

## **Impact of Oxygen-Containing Groups of Pd/C on Hydrogenation of Acetophenone and Phenylacetylene**

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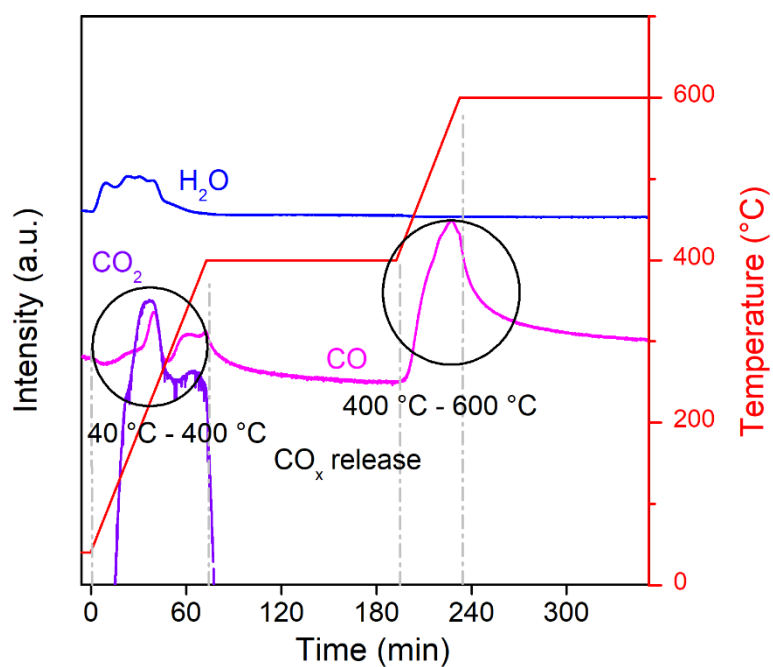
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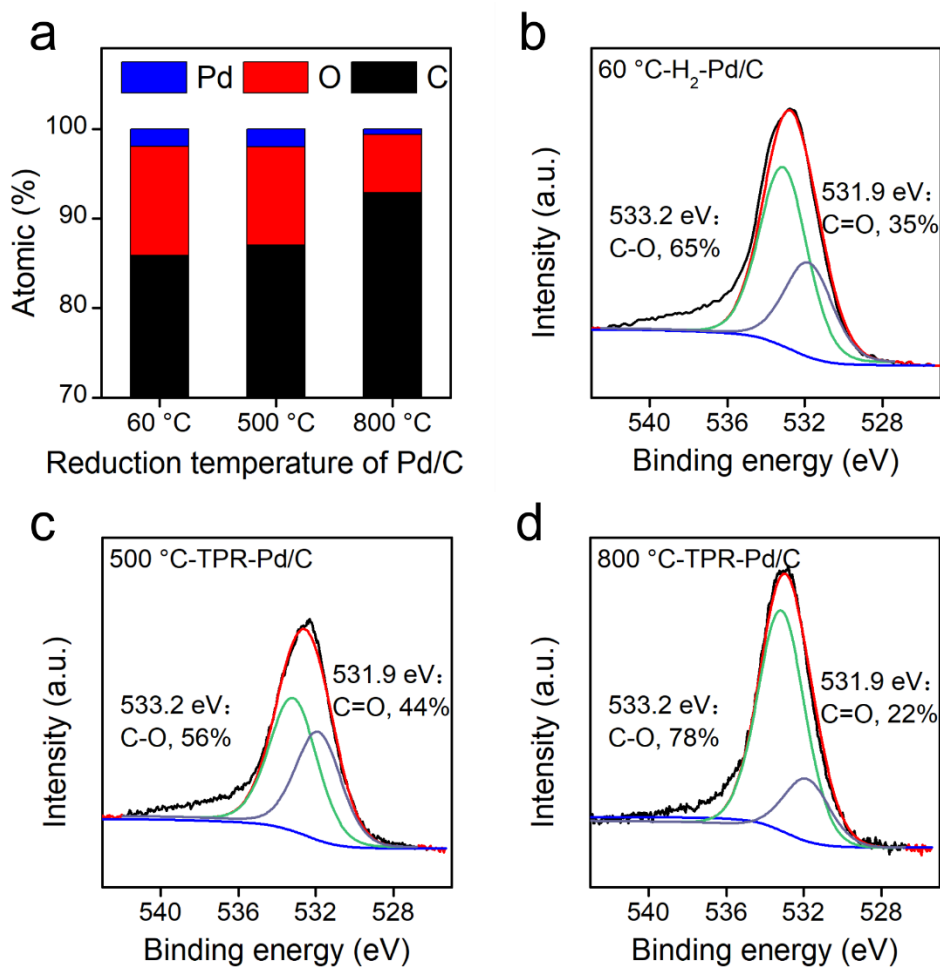
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**Table S1.** Summary of treatment of the samples.

Sample	Chemical treatment	T (°C)	Holding time (h)
60 °C-H <sub>2</sub> -Pd/C	5% H <sub>2</sub> /Ar	60	2
500 °C-TPR-Pd/C	5% H <sub>2</sub> /Ar	500	0
800 °C-TPR-Pd/C	5% H <sub>2</sub> /Ar	800	0
400 °C-N <sub>2</sub> -Pd/C	N <sub>2</sub>	400	2
600 °C-N <sub>2</sub> -Pd/C	N <sub>2</sub>	600	2
60 °C-H <sub>2</sub> -Pd/C2	5% H <sub>2</sub> /Ar	60	2
500 °C-TPR-Pd/C2	5% H <sub>2</sub> /Ar	500	0



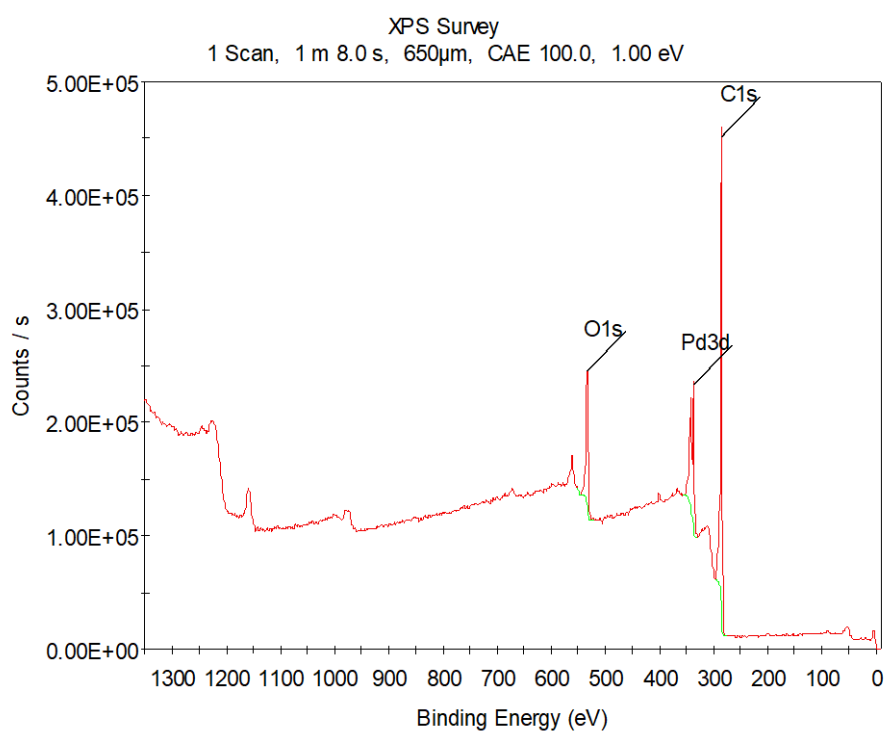
**Figure S1** The MS signals of the TPD process for the Pd/C in N<sub>2</sub>.

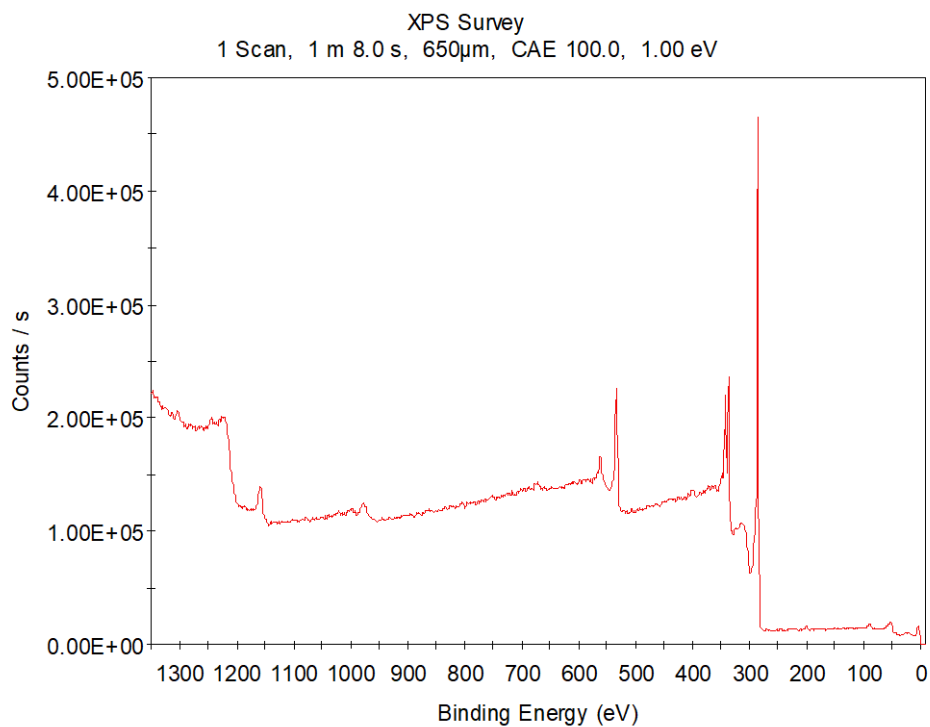


**Figure S2** (a) The elemental content ratios analyzed by XPS of the Pd/C catalyst reduced at 60 °C in 5% H<sub>2</sub>/Ar and then temperature-programmed to 500 °C and 800 °C for reduction. Peak analysis results of the O 1s XPS spectra for (b) the Pd/C catalyst reduced at 60 °C in 5% H<sub>2</sub>/Ar and temperature-programmed to (c) 500 °C and (d) 800 °C for reduction.

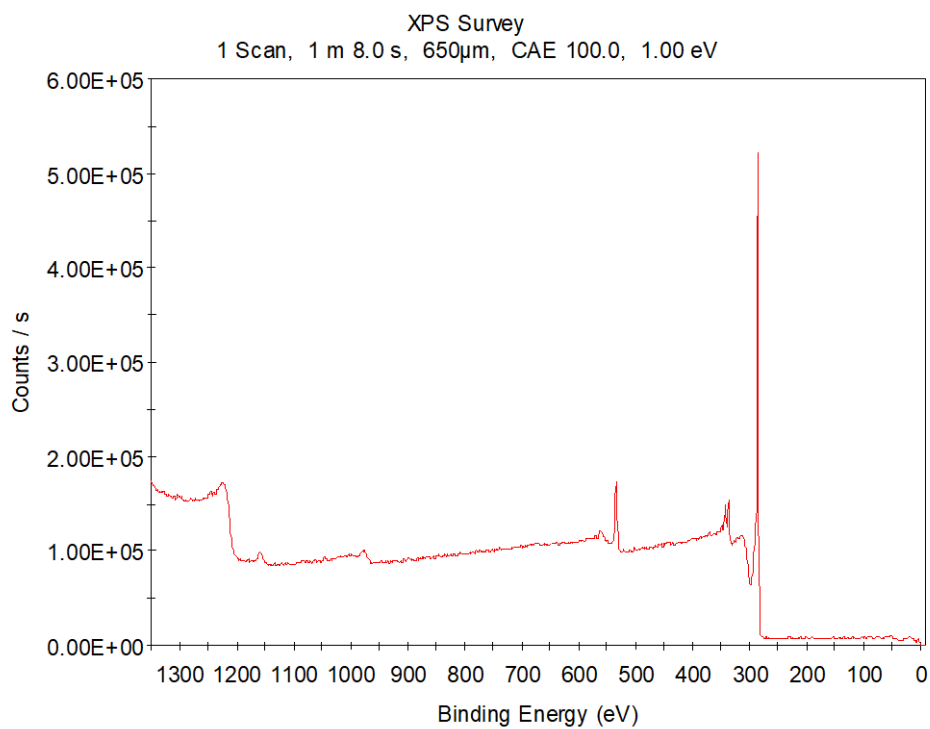
**Table S2** The XPS analysis of Pd/C catalyst after reduction at different temperatures.

Reduction temperature	Peak	Peak position (eV)	Peak width at half height (eV)	Peak area CPS. (eV)	Atomic (%)
60 °C	C 1s	284.78	1.08	141000	85.9
	O 1s	532.8	3.39	53600	12.1
	Pd 3d	335.68	1.56	61900	2.0
500 °C	C 1s	284.79	0.97	13400	87.0
	O 1s	532.47	3.16	45400	11.0
	Pd 3d	335.53	1.42	58900	2.0
800 °C	C 1s	284.82	0.97	153000	92.9
	O 1s	532.96	2.97	28800	6.5
	Pd 3d	335.83	1.21	20700	0.6

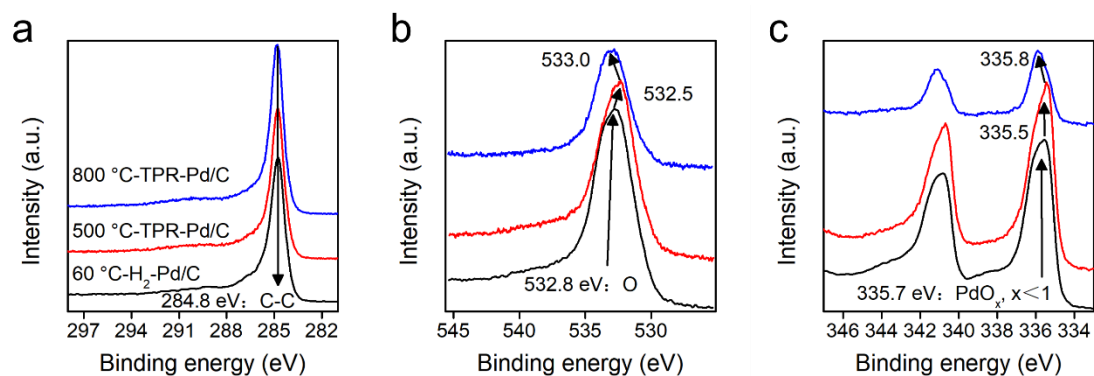
**Figure S3** XPS spectrum of Pd/C catalyst reduced at 60 °C in 5% H<sub>2</sub>/Ar.



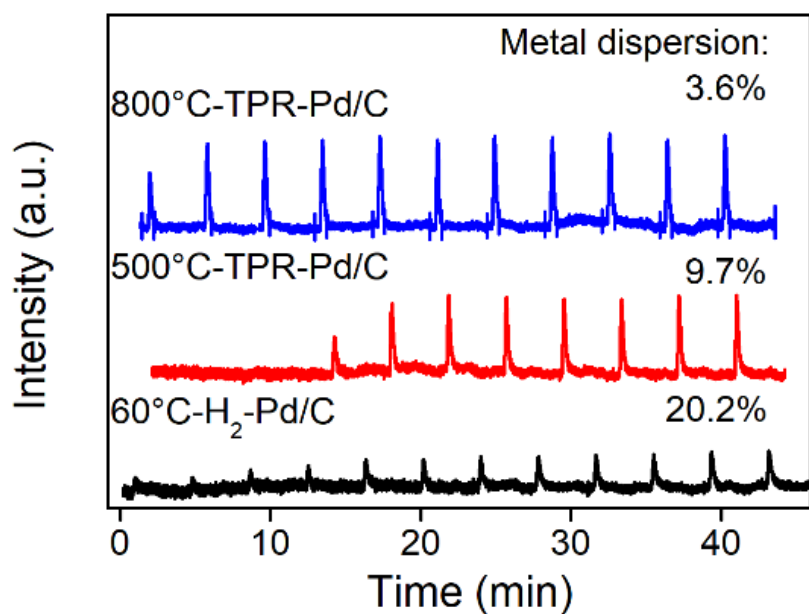
**Figure S4** XPS spectrum of Pd/C catalyst reduced at 500 °C in 5% H<sub>2</sub>/Ar.



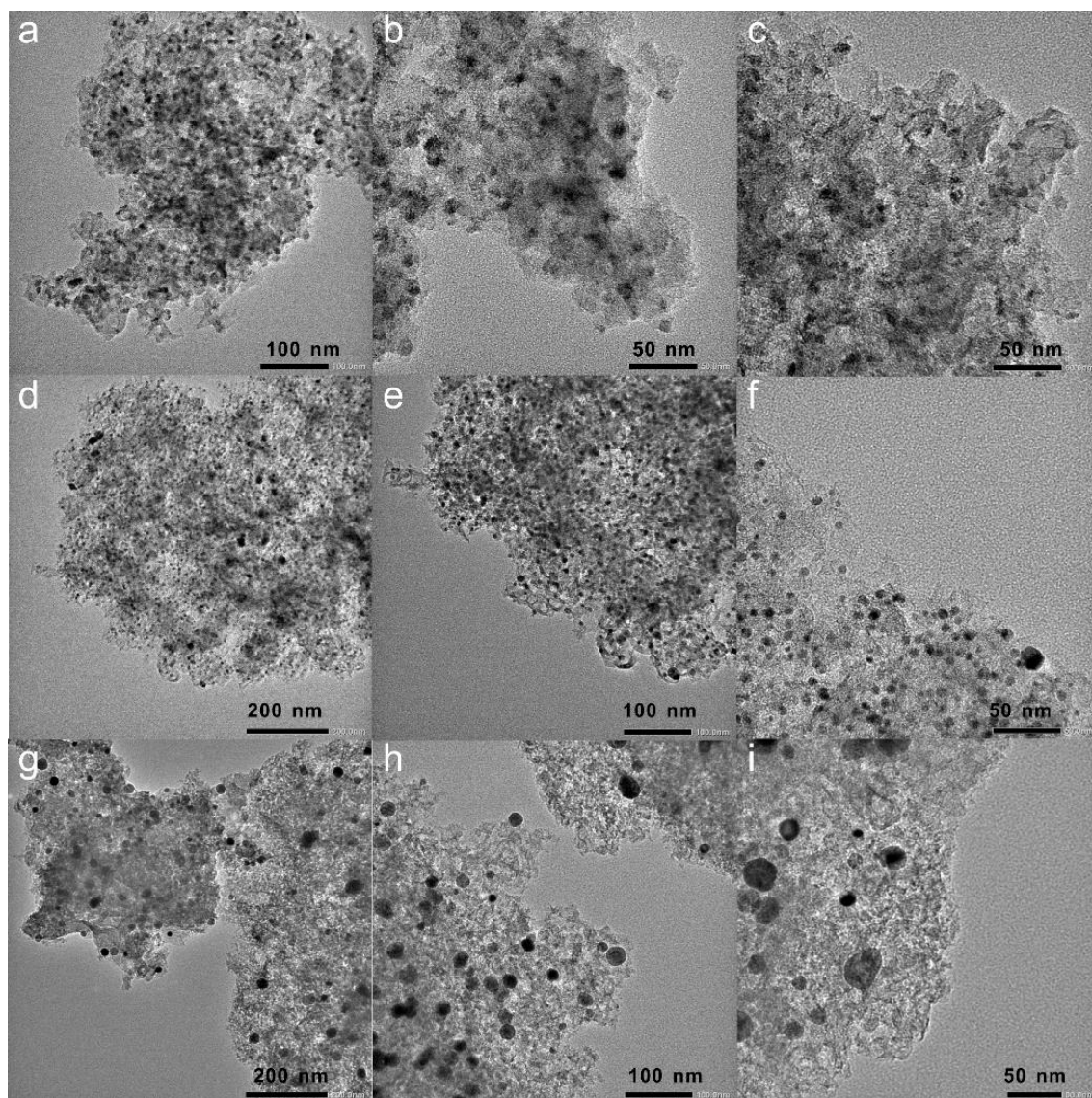
**Figure S5** XPS spectrum of Pd/C catalyst reduced at 800 °C in 5% H<sub>2</sub>/Ar.



**Figure S6** (a) C 1s XPS spectra, (b) O 1s XPS spectra, and (c) Pd 3d XPS spectra of the Pd/C catalyst reduced at 60 °C in 5% H<sub>2</sub>/Ar and then temperature-programmed to 500 °C and 800 °C for reduction.

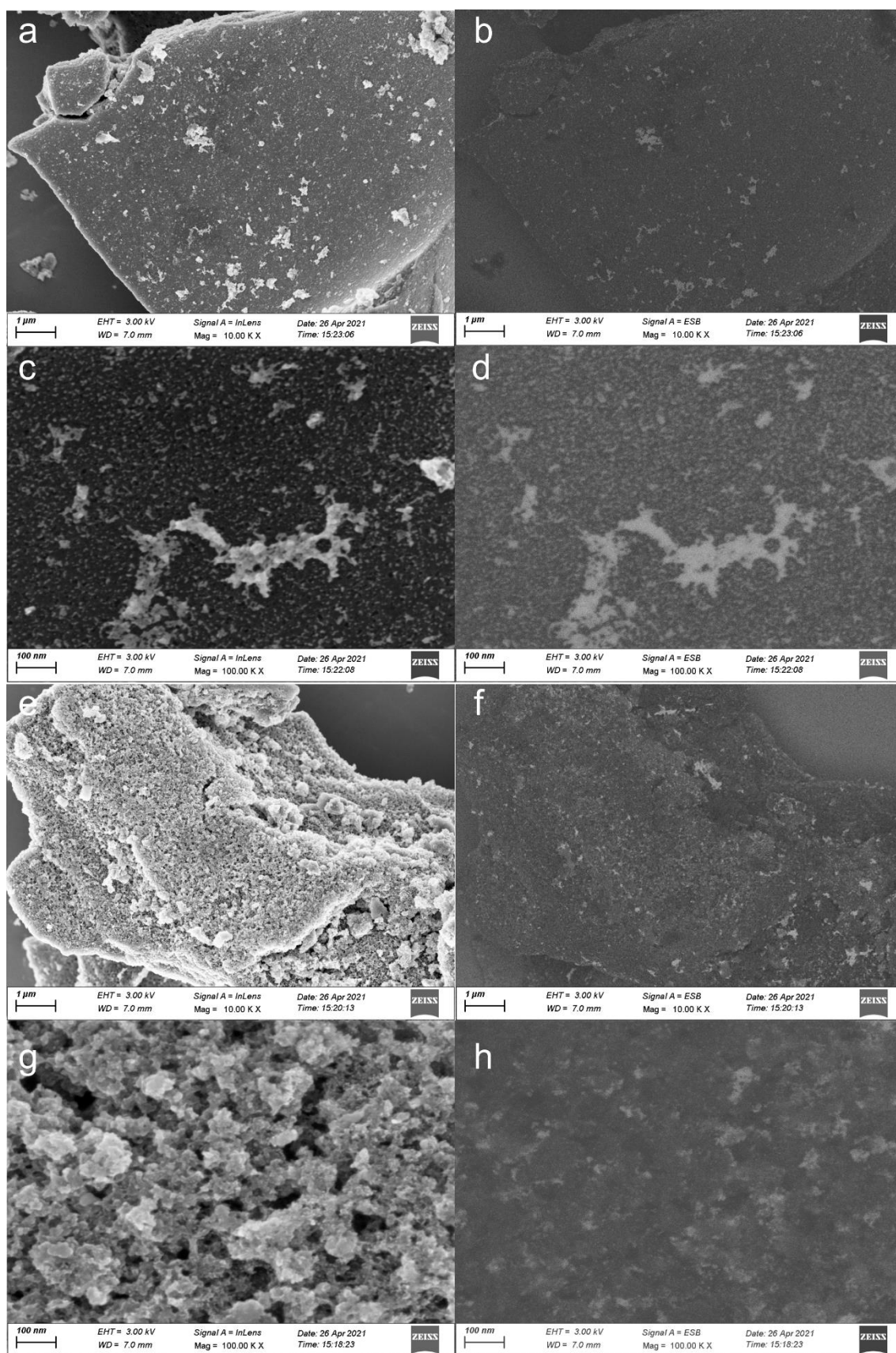


**Figure S7** CO titration analysis s of 60 °C-H<sub>2</sub>-Pd/C, 500 °C-TPR-Pd/C and 800 °C-TPR-Pd/C.

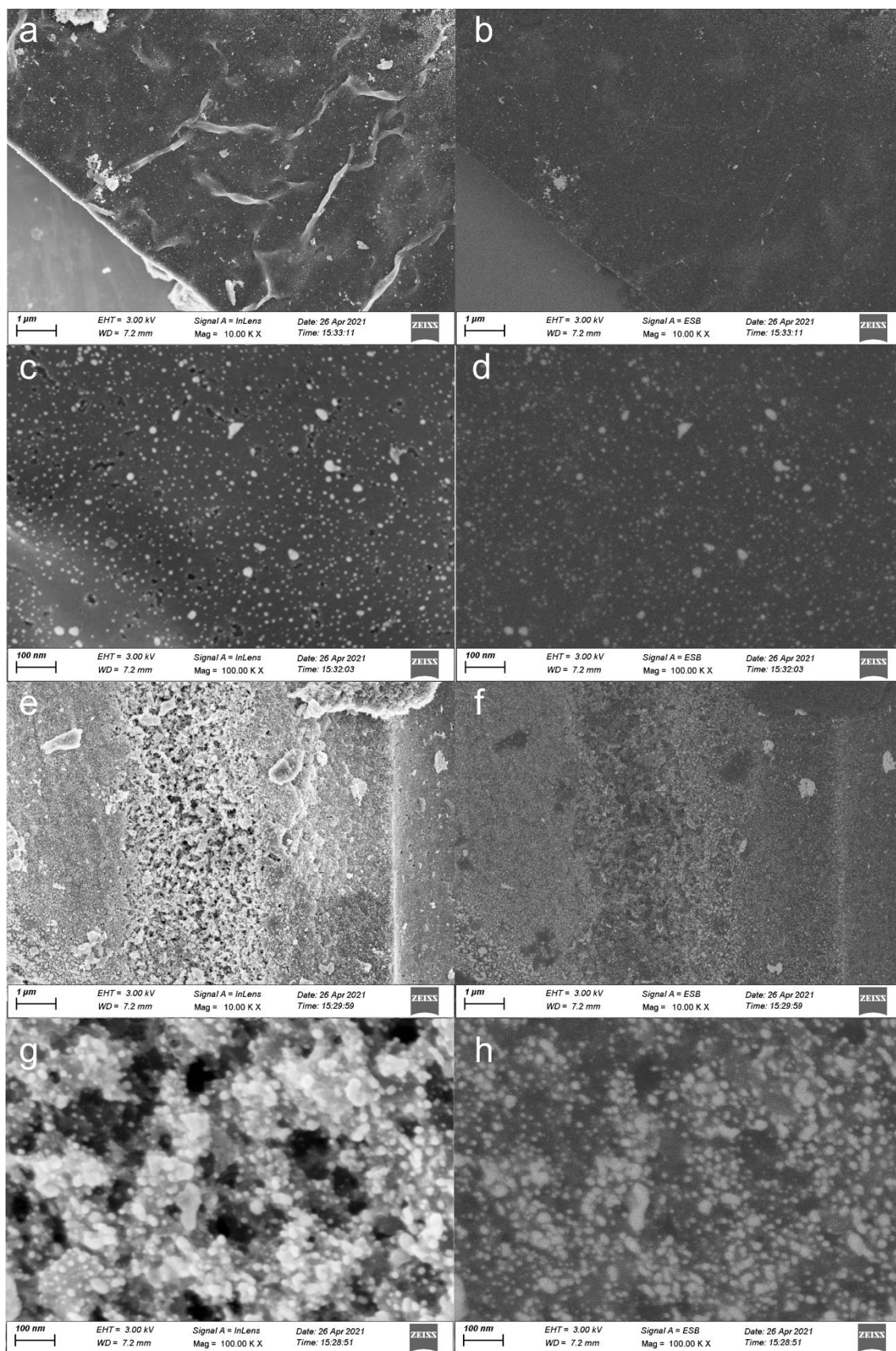


**Figure S8** TEM images of Pd/C catalyst reduced at (a–c) 60 °C in 5% H<sub>2</sub>/Ar and temperature-programmed to (d–f) 500 °C and (g–i) 800 °C for reduction.

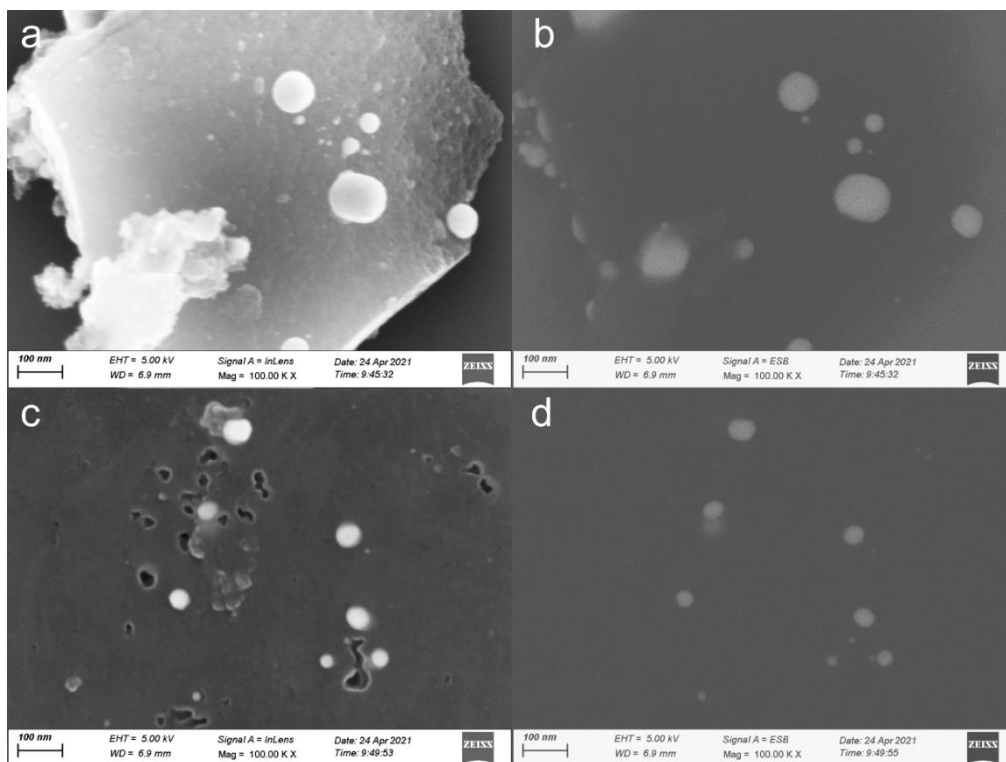




**Figure S9** SEM images of Pd/C catalyst reduced at 60 °C in 5% H<sub>2</sub>/Ar. The detectors are (a, c, e, g) InLens and (b, d, f, h) ESB.



**Figure S10** SEM images of Pd/C catalyst temperature-programmed to 500 °C in 5%  $\text{H}_2/\text{Ar}$  for reduction. The detectors are (a, c, e, g) InLens and (b, d, f, h) ESB.



**Figure S11** SEM images of Pd/C catalyst temperature-programmed to 800 °C in 5% H<sub>2</sub>/Ar for reduction. The detectors are (a, c) InLens and (b, d) ESB.

**Table S3** The values of the data points in Figure 4a (FCC, regular tetrahedron) and their corresponding calculation formulas

Entry	D	$N = \frac{D(D+1)(D+2)}{6}$	$X(\text{surface}) = 3(D-2)(D-1)/2+1$	$X(\text{perimeter}) = 3(D-2)$	$X(\text{corner}) = 3$	$\ln k = \ln (X/N)$			$\Delta = D$	$d = \frac{0.275}{\Delta}$	$\ln d$
1	10	220	109	24	3	-0.702	-2.216	-4.295	10	2.75	1.012
2	20	1540	514	54	3	-1.097	-3.351	-6.241	20	5.5	1.705
3	40	11480	2224	114	3	-1.641	-4.612	-8.250	40	11	2.398
4	80	88560	9244	234	3	-2.260	-5.936	-10.293	80	22	3.091
5	160	695520	37684	474	3	-2.915	-7.291	-12.354	160	44	3.784
6	15	680	274	39	3	-0.909	-2.859	-5.423	15	4.125	1.417
7	30	4960	1219	84	3	-1.403	-4.078	-7.411	30	8.25	2.110
8	60	37820	5134	174	3	-1.997	-5.382	-9.442	60	16.5	2.803
9	120	295240	21064	354	3	-2.640	-6.726	-11.497	120	33	3.497

D: the number of atoms on the edge of the model particle; N: the number of atoms in the model particle; X(surface), X(perimeter), and X(corner): the number of atoms on the surface, perimeter, and corner of the model particle; k: activity per amount of substance;  $\Delta$ : the particle edge length in atomic diameter units; d: the Pd particle edge length in nanometer units.

**Table S4** The values of the data points in Figure 4b (FCC, regular tetrahedron) and their corresponding calculation formulas

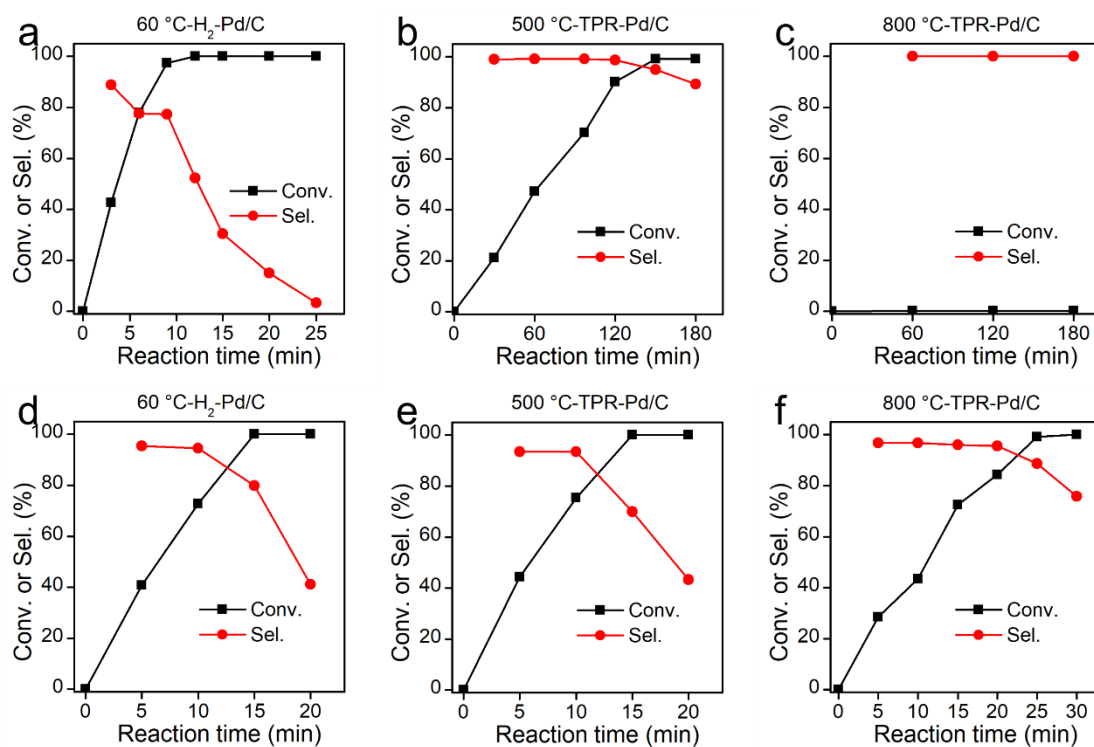
Entry	D	$N = (2D-1)(2D)(2D+1)/6 - 4(D-1)D(D+1)/6$	$X(\text{surface}) = 7(D-2)(D-1)/2 + (2D-1)$	$X(\text{perimeter}) = 3(D-2)$	$X(\text{corner}) = 3$	$\ln k = \ln (X/N)$			$\Delta = D$	$d = 0.275\Delta$	$\ln d$
1	10	670	271	24	3	-0.905	-3.33	-5.409	10	2.75	1.012
2	20	5340	1236	54	3	-1.463	-4.59	-7.484	20	5.5	1.705
3	40	42680	5266	114	3	-2.092	-5.93	-9.563	40	11	2.398
4	80	341360	21726	234	3	-2.754	-7.29	-11.64	80	22	3.091
5	160	2730720	88246	474	3	-3.432	-8.66	-13.72	160	44	3.784
6	15	2255	666	39	3	-1.22	-4.06	-6.622	15	4.125	1.417
7	30	18010	2901	84	3	-1.826	-5.37	-8.7	30	8.25	2.11
8	60	144020	12096	174	3	-2.477	-6.72	-10.78	60	16.5	2.803
9	120	1152040	49386	354	3	-3.15	-8.09	-12.86	120	33	3.497

**Table S5** The values of the data points in Figure 4c (FCC, cube) and their corresponding calculation formulas

Entry	D	$N = D[D^2 + (D-1)^2] + (D-1)[D(D-1) + D(D-1)]$	$X(\text{surface}) = 5 \cdot 2(D-1)^2 - (2D-3)$	$X(\text{perimeter}) = 4(D-2)$	$X(\text{corner}) = 4$	$\ln k = \ln (X/N)$			$\Delta = (2D-2)/\sqrt{2}+1$	$d = 0.275\Delta$	$\ln d$
1	8	1688	477	24	4	-	-	-	10.899	2.997	1.098
2	16	14896	2221	56	4	-	-	-	22.213	6.109	1.81
3	32	125024	9549	120	4	-	-	-	44.841	12.33	2.512
4	64	1024192	39565	248	4	-	-	-	90.095	24.78	3.21
5	128	8290688	161037	504	4	-	-	-	180.61	49.67	3.905
6	12	6084	1189	40	4	-	-	-	16.556	4.553	1.516
7	24	51912	5245	88	4	-	-	-	33.527	9.22	2.221
8	48	428688	21997	184	4	-	-	-	67.468	18.55	2.921
9	96	3483936	90061	376	4	-	-	-	135.35	37.22	3.617

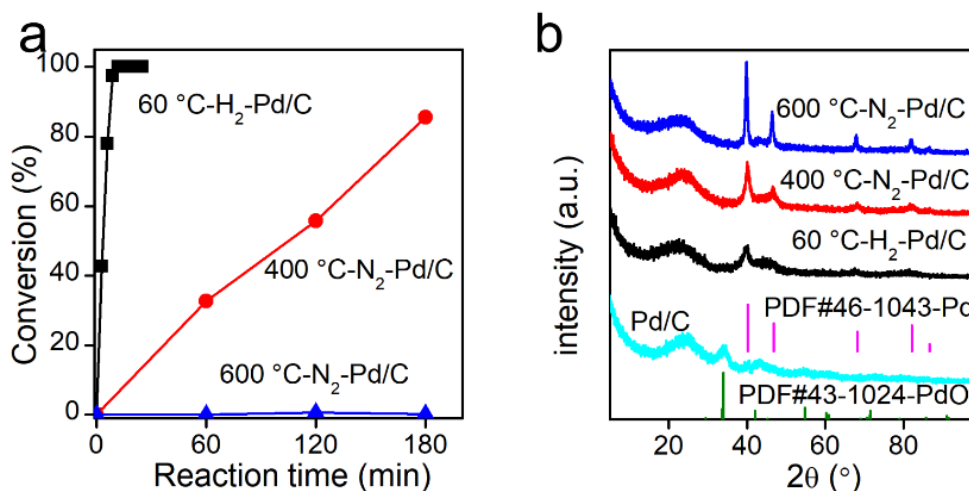
**Table S6** The values of the data points in Figure 4d (BCC, cube) and their corresponding calculation formulas

Entry	D	$N = D^3 + (D-1)^3$	$X(\text{surface}) = 5(D-1)^2 - (2D-3)$	$X(\text{perimeter}) = 4(D-2)$	$X(\text{corner}) = 4$	$\ln k = \ln (X/N)$			$\Delta = (2D-2)/\sqrt{3}+1$	$d = 0.275\Delta$	$\ln d$
1	8	855	232	24	4	-	-	-	9.0829	2.498	0.915
2	16	7471	1096	56	4	-	-	-	18.321	5.038	1.617
3	32	62559	4744	120	4	-	-	-	36.796	10.12	2.314
4	64	512191	19720	248	4	-	-	-	73.746	20.28	3.01
5	128	4145535	80392	504	4	-	-	-	147.65	40.6	3.704
6	12	3059	584	40	4	-	-	-	13.702	3.768	1.327
7	24	25991	2600	88	4	-	-	-	27.558	7.578	2.025
8	48	214415	10952	184	4	-	-	-	55.271	15.2	2.721
9	96	1742111	44936	376	4	-	-	-	110.7	30.44	3.416

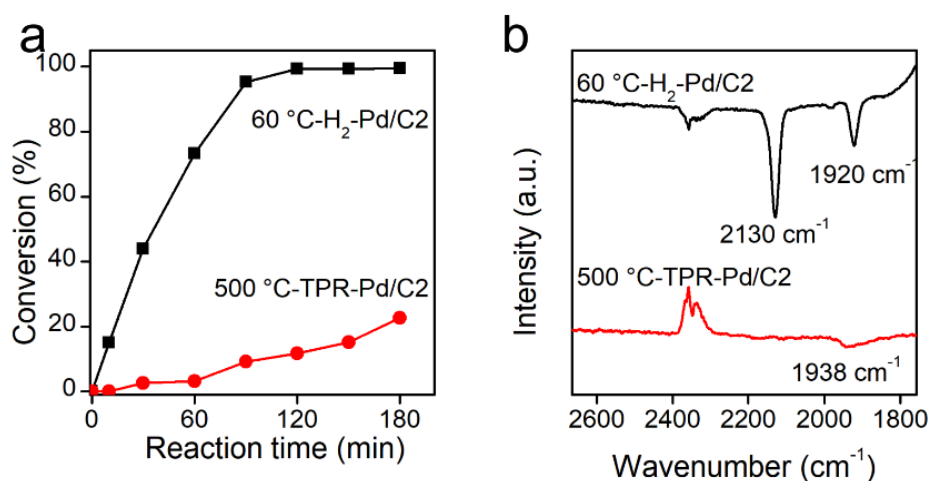


**Figure S12** Catalytic activity for (a–c) acetophenone and (d–f) phenylacetylene hydrogenation of Pd/C catalysts reduced at 60 °C in 5% H<sub>2</sub>/Ar and via temperature programming to 500 °C and 800 °C. Reaction conditions: 60 °C, 1 bar H<sub>2</sub>, 5 mL ethanol, n(acetophenone):n(Pd) = 500:1; n(phenylacetylene):n(Pd) = 2000:1.

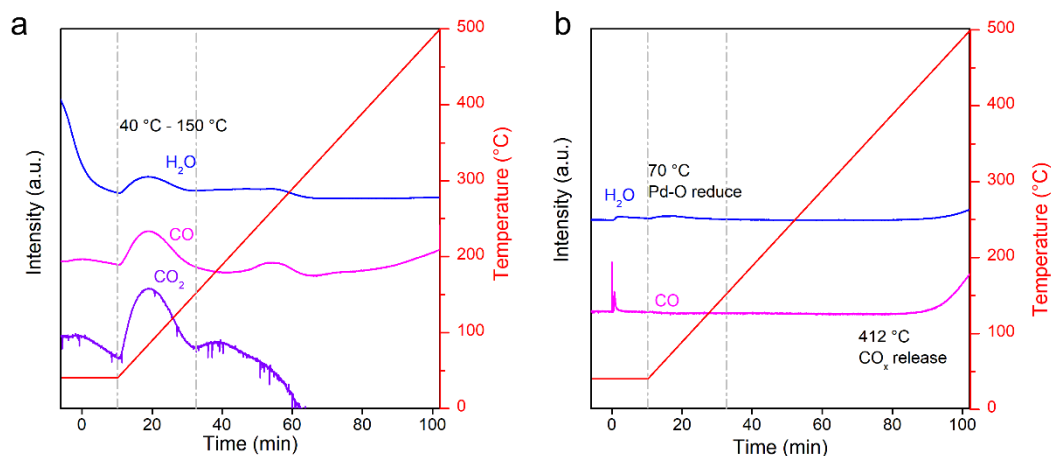




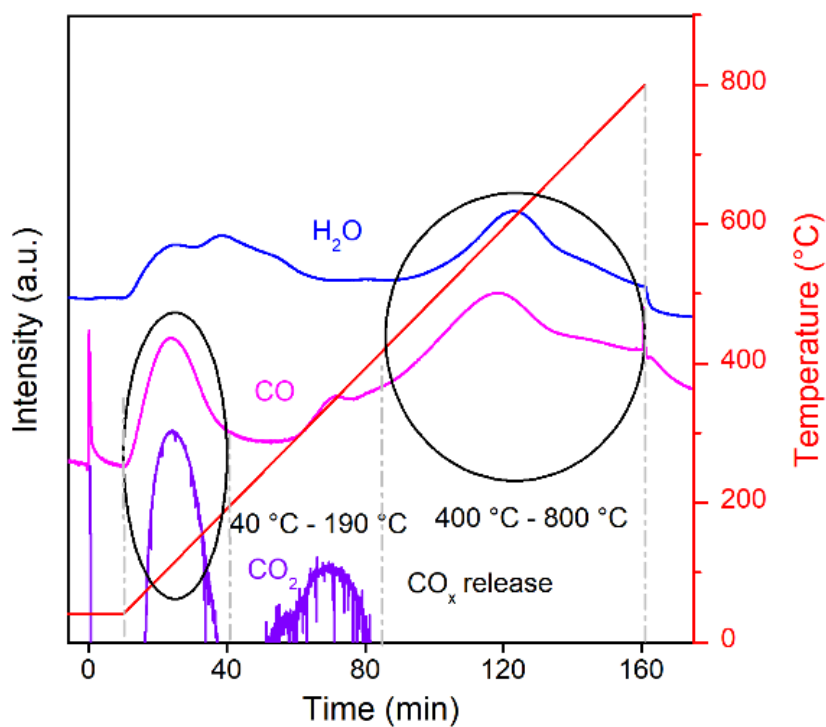
**Figure S13** (a) Catalytic activity for acetophenone hydrogenation of Pd/C catalyst reduced at 60 °C in 5% H<sub>2</sub>/Ar and at 400 °C and 600 °C in N<sub>2</sub> for 2 hours. Reaction conditions: 60 °C, 1 bar H<sub>2</sub>, 5 mL ethanol, n(acetophenone):n(Pd) = 500:1. (b) XRD of initial Pd/C, Pd/C reduced at 60 °C in 5% H<sub>2</sub>/Ar, and Pd/C reduced at 400 °C and 600 °C in N<sub>2</sub> for 2 hours.



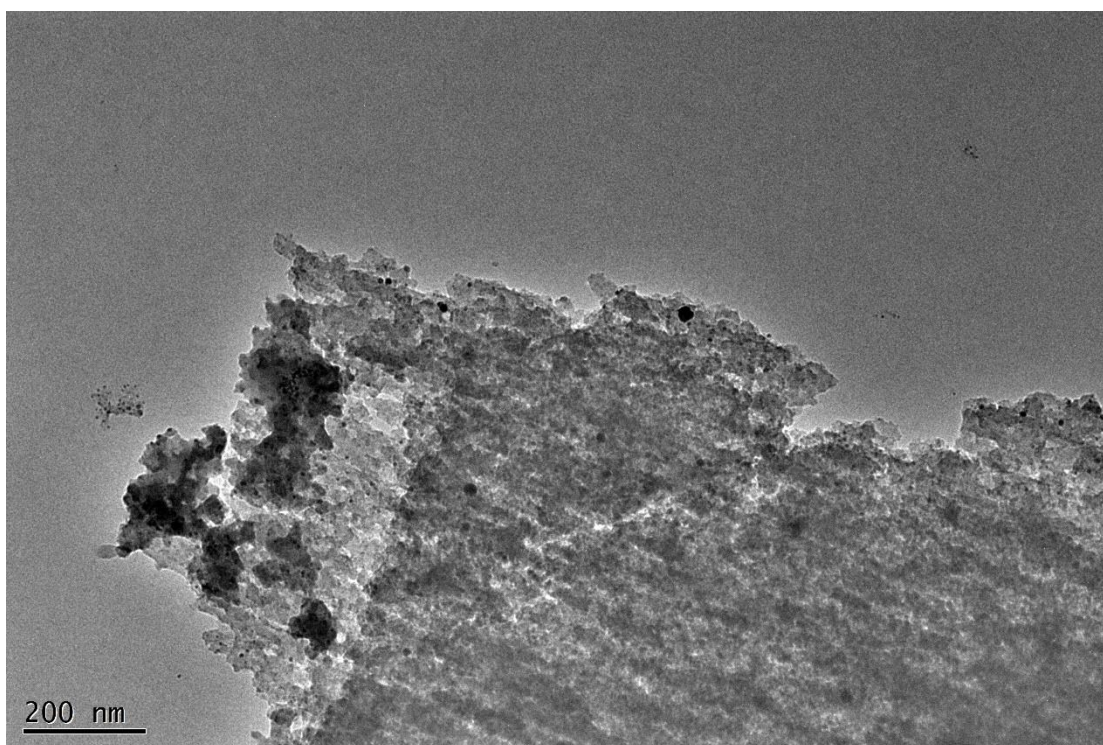
**Figure S14** (a) Catalytic activity for acetophenone hydrogenation and (b) CO-DRIFTS of 60 °C-H<sub>2</sub>-Pd/C<sub>2</sub> and 500 °C-TPR-Pd/C<sub>2</sub>. Reaction conditions: 60 °C, 1 bar H<sub>2</sub>, 5 mL ethanol, n(acetophenone):n(Pd) = 500:1. Prior to CO-DRIFTS collection, the sample was purged successively with Ar, 5% CO/Ar, and Ar for 10 min each.



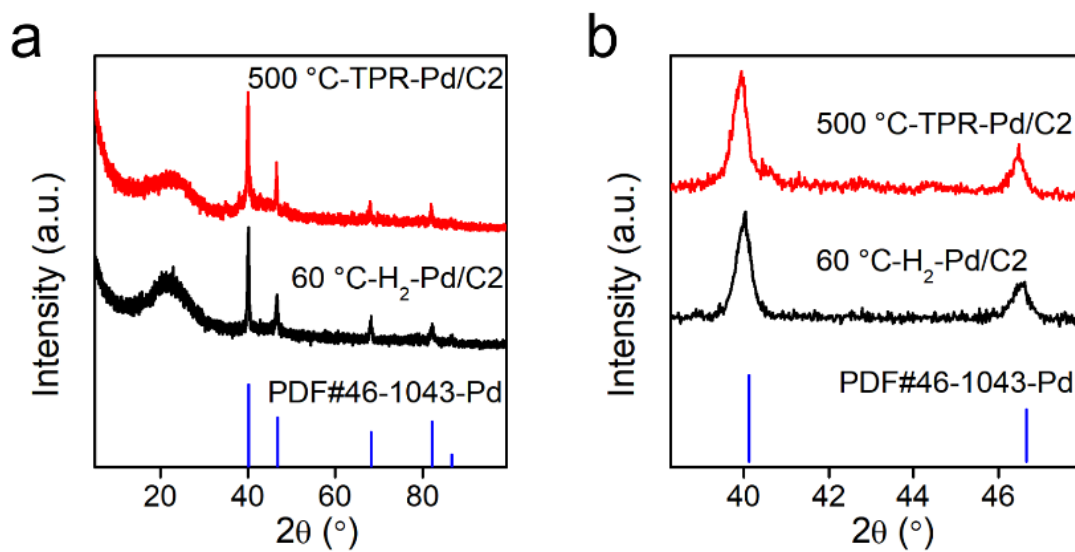
**Figure S15** (a) The *in-situ* MS signals of the TPD process for the Pd/C2 in N<sub>2</sub>. (b) The *in-situ* MS signals of the TPR process for the 500 °C-TPD-Pd/C2 in H<sub>2</sub>. The test of (b) is immediately followed by (a), and the vertical coordinates used in the two graphs of (a) and (b) are exactly the same.



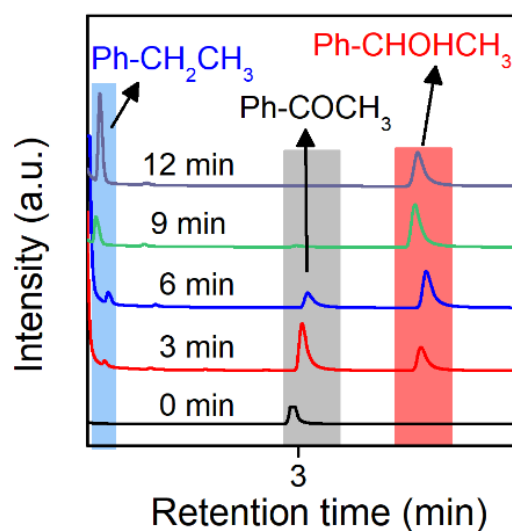
**Figure S16** The *in-situ* MS signals of the TPR process for the C2 in H<sub>2</sub>.



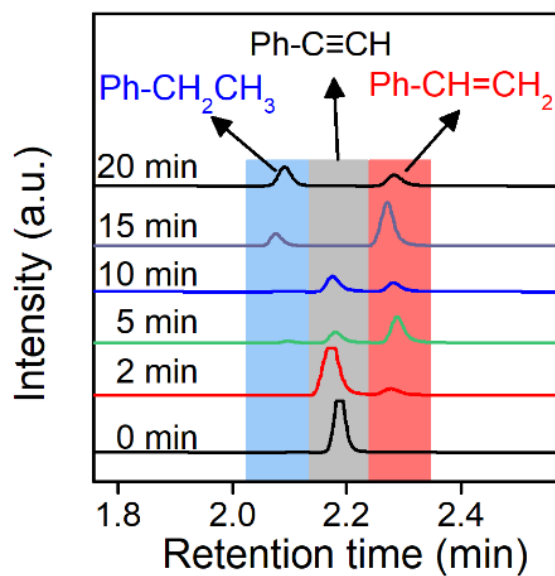
**Figure S17** TEM images of 60 °C-H<sub>2</sub>-Pd/C<sub>2</sub> catalyst.



**Figure S18** (a) Original XRD and (b) partially enlarged XRD of 60 °C-H<sub>2</sub>-Pd/C<sub>2</sub> and 500 °C-TPR-Pd/C<sub>2</sub>.



**Figure S19** Chromatographic spectrum for acetophenone hydrogenation of Pd/C catalysts reduced at 60 °C in 5% H<sub>2</sub>/Ar. Reaction conditions: 60 °C, 1bar H<sub>2</sub>, 5 mL ethanol, n(acetophenone):n(Pd) = 500:1.



**Figure S20** Chromatographic spectrum for phenylacetylene hydrogenation of Pd/C catalysts reduced at 60 °C in 5% H<sub>2</sub>/Ar. Reaction conditions: 60 °C, 1bar H<sub>2</sub>, 5 mL ethanol, n(phenylacetylene):n(Pd) = 2000:1.