Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Facile construction of ultrastable alumina anchored palladium catalysts via a designed one pot strategy for enhanced methane oxidation

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Catalyst characterization

Dispersion and particle diameter of palladium was calculated through conducting the in-situ DRIFTS of adsorbed CO (CO-DRIFTS) and Chemisorption of CO experiments. CO-DRIFTS on catalysts was measured at 30 ℃. Before CO adsorption, the catalyst was pretreated for 1 h in H_2 stream at 300 ℃, and then cooled to 30 ℃ under He flow. After background spectra were recorded, CO was introduced until the catalyst was saturated, afterward the sample was purged by He for 30 min to obtain the desorption spectra. The reaction stoichiometry of CO absorbing on Pd (n) was determined in terms of the peak area ratio of linear adsorbed CO bonds, compressed-bridge and isolated-bridge bonds, in consideration of different Pd/CO atomic ratio.[1] Chemisorption of CO was implemented on a Micromeritics AutoChem 2910 equipment with a thermal conductivity detector (TCD), the dosage of catalyst was 100 mg. After pretreatment (10 vol. % of H_2/Ar flow, 300 °C for 30 min), the pulse adsorption of CO (5 vol. % of CO/He) was carried out until saturation was achieved at 30 °C, then dispersion of Pd (D) and the average cluster diameter of palladium (d_{Pd}) was calculated by Eq. (1) and (2), respectively.[2, 3]

$$D(\%) = 100\frac{V_m n M_{Pd}}{22414 m_{cat} W_{Pd}} \qquad (1)$$

$$d_{Pd}(nm) = \frac{6 \cdot v}{D \cdot a} \qquad (2)$$

Where V_m (mL) is the amount of adsorbed CO on catalysts (STP), n denotes the reaction stoichiometry (determined through the CO-DRIFTS), M_{Pd} is the atomic weight of Pd (106.4 g mol^{-1}), m_{cat} is the mass of the catalysts (g), W_{Pd} denotes the loading amount of Pd (0.5 %). Where v is the average volume occupied by a single metal atom in the bulk phase (14.70×10^{-3} nm^3 for Pd), *a* is the average surface area occupied by an exposed metal surface atom (7.93×10^{-2} nm^2 for Pd).

Temperature programmed desorption of O_2 (O_2-TPD), temperature programmed oxidation (TPO) and temperature programmed reduction of CH_4 (CH_4-TPR) were implemented on a Micromeritics AutoChem II 2920 instrument equipped with a TCD and a Hiden QIC-20 mass spectrometer. The gas flow rate in each case was set to 30 mL min^{-1}. For O_2-TPD tests, 150 mg catalyst was pretreated under He flow at 350 °C for 30 min. Then 2 vol.% O_2/He was switched on and held for another 30 min. Afterward, the catalyst was cooled to 50 °C under 2 vol.% O_2/He then heated to 950 °C under He flow, the mass signal of O_2 (m/z=32) was recorded. The dosage of catalyst was 200 mg for TPO and CH_4-TPR experiments. In TPO tests, samples were heated up to 350 °C under He flow and held for 30 min, then cooled to 100 °C. Afterward, two consecutive heating/cooling cycles between 100 and 900 °C at a rate of 10 °C min^{-1} were performed under 2 vol. % O_2/He gas flow, and the oxygen concentration was monitored by the TCD. For CH_4-TPR, the sample was pretreated in a He flow at 300 °C for 30 min, then cooled to 30 °C. Afterward, the sample was heated from 30 °C to 900 °C with a heating rate of 10 °C/min under 10 vol. % CH_4/Ar gas flow, and the characteristic signals of CH_4 (m/z=16), CH_3 (m/z=15), CO_2 (m/z=44), H_2O (m/z=18), CO (m/z=28), H_2 (m/z=2) were continuously monitored by mass spectrometer as a function of time and temperature.

Table S1. Textural parameters of catalysts.

Sample	O-500	I-500	O-800	I-800	O-900	I-900
S_{BET} (m^2 g^{-1})	370.2	352.1	239.4	218.1	181.1	159.0
V_P (cm^3 g^{-1})	0.7	0.8	0.6	0.8	0.6	0.7
D_P (nm)	5.5	7.3	7.5	10.4	9.7	12.8

Table S2. Dispersion and particle size of palladium species determined through IR Bands of CO absorbed and CO chemisorption

Catalyst	Peak center (cm^{-1})	Peak assignment [1]	Pd/CO atomic ratio [1]	Proportion (%)	CO uptake (μmol/g) [a]	Dispersion (%) [b]	d $_{Pd}$ (nm) [c]
O-500	1854	Isolated-bridge	2	15.5	26.2	81.7	1.4
	1905	Compressed-bridge	1.5	62.1			
	2058/ 2076	Linear	1	22.4			
I-500	1890	Isolated-bridge	2	6.6	30.5	77.0	1.4
	1920	Compressed-bridge	1.5	24.0			
	2055/ 2082	Linear	1	69.4			
O-800	1863	Isolated-bridge	2	7.9	27.2	80.4	1.4
	1912	Compressed-bridge	1.5	61.7			
	2054/ 2076	Linear	1	30.4			
I-800	1882	Isolated-bridge	2	4.8	27.0	71.4	1.6
	1917	Compressed-bridge	1.5	38.8			
	2054/ 2080	Linear	1	56.4			
O-900	1857	Isolated-bridge	2	16.7	11.1	35.9	3.1
	1919	Compressed-bridge	1.5	71.4			
	2040/ 2069	Linear	1	11.9			
I-900	1900	Isolated-bridge	2	12.7	9.2	24.2	4.6
	1947	Compressed-bridge	1.5	22.0			
	2077/ 2125/ 2161	Linear	1	65.3			

a. Determined by CO-Chemisorption.

b. Determined by CO-Chemisorption and CO-DRIFTS according to Eq. (1), where the peak assignment and Pd/CO atomic ratio was referred to Ref. [1].

c. Determined through Eq. (2).

Table S3. Comparison with literatures about the performance of catalysts for methane oxidation.

Catalysts	Pd wt.%	Calcination temperature (°C)	Synthesis method	Pretreatment	Reaction conditions		T_{99} (℃)
					CH_4 (%)	GHSV (mL g^{-1} h^{-1})	
O-800 (Pd-Al_2O_3) This work	0.5	800	One pot method	On-stream test in the presence and absence of water, then activated with methane (400 ℃, 1 vol. % CH_4, 20 min)	1	50,000	355
Pd/Al_2O_3 [4]	2	500	Impregnation method	500 ℃ (10 vol. % O_2/N_2, 10 min), and 500 ℃ (3 vol. % H_2/N_2, 10 min)	0.4	300,000	450
Pd/Al_2O_3 (commercial catalyst) [5]	2	-	-	-	1	36,000	425
Pd/6P-OMA [6]	0.5	500	Incipient wetness impregnation method with phosphorus doped alumina carrier	400 °C (10 vol % H_2/Ar, 30 min)	1	50,000	321
$Pd@CeO_2/H-Al_2O_3$ [7]	1	850	Adsorption of $Pd@CeO_2$ particles onto hydrophobic Al_2O_3	250 °C (5 vol. % O_2/Ar, 30 min); 850 °C (reaction atmosphere, 1h)	0.5	200,000	400
PdCeM [8]	0.81	900 (in a mini ball mill)	One-step dry ball-milling method	Cycled under reaction conditions between room temperature and 1173 K for 2 heating/cooling cycles	0.5	200,000	627
Pd-Ce $NW@SiO_2$ [5]	1.5	600	All-in-one strategy (aqueous solution mixed)	-	1	36,000	350
PdO/CeO_2-0.1/Co_3O_4 [9]	5.37	400	Synthesis of $Pd/Co(OH)_2$, then mixed with $Ce(NO_3)_3$	-	0.5	-	350

Table S4. XPS spectra analysis of Pd $3d_{5/2}$ for catalysts

Catalyst	Binding energy (eV)						Peak area ratio		
	Pd^0			Pd^{2+}			Pd^{2+} / Pd^0		
	a	b	c	a	b	c	a	b	c
O-500	335.40	335.40	335.38	336.54	336.30	336.76	2.78	2.49	2.29
I-500	335.36	335.40	335.16	336.93	336.73	336.46	3.78	5.85	1.91
O-800	335.40	335.36	335.32	336.30	336.31	336.54	3.22	2.64	1.52
I-800	335.17	335.38	335.27	336.60	336.69	336.39	4.11	5.34	1.43
O-900	335.26	335.33	335.12	336.39	336.43	336.31	4.24	4.14	0.83
I-900	335.40	335.38	335.10	336.83	336.73	336.32	5.46	5.72	0.66

(a) for the fresh catalysts before reaction.

(b) for the used catalysts after the catalytic activity testing.

(c) for the catalysts after CH_4 reduction treatment (400 ℃, 20 min).

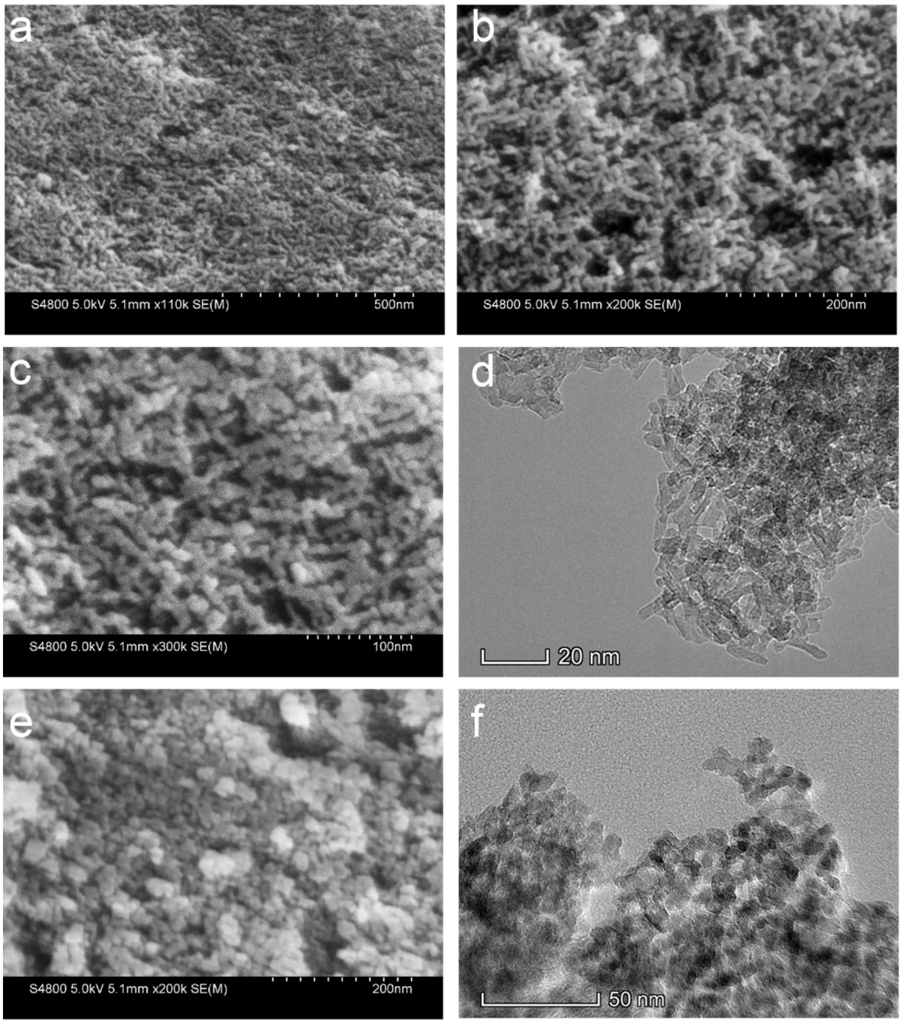
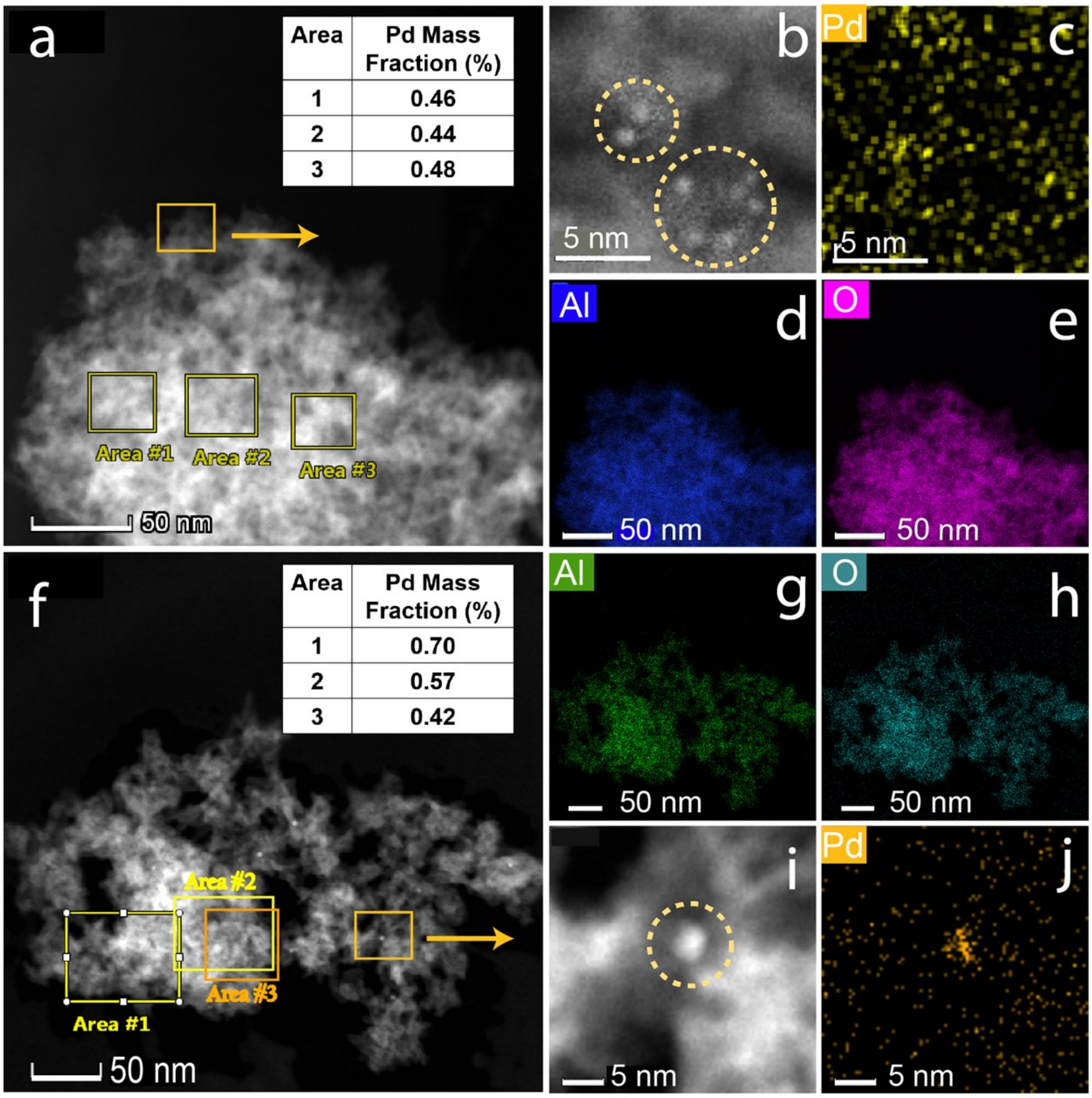


Fig. S1. SEM images (a-c) and TEM image (d) of O-800 catalyst, SEM image (e) and TEM (f) image of I-800 catalyst.



Area	Pd Mass Fraction (%)
1	0.46
2	0.44
3	0.48

Area	Pd Mass Fraction (%)
1	0.70
2	0.57
3	0.42

Fig. S2. HAADF-STEM images and EDS element-mapping analysis of the fresh O-800 (a-e) and I-800 catalyst (f-j).

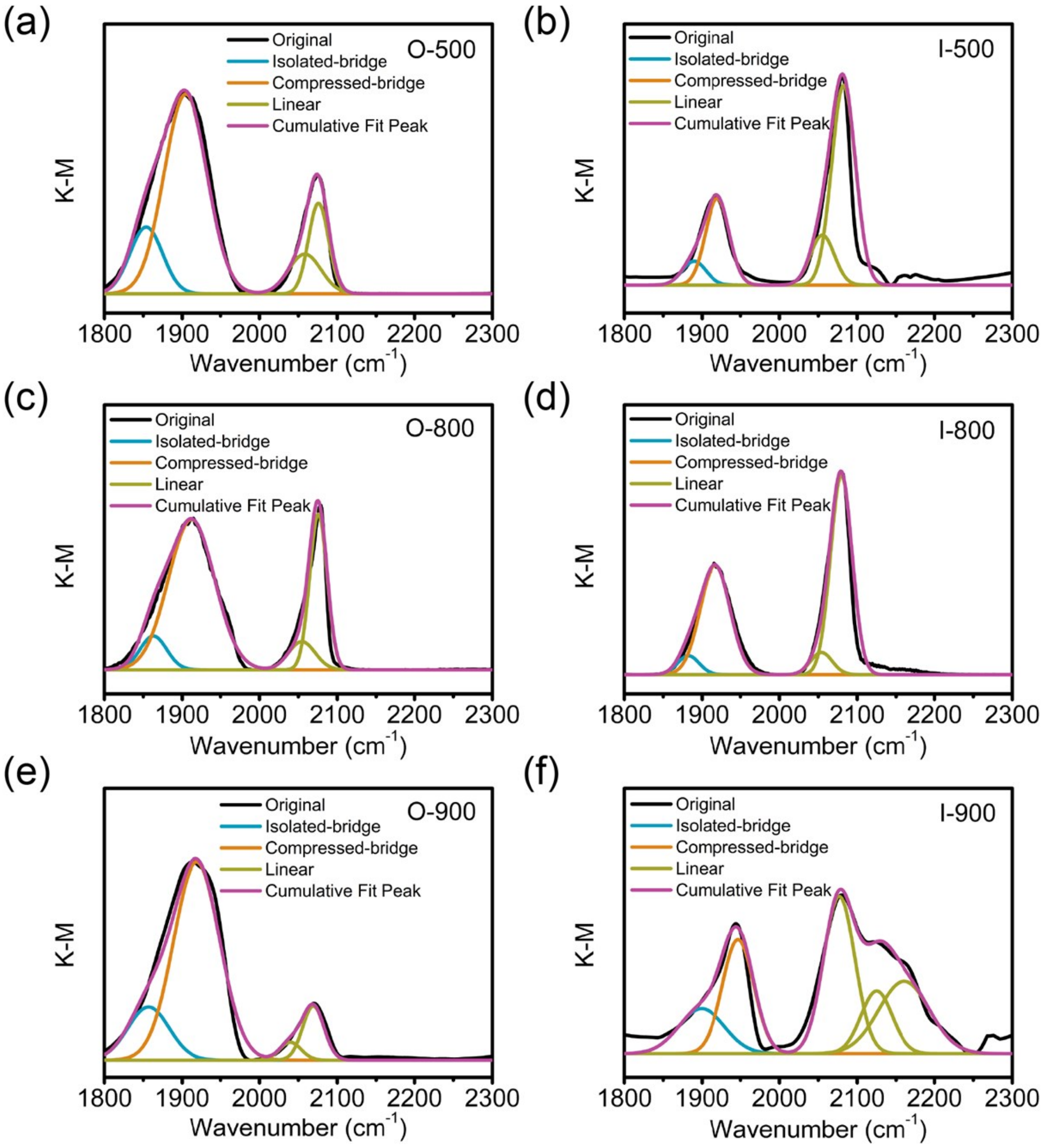
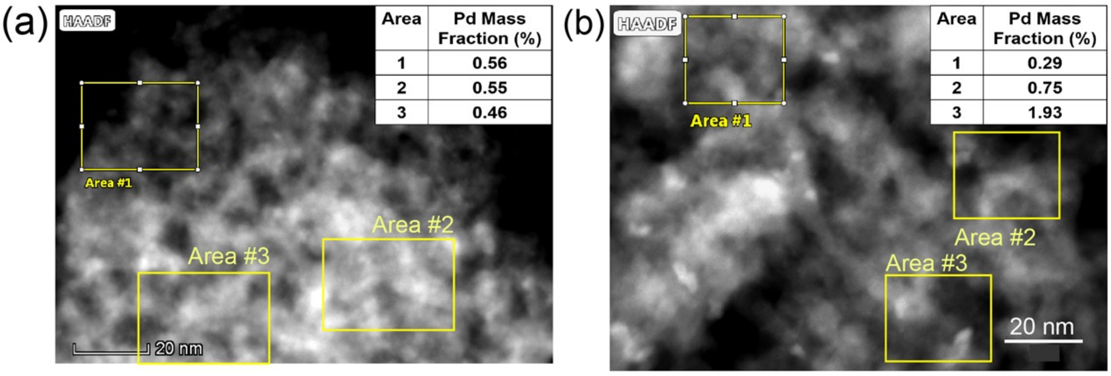


Fig. S3. In situ DRIFT spectra of the adsorption of CO on catalysts and deconvolution results.



Area	Pd Mass Fraction (%)
1	0.56
2	0.55
3	0.46

Area	Pd Mass Fraction (%)
1	0.29
2	0.75
3	1.93

Fig. S4. HAADF-STEM images and EDS analysis of the used O-800 (a) and I-800 catalyst (b).

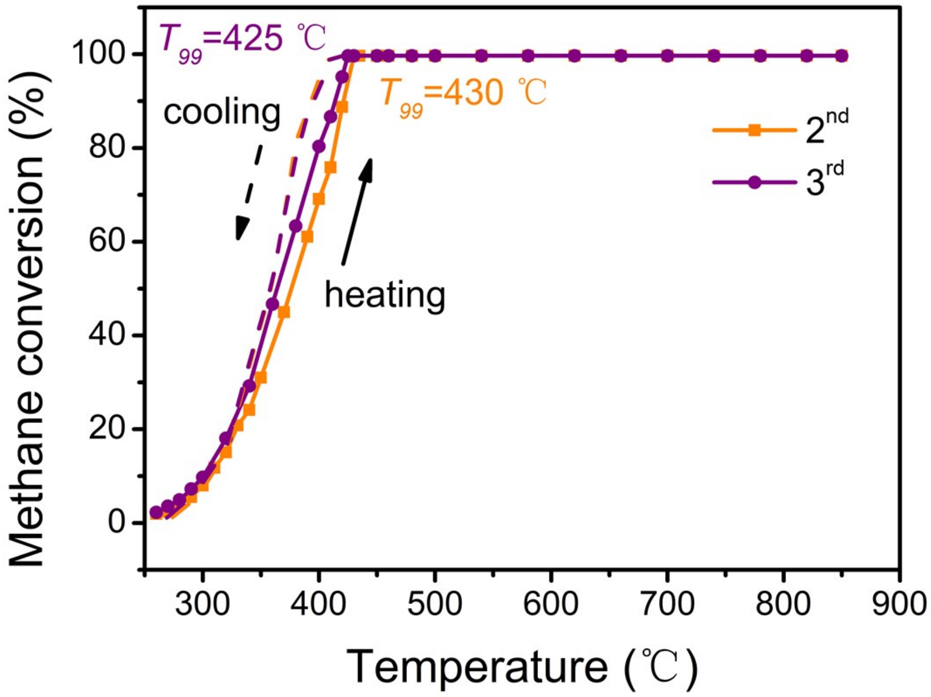


Fig. S5. Cycling stability test over O-800 catalyst; Reaction condition: 1 vol. % CH_4, 5 vol.% O_2 in N_2 as balance gas, GHSV = 50,000 mL h^{-1} g^{-1}.

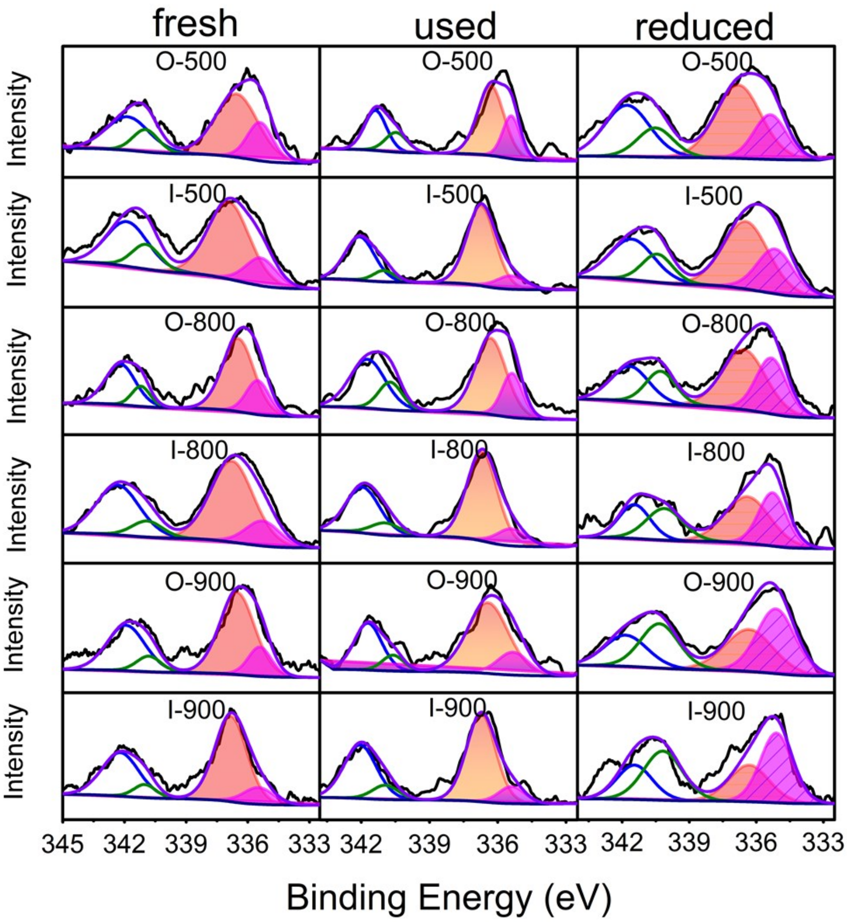


Fig. S6. Pd 3d XPS spectra of catalysts. left panel: fresh catalysts, middle panel: used catalysts, right panel: catalysts reduced by CH_4 (400 ℃, 20 min).

References

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