Supporting Information for

Green Catalytic Synthesis of 5-Methylfurfural by Selective Hydrogenation of 5-Hydroxymethylfurfural over Size-controlled Pd Nanoparticle Catalysts

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1 Experimental Section

1.1.1 GC-Mass analysis methods

The initial and finish temperature of the oven, both of which were held for 2 min, were 45 °C and 300 °C respectively at the heating rate of 5 °C/min. The total time of the GC-Mass procedure was 55 min. The temperature of injector was 300 °C with a split of 20:1. The auxiliary temperature was 250 °C and the rate of the helium flow was 1.0 mL/min.

1.1.2 HPLC-Mass analysis methods

The mobile phase consists of 1‰ aqueous acetic acid solution and pure acetonitrile. The volume ratio of them was 80:20. The flow rate of the mobile phase was 0.5 mL/min. The temperature of the column was constant at 30 °C. The maximum absorption wavelength of the UV detector was set to 265 nm. The total elapsed time was 35 min.

The HMF standard curve eqution:

Peak Area = 33627.57299*C_1 + 358.856, R^2 = 0.99941,

C_1 represents the concentration of HMF, mg/mL.

The MF standard curve eqution:

Peak Area = 21904.93112*C_2 + 2580.76515, R^2 = 0.99779,

C_2 represents the concentration of MF, mg/mL.

All the samples were diluted ten times before the injection.

2 Supplementary Results

2.1 Reaction results

Table S1. The reaction results of the catalysts with different supports and annealing temperatures.

Entry	Catalyst	Temperature [°C]	Time [h]	Conversion [%]	Yield [%]	Selectivity [%]
1a	5%Pd/C(comm.)	120	7.5	29	15	52
1b	5%Pd/C(comm.)	160	7.5	78	25	32
1c	5%Pd/C(comm.)	220	7.5	100	-	-
2	1%Pd-PVP/ZrO_2(1:2)	220	7.5	86	62	72
3	1%Pd-PVP/SiO_2(1:2)	220	7.5	92	37	40
4	1%Pd-PVP/C (1:2, 350°C)	220	7.5	90	59	66
5	1%Pd-PVP/C (1:2, 450°C)	220	7.5	87	66	76
6	1%Pd-PVP/C (1:2, 550°C)	220	7.5	82	77	94

Reaction conditions: 250 mg HMF, 50 mg catalyst, 10 mL THF, 1 mL HCOOH, 5 bar N_2.

As can be seen in entry 1a, 1b and 1c, after the experimental condition optimization, the yield and selectivity of MF is still low when using commercial Pd/C catalyst because it has a very strong hydrogenation performance. When utilizing ZrO_2 (entry 2) or SiO_2 (entry 3) instead of carbon as support, the conversion of HMF increased but the selectivity of MF decreased, causing the drop of MF yield. Different annealing tempratures have also been tested (entry 4, 5 and 6). The results show that the catalyst 1%Pd-PVP/C(1:2, 550°C) can achieve a relatively high yield and selectivity.

2.2 Characterization of the products

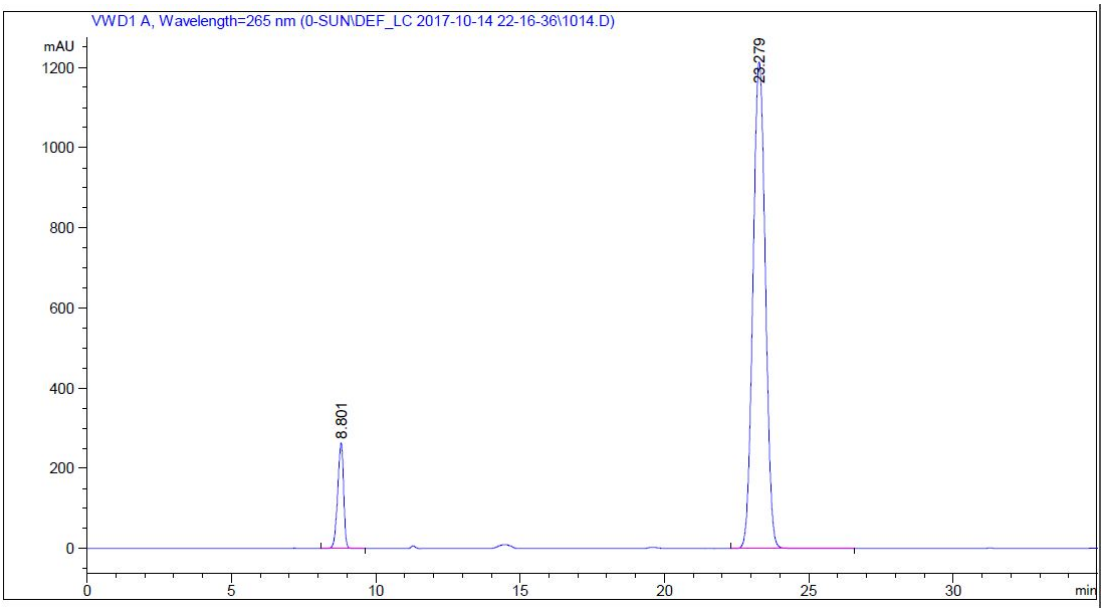


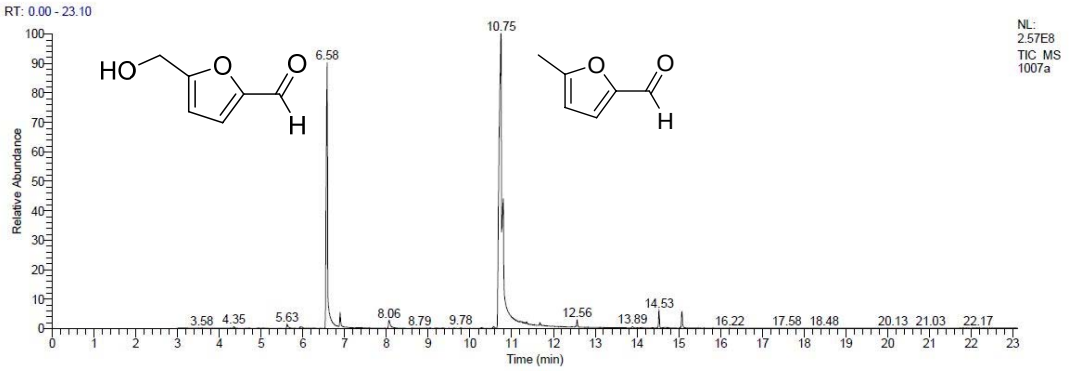
Figure S1. HPLC result of the reaction product using catalyst 2.5%Pd-PVP/C(1:2).

The reaction condition

Temperature [℃]	Pressure [bar]	Reaction time [h]
200	5	7.5

The HPLC results

Retention time [min]	8.801	23.279
Peak Area	3792.1	36048.3
Chemicals	HMF	MF



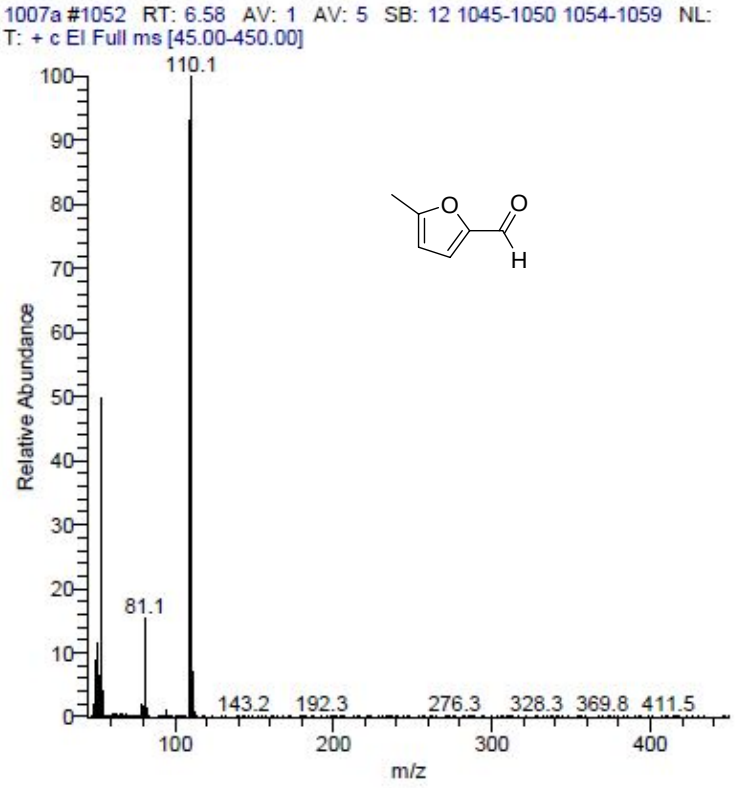


Figure S2. GC-Mass spectra of MF.

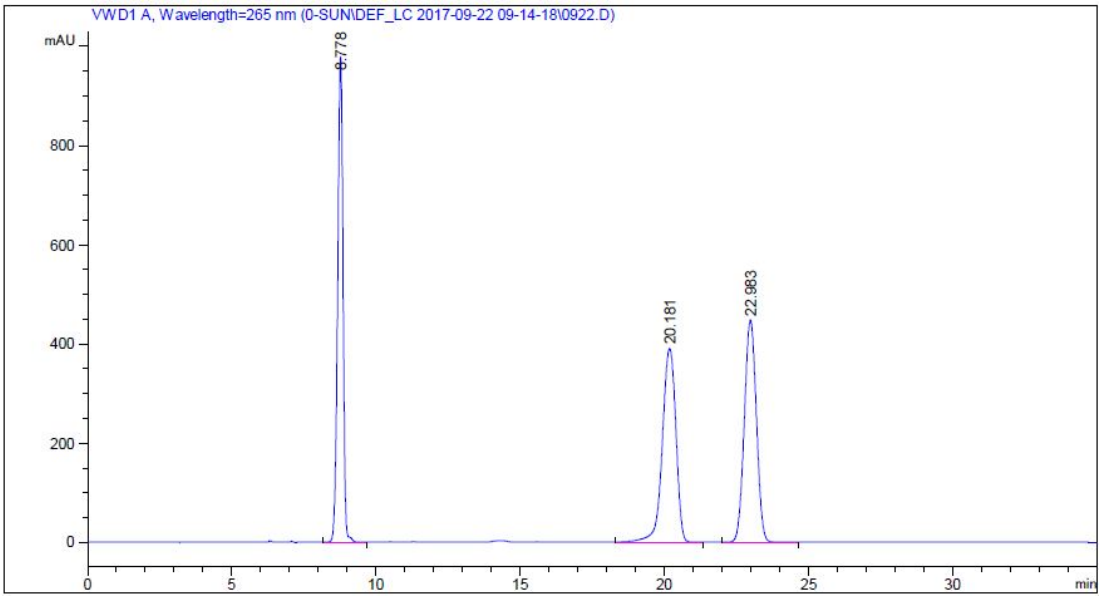


Figure S3. HPLC result of the reaction products under low temperature.

The reaction condition

Temperature [℃]	Pressure [bar]	Reaction time [h]
160	5	7.5

The HPLC results

Retention time [min]	8.778	20.181	22.983
Peak Area	12627.0	12785.9	13030.6
Chemicals	HMF	FFMF	MF

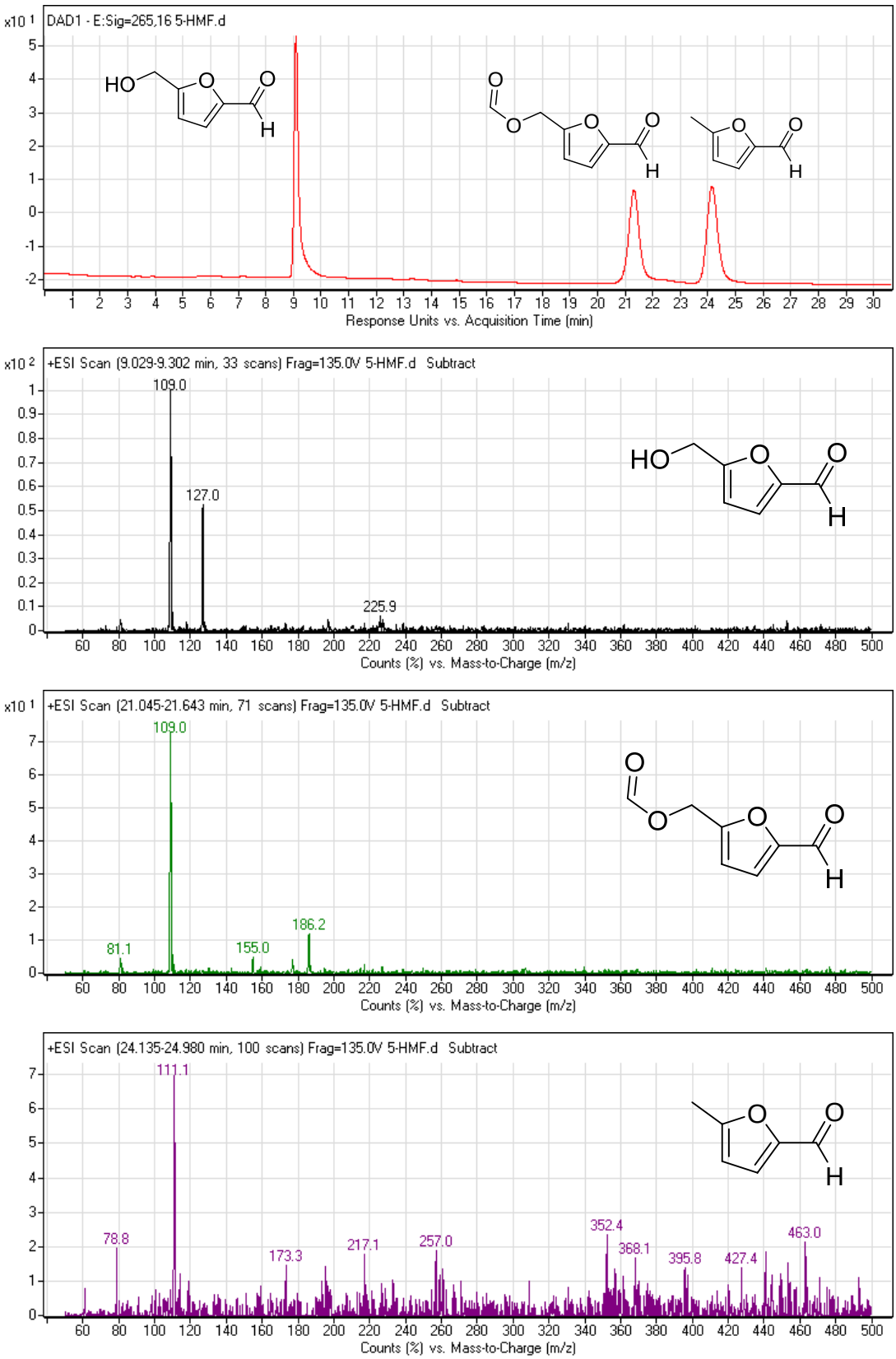


Figure S4. HPLC-Mass spectra of HMF, FFMF and MF.

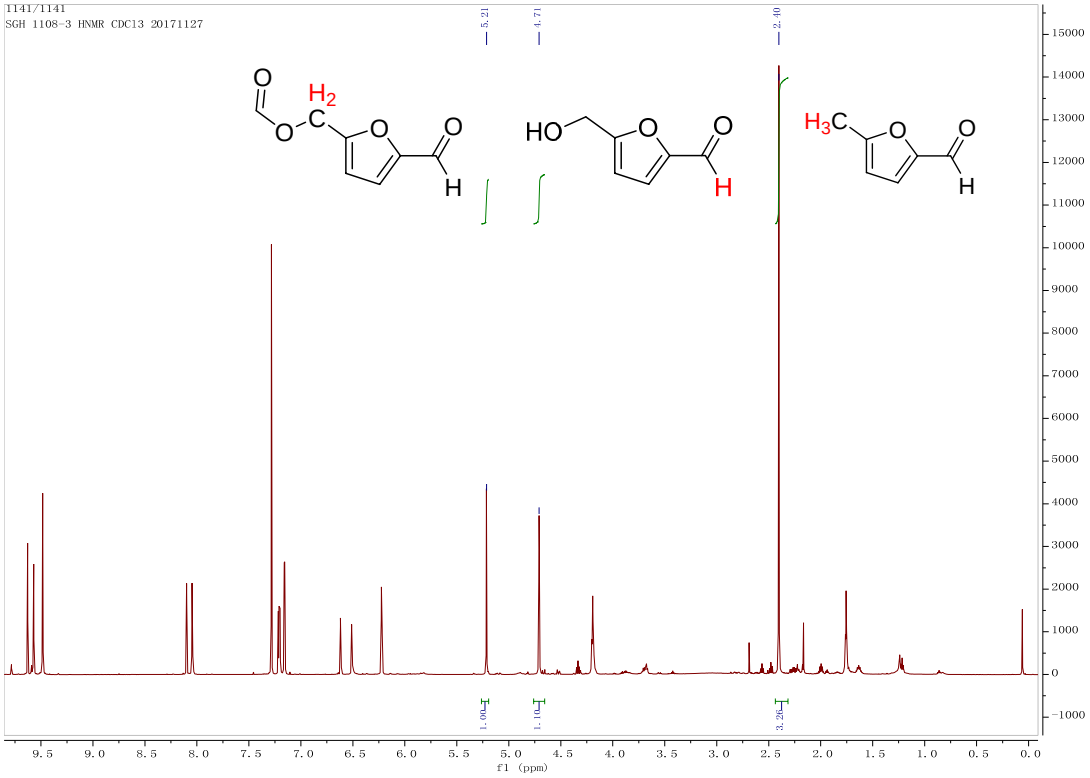
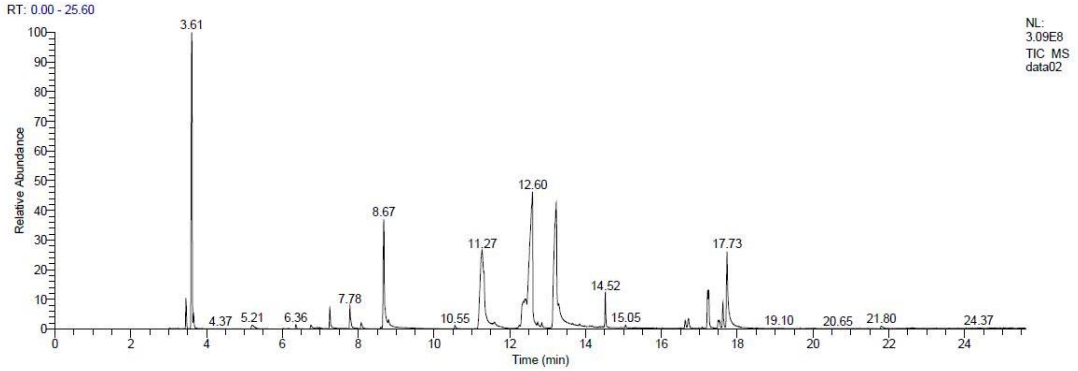
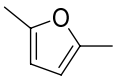
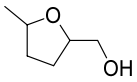
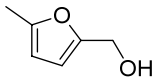
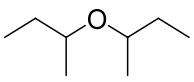
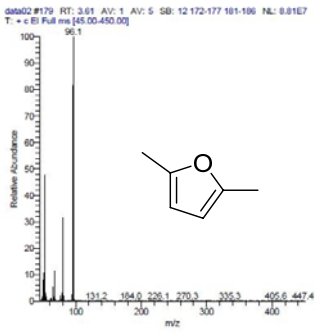
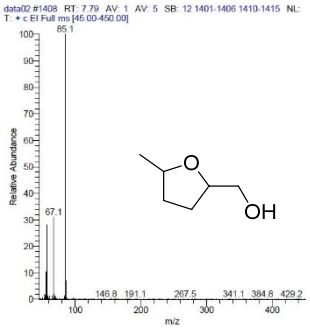


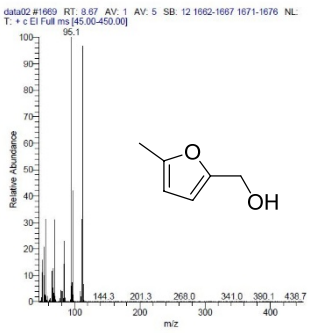
Figure S5. H^1 NMR spectra of the reaction product.



Retention time [min]	3.61	7.78	8.67	12.60
Products				







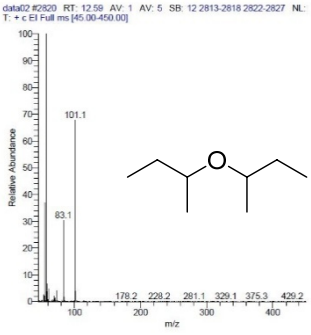


Figure S6. GC-Mass spectra of the overhydrogenation products obtained from using the commericial Pd/C as the catalyst..

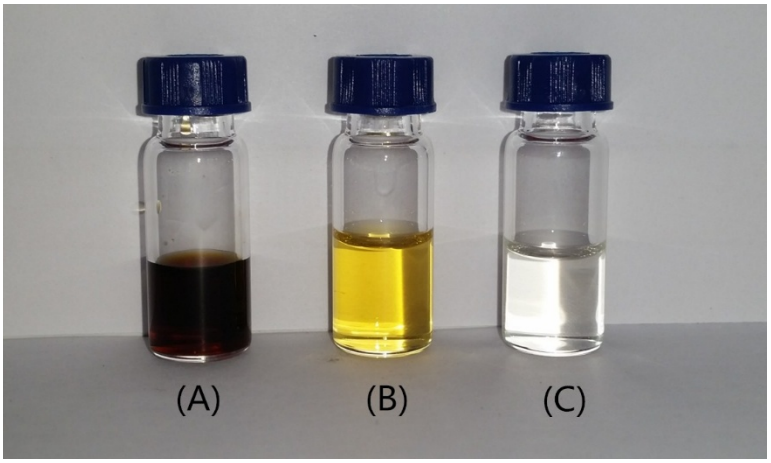


Figure S7 The photos of the products: (A) The reaction product without any catalyst; (B) The reaction product using catalyst 1%Pd-PVP(1-2); (C) The reaction product using catalyst commercial Pd

The reaction condition

Temperature [℃]	Pressure [bar]	Reaction time [h]
220	5	7.5

All the reactions are under the same condition.

Figure S6 shows the photos of the products. Without the catalyst, HMF was easily degraded under reaction the condition and the reaction product presents a dark brown colour because of the complex components. When using the catalyst 1%Pd-PVP(1-2), the main components of the mixture is MF which shows a light yellow colour. It is obvious that HMF has been over hydrogenated using the commercial catalyst since the reaction product is nearly colorless.

2.3 Characterization of the catalysts.

2.3.1 TEM micrographs and corresponding particle size distributions of the carbon-supported catalysts.

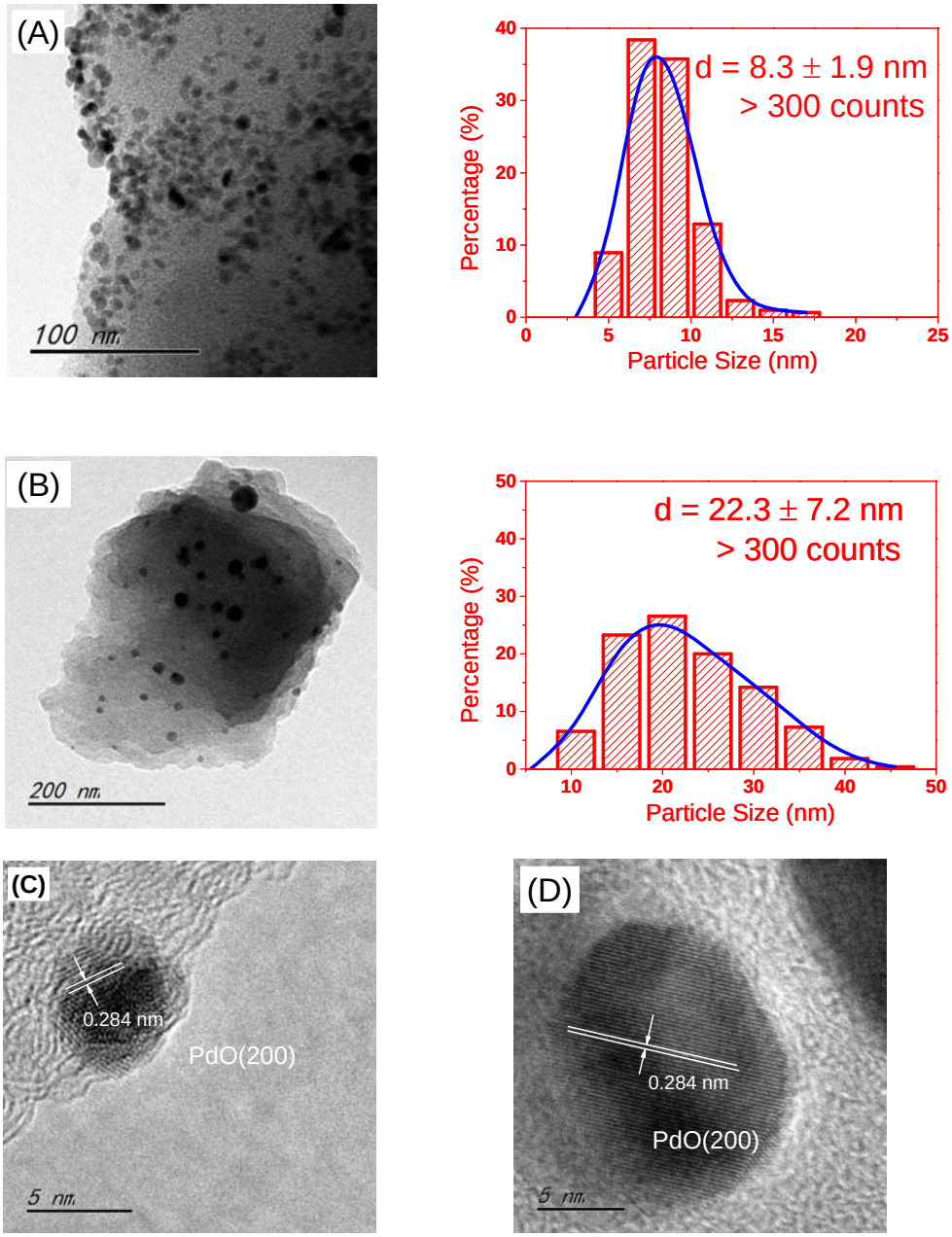


Figure S8. TEM images of the catalysts: (A) 1%Pd-PVP/C(1:1); (B) 1%Pd-PVP/C(1:1, 550℃); (C) lattice fringe of Pd NPs on the catalyst 1%Pd-PVP/C(1:1); (D) lattice fringe of Pd NPs on the catalyst 1%Pd-PVP/C(1:1, 550℃).

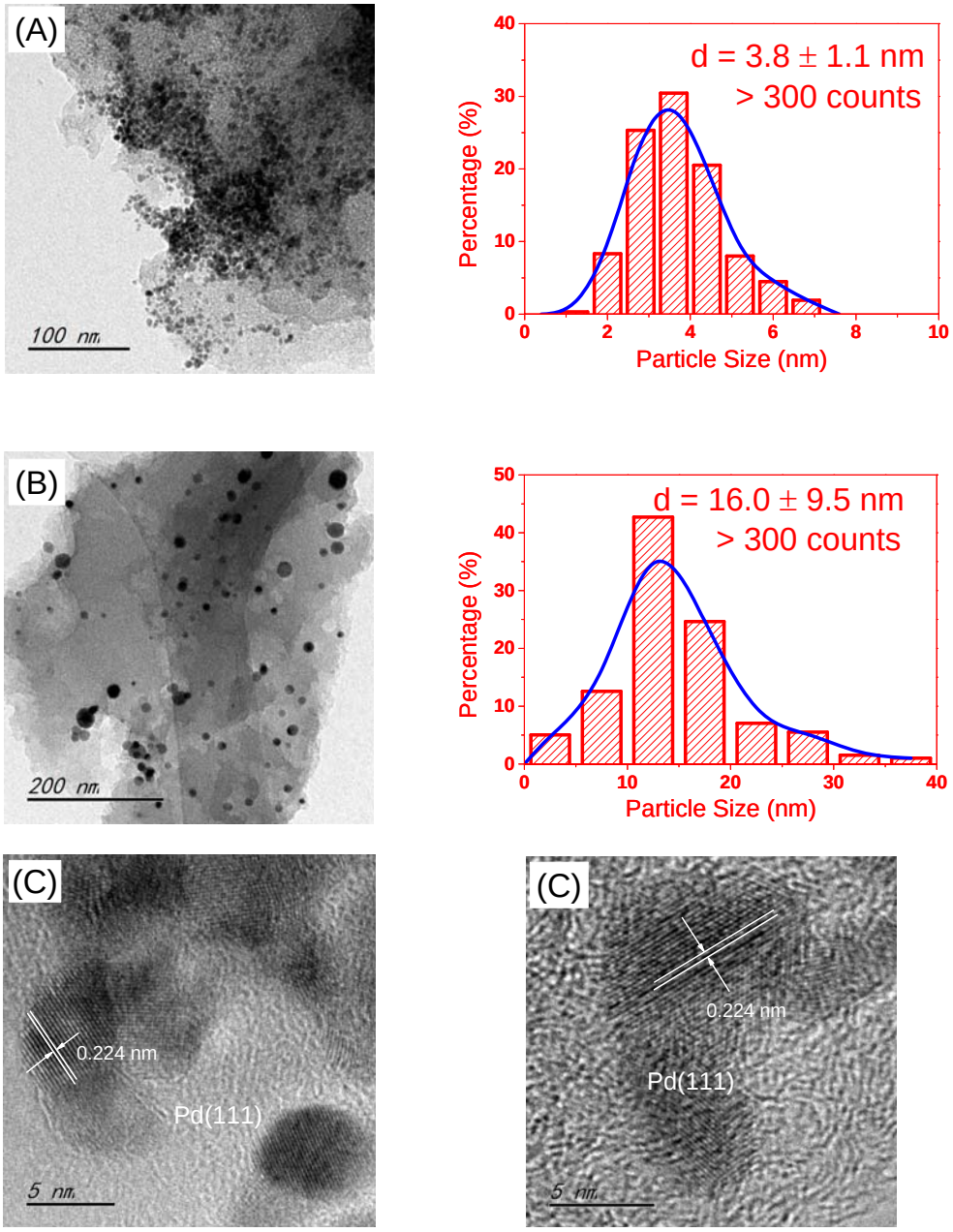


Figure S9. TEM images of the catalysts: (A) 1%Pd-PVP/C(1:2); (B) 1%Pd-PVP/C(1:2, 550℃); (C) lattice fringe of Pd NPs on the catalyst 1%Pd-PVP/C(1:2); (D) lattice fringe of Pd NPs on the catalyst 1%Pd-PVP/C(1:2, 550℃).

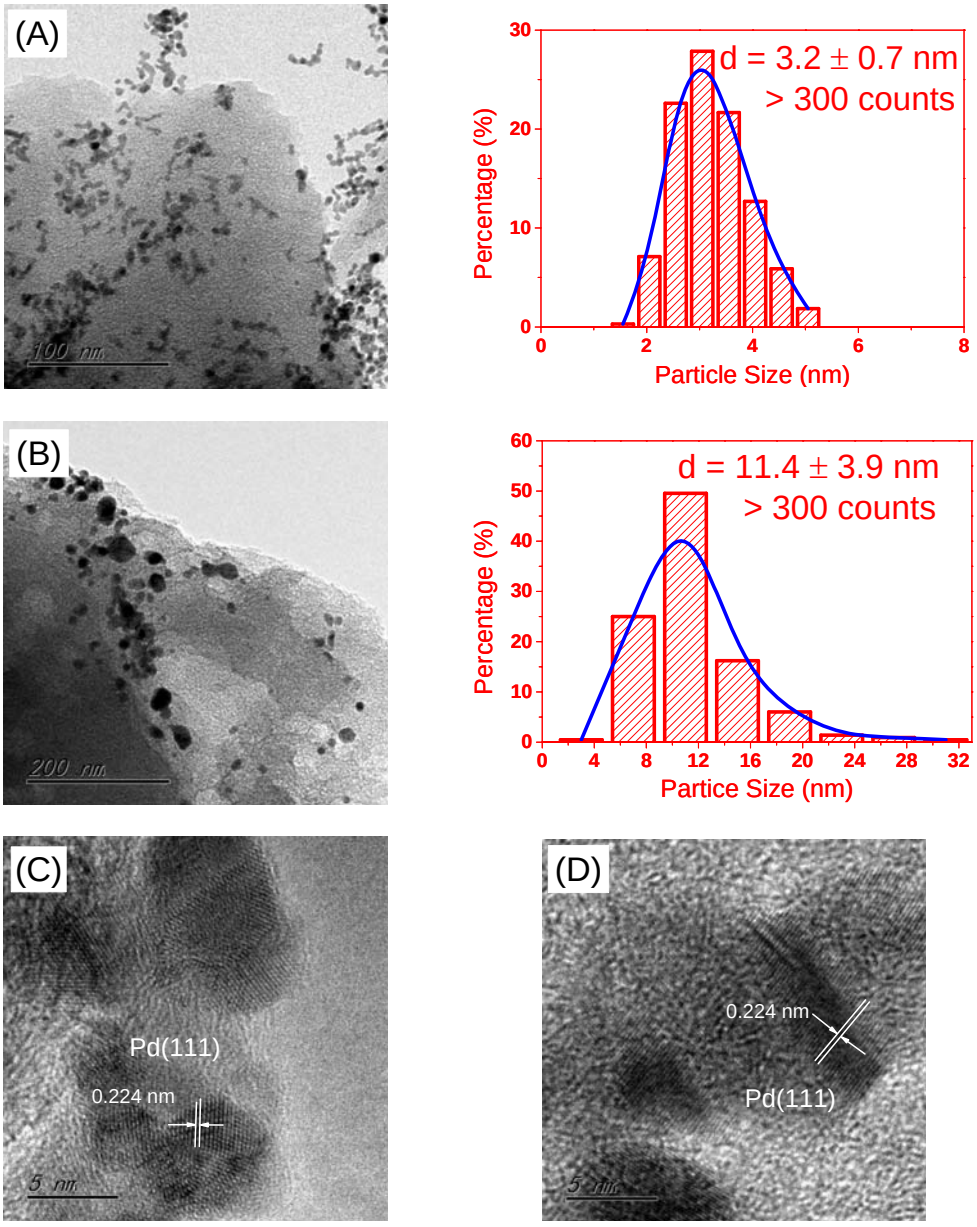
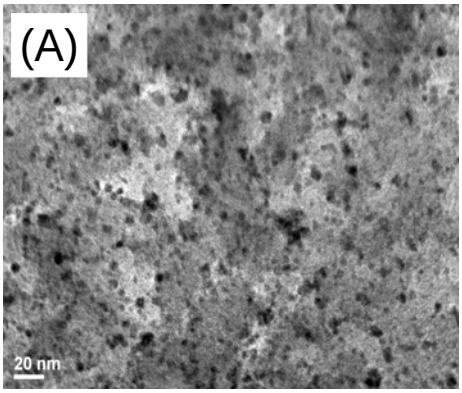
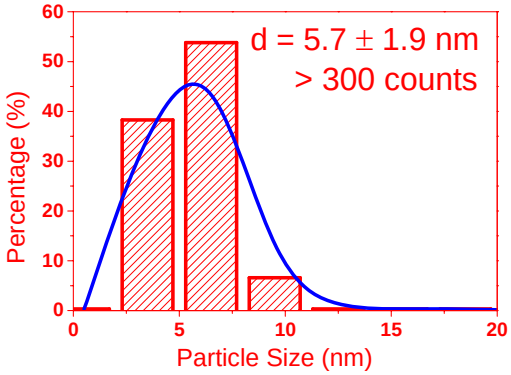


Figure S10. TEM images of the catalysts: (A) 1%Pd-PVP/C(1:4); (B) 1%Pd-PVP/C(1:4, 550℃); (C) lattice fringe of Pd NPs on the catalyst 1%Pd-PVP/C(1:4); (D) lattice fringe of Pd NPs on the catalyst 1%Pd-PVP/C(1:4, 550℃).





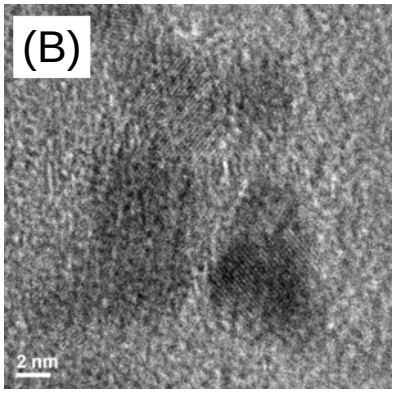


Figure S11. TEM images of the catalysts: (A) commercial Pd/C; (B) lattice fringe of Pd NPs on the commercial Pd/C

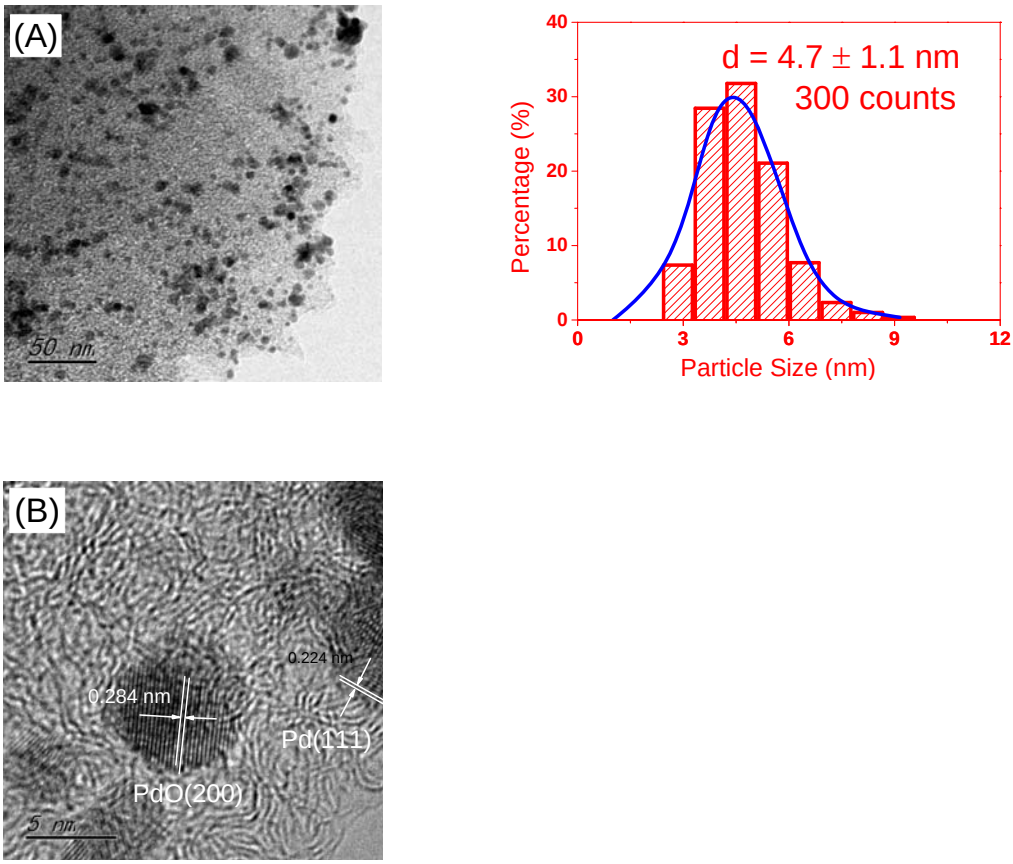


Figure S12. TEM images of the catalysts: (A) 2.5%Pd-PVP/C(1:2); (B) lattice fringe of Pd NPs on the catalyst 2.5%Pd-PVP/C(1:2).

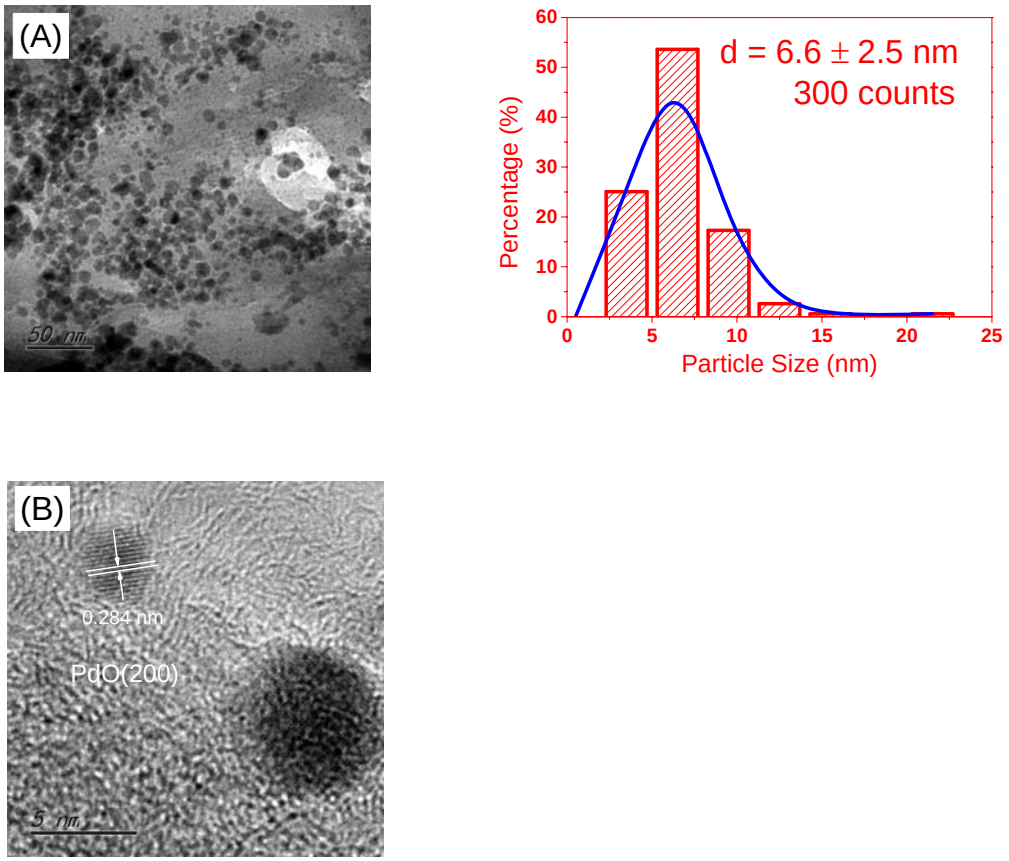


Figure S13. TEM images of the catalysts: (A) 5%Pd-PVP/C(1:2); (B) lattice fringe of Pd NPs on the catalyst 5%Pd-PVP/C(1:2).

2.3.2 XRD patterns of the catalysts.

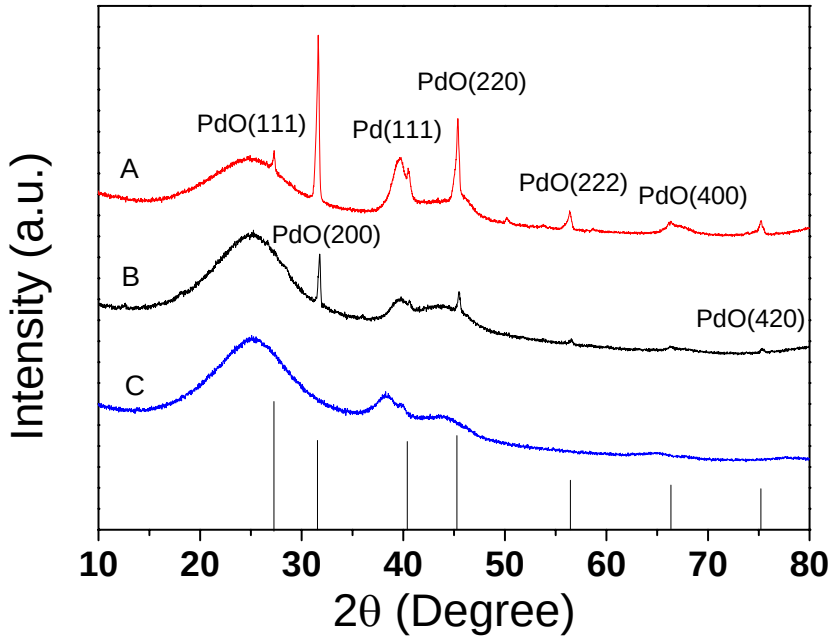


Figure S14. XRD patterns of the catalysts: (A) commercial Pd/C; (B) 5%Pd-PVP/C(1:2); (C) 2.5%Pd-PVP/C(1:2).

2.3.3 XPS spectra for Pd (3d) and N (1s) of the catalysts.

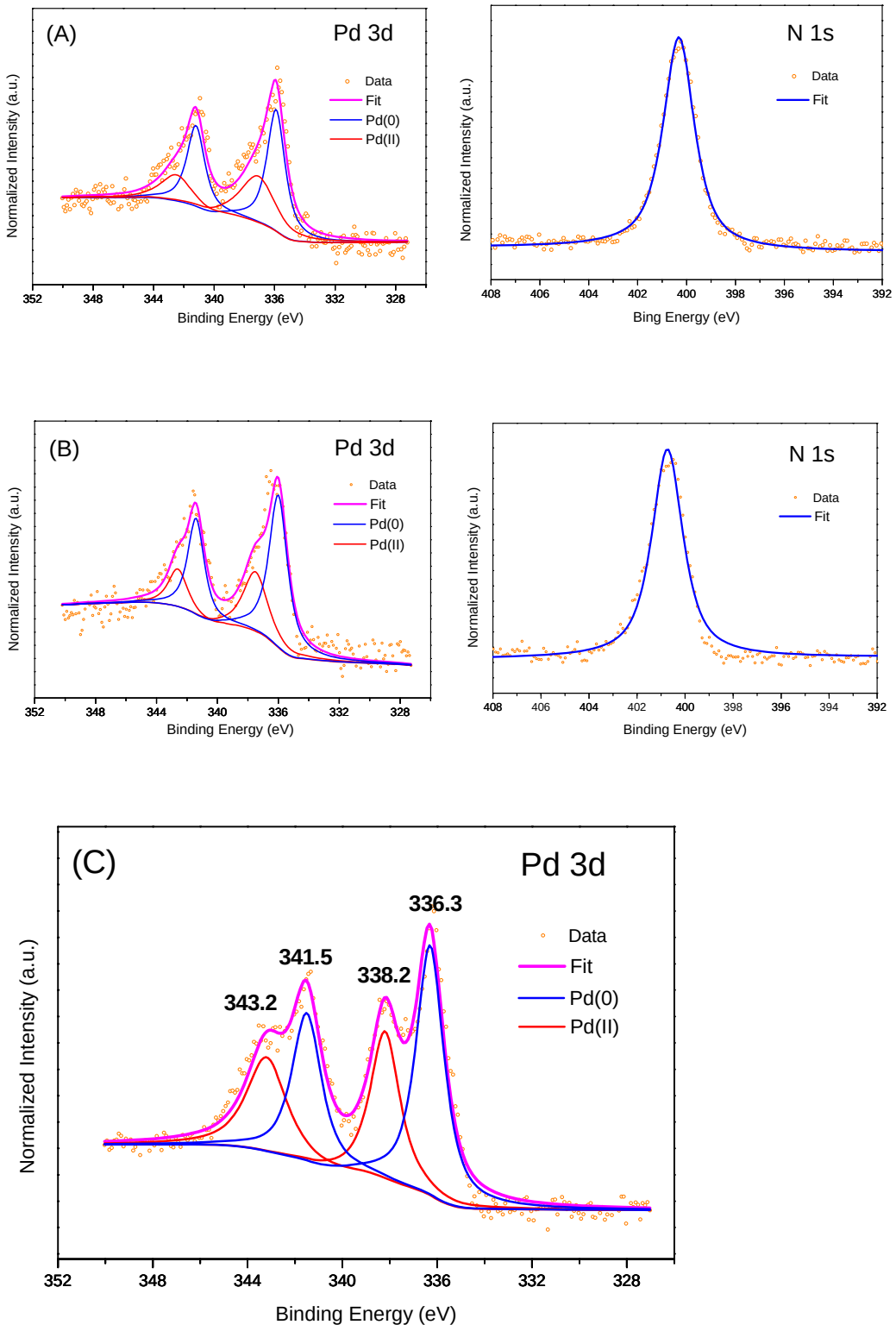


Figure S15. XPS spectra for Pd (3d) and N (1s) of the catalysts: (A) 2.5%Pd-PVP/C(1:2); (B) 5%Pd-PVP/C(1:2); (C) commercial Pd/C.

2.4 The comparison test using different hydrogen donors and acid

Table S2. The reaction results using other hydrogen donors and acid

Catalyst	Hydrogen donor [a]	Acid	Conversion [%]	Yield [%]	Selectivity [%]
1%Pd-PVP/C(1:2)	H_2	-	100	-	-
1%Pd-PVP/C(1:2)	isopropanol	-	77	-	-
1%Pd-PVP/C(1:2)	-	acetic acid	47	8	17

a- H_2: 1 MPa

2.5 The reusability of the catalyst 1%Pd-PVP/C(1:2)

The recycle experiments were performed since the reusability of the catalyst is very improtant. After three-time usages, the yield of MF has a slight decline but still with high selectivity (see Table S3). According to the ICP-OES results of the fresh catalyst and the spent catalyst, the Pd content in the filtrate collected from the first run was about 0.40 ppm, demonstrating that the Pd leaching could be neglected. The STEM result showed that the particle size became bigger, which could be responsible for a reduction in catalytic activity of 1%Pd-PVP/C(1:2) (not shown).

Table S3. Recycle experiments for 1%Pd-PVP/C(1:2)

Recovery times	Conversion [%]	Yield [%]	Selectivity [%]
0	78	73	94
1	67	58	85
2	69	57	82
3	61	50	82

Reaction conditions: 250 mg HMF, 50 mg catalyst, 10 mL THF, 1 mL HCOOH, 5 bar N_2.

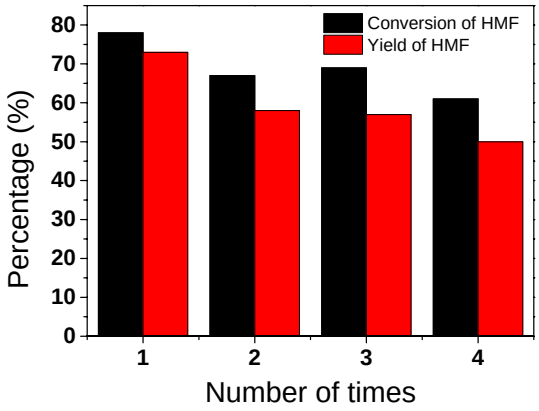


Figure S16 Recycle experiments for 1%Pd-PVP/C(1:2). Reaction conditions: 250 mg HMF, 50 mg catalyst, 10 mL THF, 1 mL HCOOH, 5 bar N_2.