Electronic Supplementary Material (ESI) for Green Chemistry.

Efficient synthesis of 5-methyl-2-furancarboxylic acid via selective hydrogenolysis of bio-renewable 5-hydroxymethyl-2-furancarboxylic acid on Pd/C catalysts at ambient temperature

Contents

Fig. S5 Effect of Pd particle sizes on turnover rates in 5-hydroxymethyl-2-furancarboxylic acid (HMFA) reaction on Pd/SiO_2. Pd particle sizes of Pd/SiO_2 catalysts were controlled by varying Pd loadings. Reaction conditions: 1 mmol HMFA, 12 mL tetrahydrofuran, 3.0 MPa H_2, 30 ^oC, 20-30% HMFA conversions obtained by varying reaction time and catalyst amounts. MFA: 5-methyl-2-furancarboxylic acid; HMTFA: 5-hydroxymethyl-2-tetrahydrofurancarboxylic acid.

Fig. S6 Transmission electron microscopy (TEM) micrographs (scale bar = 20 nm) and histograms of metal particle size distribution for (a) Pd/C-1 (3 wt% Pd), (b) Pd/C-2 (3 wt% Pd), (c) Pd/C (3 wt% Pd), (d) Pd/C-3 (3 wt% Pd), (e) Pd/C-4 (3 wt% Pd) and (f) Pd/C-5 (3 wt% Pd).

Fig. S7 Transmission electron microscopy (TEM) micrograph (scale bar = 20 nm) and histograms of metal particle size distribution for spent Pd/C (3 wt% Pd) catalyst.

Experimental section: general procedure for the preparation of Pd/C and Pd/SiO2 catalysts with different Pd particle sizes.

As shown in Table S1, the Pd particle sizes of the Pd/C catalysts were controlled by varying the Pd loadings and the pH values of $PdCl_2$ aqueous solutions using NaOH and HCl as pH regulators before adding support C. Taking Pd/C, prepared at the pH value of 1, as an example, adding 0.1 mmol HCl to $PdCl_2$ aqueous solution, the pH value was detected by pH meter. Support C was added into the aqueous solution of $PdCl_2$ with vigorous stirring at room temperature. The resultant suspension was stirred vigorously at a speed of 600 rpm at room temperature for 2 h, and then an aqueous solution of $NaBH_4$ (1.0 mol/L) was added dropwise. After stirring for 4 h, the solution was filtered and washed with deionized water for three times. Afterwards, the resulting powder was dried at 120 ^{o}C overnight. By the same method, the other Pd particle sizes of the Pd/C catalysts were prepared.

Table S1 Specific preparation protocols for Pd/C catalysts with different Pd particle sizes

Catalyst Pd/C-X [a]	Pd loading (%)	pH value [b]	Pd particle size [c] (nm)
Pd/C-0.9	0.5	0.5	0.9±0.2
Pd/C-2.1	1	0.5	2.1±0.5
Pd/C-2.6	2	0.5	2.6±0.6
Pd/C-3.3	3	0.5	3.3±0.5
Pd/C-4.1	2	1	4.1±0.9
Pd/C-4.7	3	1	4.7±1.4
Pd/C-5.2	4	1	5.2±1.4
Pd/C-6.1	3	2	6.1±1.4

[a]X denotes average Pd particle size of Pd/C catalysts. [b]pH values of $PdCl_2$ aqueous solution using NaOH and HCl as a pH regulators after adding support C. [c]Measured by transmission electron microscope (TEM, Fig. S2).

As shown in Table S2, the Pd particle sizes of the Pd/SiO_2 catalysts were controlled by varying the Pd loadings. SiO_2 was added into an aqueous solution of $PdCl_2$ with vigorous stirring at room temperature. The resultant suspension was stirred vigorously at a speed of 600 rpm at room temperature for 2 h, and then an aqueous solution of $NaBH_4$ (1.0 mol/L) was added dropwise. After stirring for 4 h, the solution was filtered and washed with deionized water for three times. Afterwards, the resulting powder was dried at 120 ^oC overnight.

Table S2 Specific preparation protocols for Pd/SiO_2 catalysts with different Pd particle sizes

Catalyst Pd/SiO_2-X [a]	Pd loading (%)	Pd particle size [c] (nm)
Pd/ SiO_2-0.9	0.5	0.9±0.2
Pd/ SiO_2-1.2	1	1.2±0.3
Pd/ SiO_2-2.3	2	2.3±0.8
Pd/ SiO_2-3.0	3	3.0±0.6

[a]X denotes average Pd particle size of Pd/SiO_2 catalysts. [b]pH values of $PdCl_2$ aqueous solution using NaOH and HCl as a pH regulators after adding support SiO_2. [c]Measured by transmission electron microscope (TEM, Fig. S3).

Table S3 Pd dispersion and particle size of supported Pd catalysts (2 wt% Pd)

Catalyst	Pd dispersion (%) [a]	Size (nm) [a]	Size (nm) [b]
Pd/C	38.0	3.0	2.6
Pd/CeO_2	37.6	3.0	2.6
Pd/SiO_2	39.1	2.8	2.3
Pd/ZrO_2	36.8	3.1	2.7
Pd/TiO_2	44.0	2.6	2.3

[a]Pd particle size measured by CO-chemisorption. [b]Pd particle size measured by TEM.

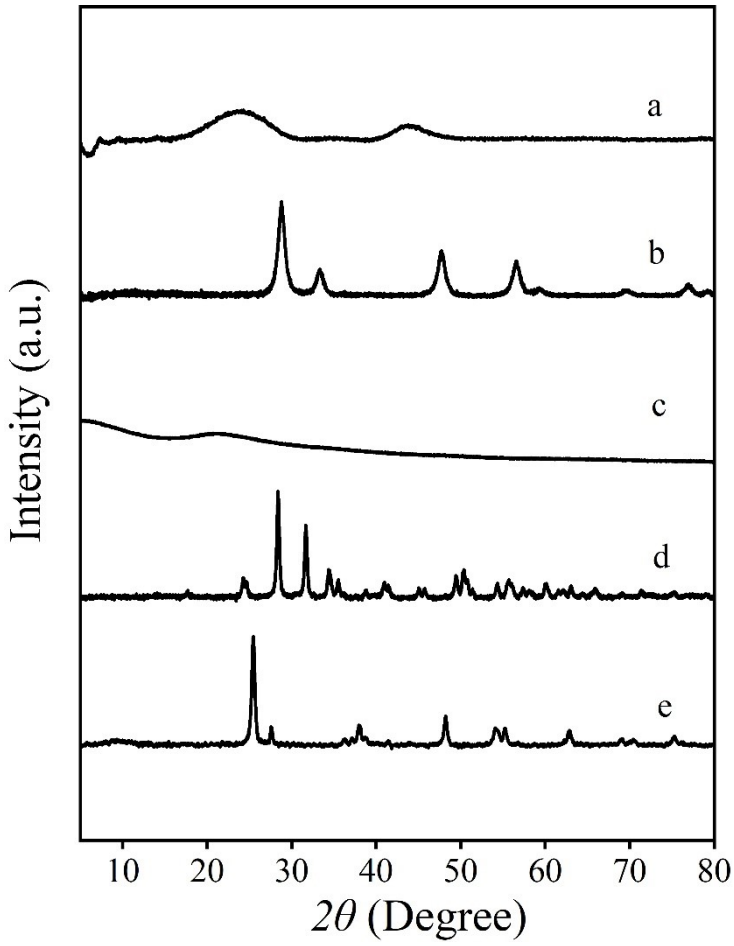

Fig. S1 X-ray diffraction patterns of (a) Pd/C (2 wt% Pd), (b) Pd/CeO_2 (2 wt% Pd), (c) Pd/SiO_2 (2 wt% Pd), (d) Pd/ZrO_2 (2 wt% Pd) and (e) Pd/TiO_2 (2 wt% Pd).

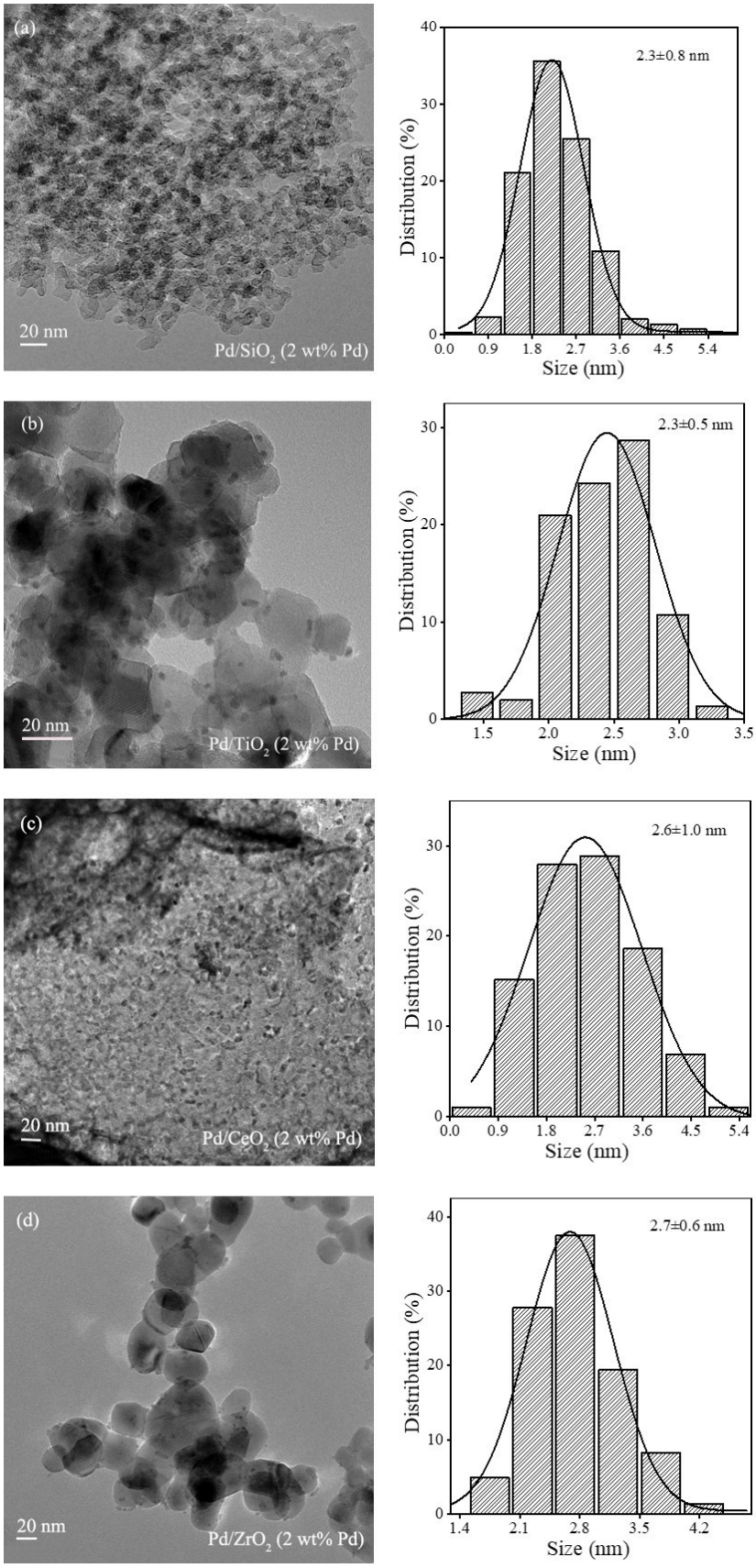

Fig. S2 Transmission electron microscopy (TEM) micrographs (scale bar = 20 nm) and histograms of metal particle size distribution for oxide-supported Pd catalysts with 2 wt% loading: (a) Pd/SiO_2, (b) Pd/TiO_2, (c) Pd/CeO_2 and (d) Pd/ZrO_2.

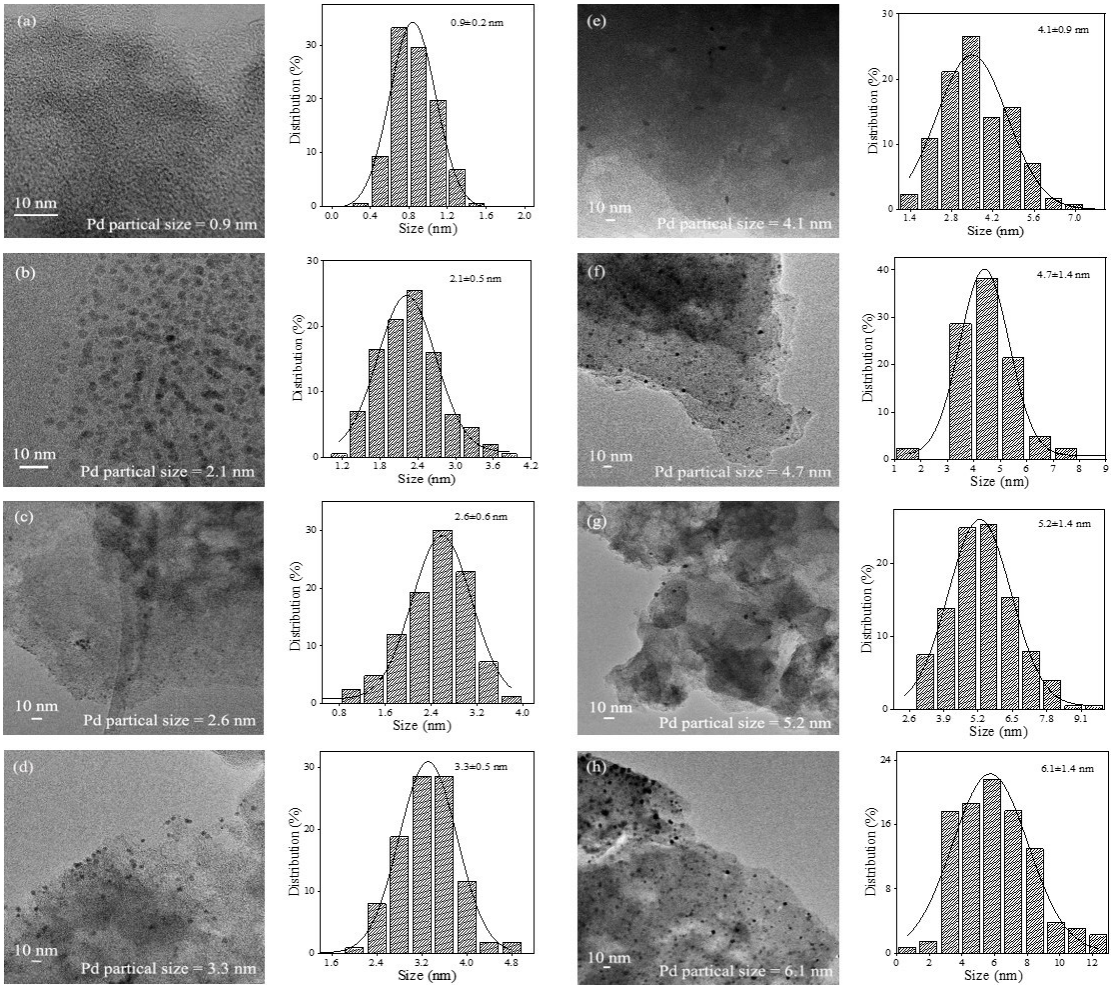

Fig. S3 Transmission electron microscopy (TEM) micrographs (scale bar = 10 nm) and histograms of metal particle size distribution for Pd/C with Pd particle sizes of (a) 0.9 nm, (b) 2.1 nm, (c) 2.6 nm, (d) 3.3 nm, (e) 4.1 nm, (f) 4.7 nm, (g) 5.2 nm and (h) 6.1 nm controlled by varying Pd loadings and pH values of $PdCl_2$ aqueous solution.

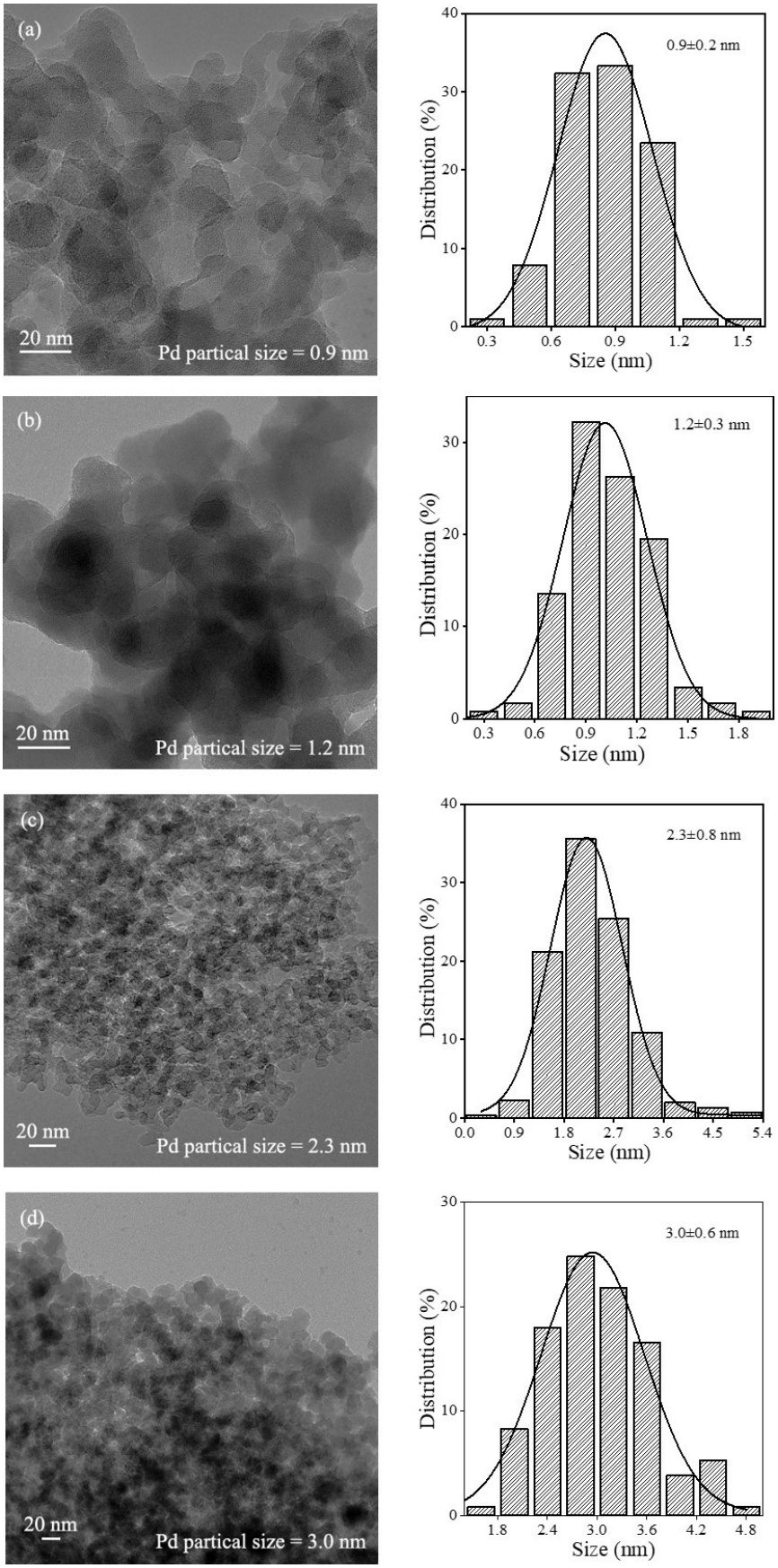

Fig. S4 Transmission electron microscopy (TEM) micrographs (scale bar = 20 nm) and histograms of metal particle size distribution for Pd/SiO_2 with Pd particle sizes of (a) 0.9 nm, (b) 1.2 nm, (c) 2.3 nm and (d) 3.0 nm controlled by varying Pd loadings.

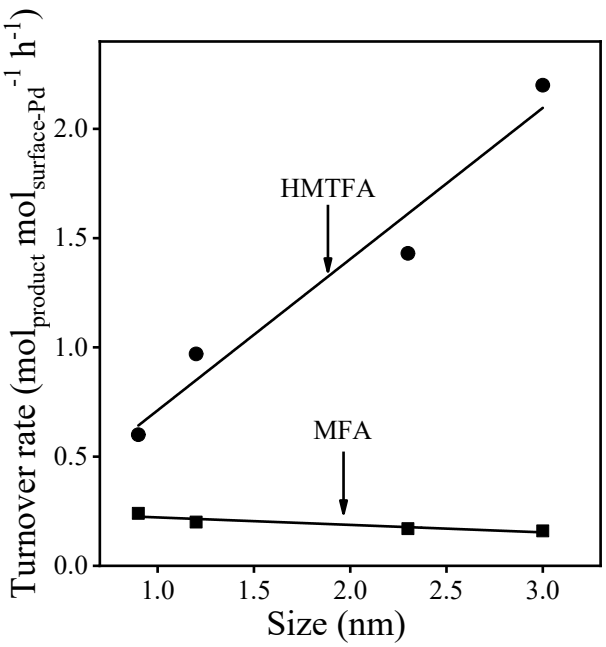

Fig. S5 Effect of Pd particle sizes on turnover rates in 5-hydroxymethyl-2-furancarboxylic acid (HMFA) reaction on Pd/SiO_2. Pd particle sizes of Pd/SiO_2 catalysts were controlled by varying Pd loadings. Reaction conditions: 1 mmol HMFA, 12 mL tetrahydrofuran, 3.0 MPa H_2, 30 ^oC, 20-30% HMFA conversions obtained by varying reaction time and catalyst amounts. MFA: 5-methyl-2-furancarboxylic acid; HMTFA: 5-hydroxymethyl-2-tetrahydrofurancarboxylic acid.

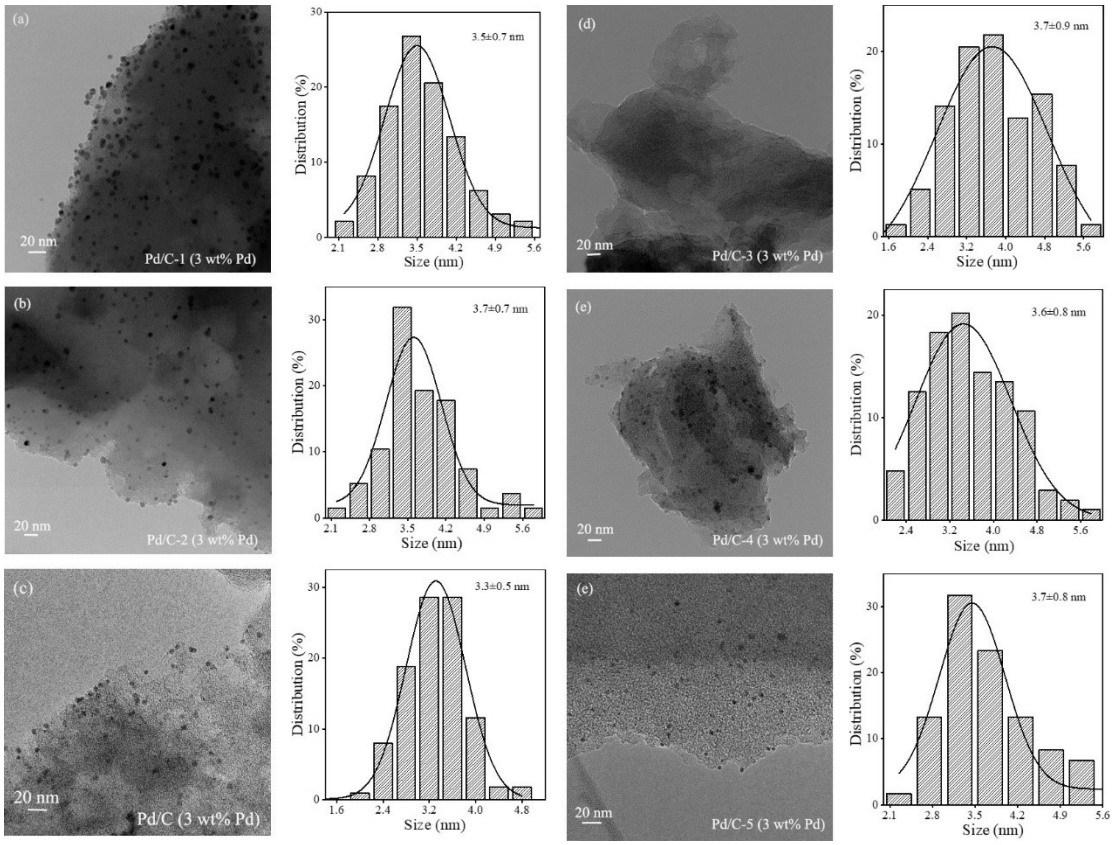

Fig. S6 Transmission electron microscopy (TEM) micrographs (scale bar = 20 nm) and histograms of metal particle size distribution for (a) Pd/C-1 (3 wt% Pd), (b) Pd/C-2 (3 wt% Pd), (c) Pd/C (3 wt% Pd), (d) Pd/C-3 (3 wt% Pd), (e) Pd/C-4 (3 wt% Pd) and (f) Pd/C-5 (3 wt% Pd).

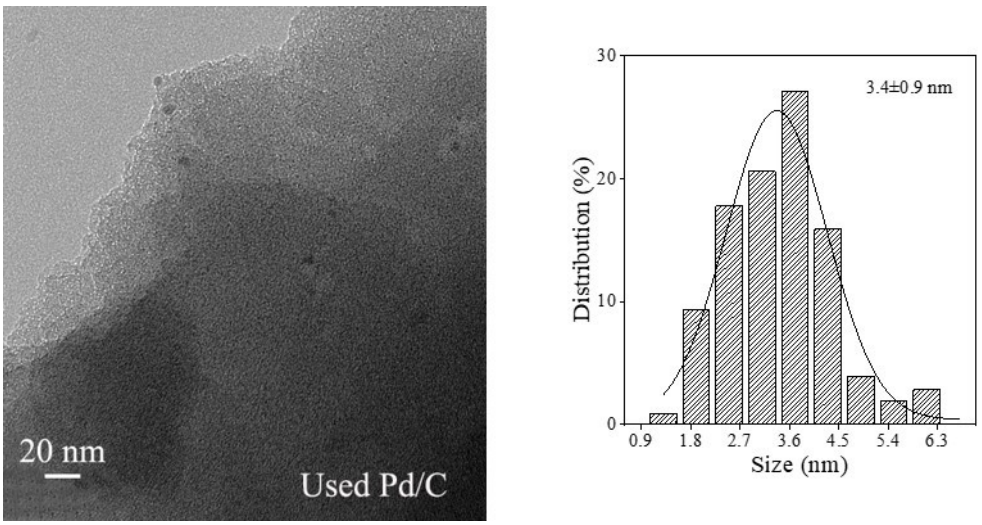

Fig. S7 Transmission electron microscopy (TEM) micrograph (scale bar = 20 nm) and histograms of metal particle size distribution for spent Pd/C (3 wt% Pd) catalyst.