

Supporting Information

Construction and Evolution of Active Palladium Species on Phase-Regulated Reducible TiO₂ for Methane Combustion

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Catalyst characterization

Temperature programmed oxidation by O₂ (O₂-TPO): samples were heated up to 350 °C under He flow and held for 30 min, then cooled to 100 °C. Subsequently, the catalyst was exposed to a mixture of 2 vol.% O₂ in He (flow rate: 30 mL min⁻¹), and the temperature was then increased to 800 °C (ramp rate: 10 °C min⁻¹) and cooled down. The oxygen concentration was monitored by the TCD.

Temperature programmed desorption of O₂ (O₂-TPD): 100 mg catalyst was pretreated under He flow at 350 °C for 30 min. Then 2 vol. % O₂/He was switched on and held for another 30 min. Afterward, the catalyst was cooled to 50 °C under 2 vol. % O₂/He then heated to 900 °C under He flow, the mass signal of O₂ (m/z = 32) was recorded.

Temperature programmed reduction by H₂ (H₂-TPR): Prior to reduction tests, each sample (100 mg) was pretreated in an argon flow (flow rate: 30 mL min⁻¹) holding at 300 °C for 30 min and was then cooled to 50 °C. The data were collected from 50 to 800 °C under 10 vol. % H₂/Ar (flow rate: 30 mL min⁻¹) at a heating rate of 10 °C min⁻¹. The results were obtained by the TCD.

Temperature programmed reduction of CH₄ (CH₄-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⁻¹ under 10 vol. % CH₄/Ar gas flow, and the characteristic signals of CH₄ (m/z = 16), CH₃ (m/z = 15), CO₂ (m/z = 44), H₂O (m/z = 18), CO (m/z = 28), H₂ (m/z = 2) were continuously monitored by mass spectrometer as a function of time and temperature.

Table S1. Performance comparison of some Pd/TiO₂ catalysts.

sample	Pd loading amount (wt %)	Reaction condition	T ₅₀ (°C)	T ₉₉ (°C)	Ref
PT-1000	0.5	1 vol. % CH ₄ , 10 vol. % O ₂ and N ₂ equilibrium gas GHSV=30 000 mL g ⁻¹ h ⁻¹	334	370	This work
Pd/TiO ₂	5	2 vol. % CH ₄ , 8 vol. % O ₂ and N ₂ equilibrium gas GHSV=150000 mL g ⁻¹ h ⁻¹	350	>500	Niu et al ¹
Pd@TiO ₂	1	5 vol. % CH ₄ , 1 vol. % O ₂ and N ₂ equilibrium gas GHSV=170000 mL g ⁻¹ h ⁻¹	350	600	Ali et al ²
Pd/TiO ₂	0.4	300 ppmv CH ₄ in air, GHSV=21000 mL g ⁻¹ h ⁻¹	375	600	Janbey et al ³
Pd/TiO ₂	1	0.3 vol. % CH ₄ , 2.4 vol. % O ₂ and He equilibrium gas, GHSV=60000 mL g ⁻¹ h ⁻¹	330	500	Venezia et al ⁴
Pd/TiO ₂	1.1	1/120 (v/v) of CH ₄ /air 120 mL min ⁻¹	430	540	Wang et al ⁵
Pd/TiO ₂	1	1 vol. % CH ₄ , 99 vol. % air, GHSV=48000 mL g ⁻¹ h ⁻¹	800	>885	Sekizawa et al ⁶
Pd/TiO ₂	2	1 vol. % CH ₄ , 10 vol. % O ₂ and He equilibrium gas, GHSV=60000 mL g ⁻¹ h ⁻¹	381	>500	Carrazán et al ⁷
Pd/TiO ₂	2	1 vol. % CH ₄ , 99 vol. % air, GHSV=33000 mL g ⁻¹ h ⁻¹	-	-	Lin et al ⁸

Table S2. Cell parameters and crystal size of T-x and PT-x catalysts.

Sample	Cell parameters (Å) ^a	Crystallite size (nm) ^b
	a=b	
PT-500	4.6019	32.1
T-500	4.5998	-
PT-600	4.5967	65.4
T-600	4.5948	-
PT-800	4.5932	75.5
T-800	4.5918	-
PT-1000	4.5944	78.3
T-1000	4.5932	-
PT-1200	4.5937	84.1
T-1200	4.5914	-
PT-1000-used	4.5994	82.6

^a Obtained from XRD (Fig. 2).

^b Crystalline size of samples was calculated by the Scherrer equation from the (111) peak of rutile.

sample	Pd ⁴⁺		Pd ²⁺		Pd ⁰		Average n(Pd)/n(Ti) ratio ($\times 10^2$)
	BE (eV)	%	BE (eV)	%	BE (eV)	%	
PT-500	337.5	25.9	336.3	67.8	335.0	6.4	0.6
PT-600	337.5	19.2	336.4	75.1	335.0	5.6	1.4
PT-800	337.5	16.1	336.5	79.3	335.1	4.5	7.3
PT-1000	337.5	15.1	336.5	81.1	335.1	3.8	11.4
PT-1200	337.5	28.1	336.5	65.5	335.0	6.5	9.8

Table S3. XPS analyses of Pd 3d_{5/2} for PT-x catalysts.

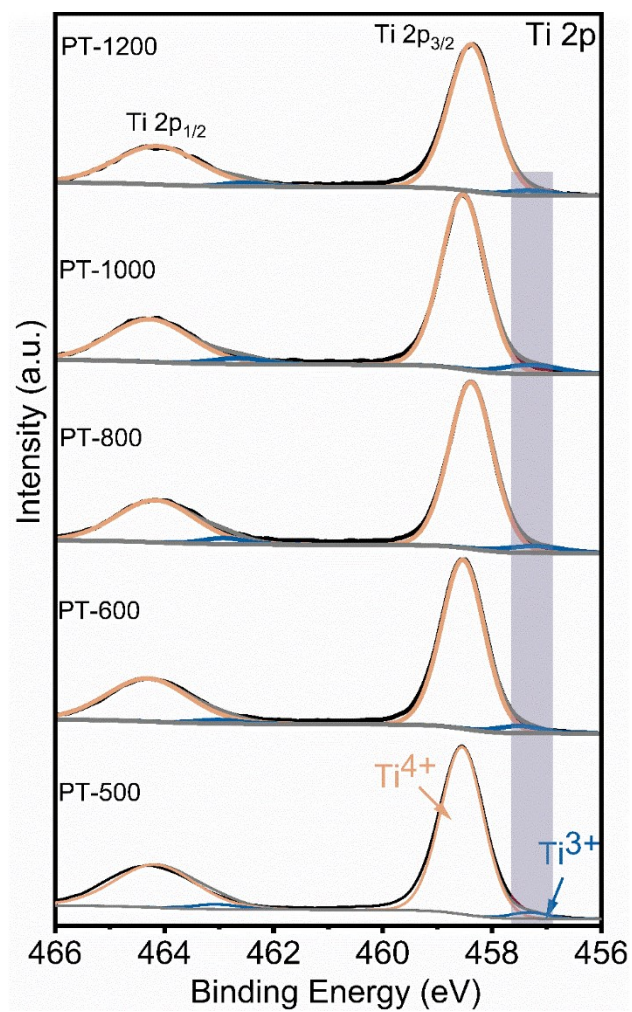


Fig. S1 Ti 2p spectra of PT-x catalysts.

Table S4. XPS analyses of Ti 2p for PT-x catalysts.

sample	Ti ⁴⁺	Ti ³⁺	Ti ³⁺ /(Ti ³⁺ +Ti ⁴⁺) ratio ($\times 10^2$)
	BE (eV)	BE (eV)	
PT-500	458.5	457.3	3.0
PT-600	458.5	457.5	4.2
PT-800	458.3	457.2	5.1
PT-1000	458.5	457.2	6.4
PT-1200	458.3	457.2	3.5

Table S5. XPS analyses of O 1s for PT-x catalysts.

sample	O _{ads}		O _{latt}		O _{ads} /O _{latt} ($\times 10^2$)
	BE (eV)	%	BE (eV)	%	
PT-500	531.9	23.2	529.9	97.7	2.4
PT-600	531.9	16.0	529.8	84.0	19.0
PT-800	531.9	21.8	529.6	78.2	27.8
PT-1000	531.9	32.2	529.8	67.8	47.5
PT-1200	531.9	18.9	529.8	81.1	23.3

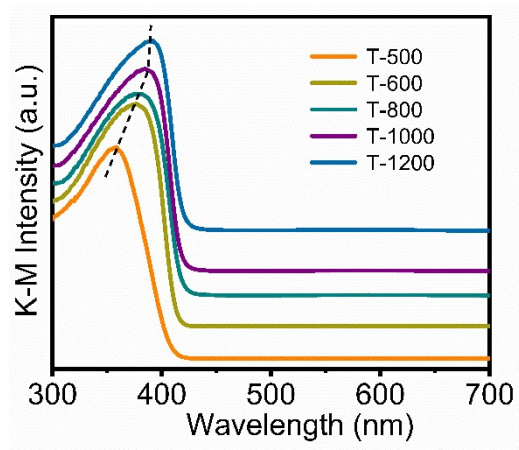


Fig. S2 UV-Vis DRS spectra of T-x supports.

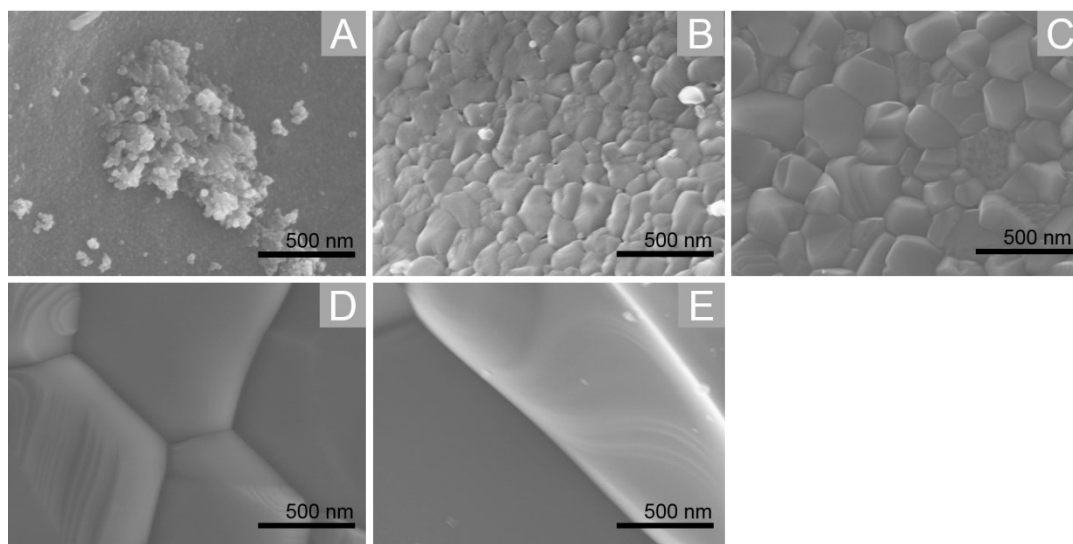


Fig. S3 SEM images of T-500 (A), T-600 (B), T-800 (C), T-1000 (D) and T-1200 (E) at different magnifications.



Fig. S4 Image of “Snow Cookie”, a Chinese snack.

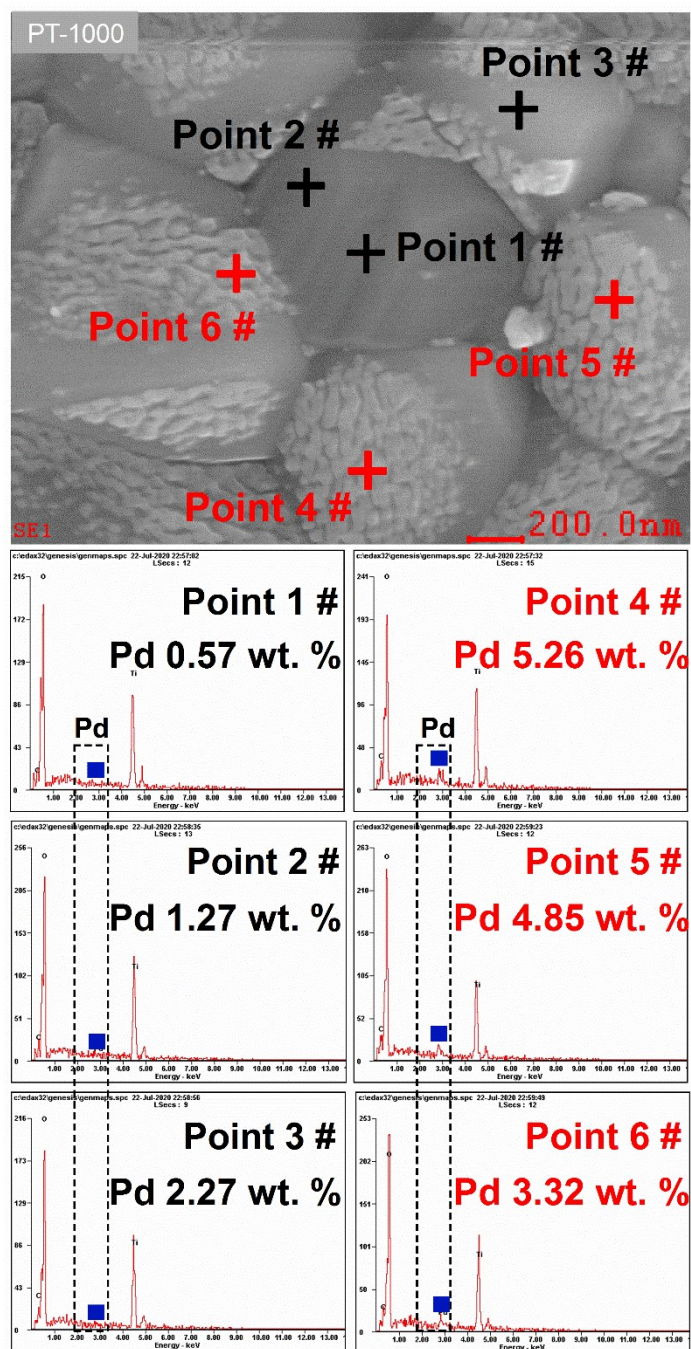


Fig. S5 EDS analysis performed on the individual particles in PT-1000 catalysts.

Table S6. Atomic percent of different elements and average n(Pd)/n(Ti) ratio over PT-x catalysts determined by XPS.

Catalysts	Atomic percent (%)			Average n(Pd)/n(Ti) ratio ($\times 10^2$)
	Pd	O	Ti	
PT-500	Area 1#	0.23	31.52	0.6
	Area 2#	0.15	30.7	
PT-600	Area 1#	0.49	68.97	1.4
	Area 2#	0.42	69.04	
PT-800	Area 1#	2.05	69.49	7.3
	Area 2#	2.13	69.03	
PT-1000	Area 1#	2.95	70.23	11.4
	Area 2#	3.03	71.3	
PT-1200	Area 1#	2.66	72.5	9.8
	Area 2#	2.58	69	
PT-1000-used	Area 1#	2.49	71.66	10.1
	Area 2#	2.64	71.95	

^a the average Pd/Ti ratio was determined based on the calculations of area 1# and area 2# (Spot: mono 500 μm).

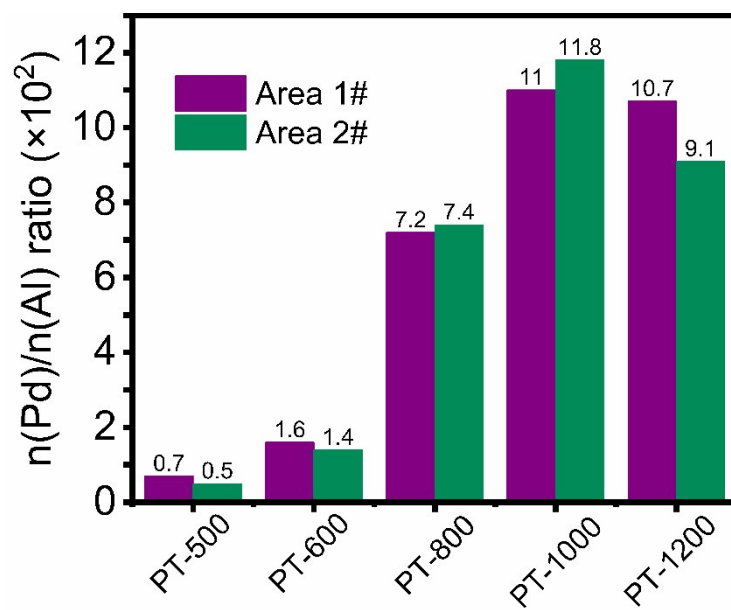


Fig. S6 n(Pd)/n(Ti) ratios determined through XPS over PT-x catalysts.

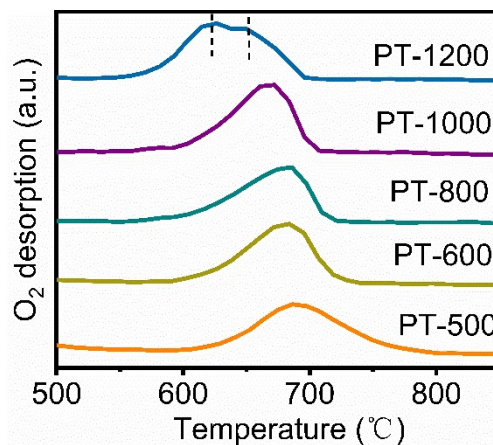


Fig. S7 O₂-TPD profiles of the PT-x catalysts.

Table S7. O₂-TPO profiles of PT-x catalysts.

sample	Decomposition peak	Decomposition	Reoxidation peak	(PdO+PdO ₂)/
	area of PdO	peak area of PdO ₂	area of Pd ⁰	Pd ⁰ ^a
PT -500	10.20	-	2.70	3.78
PT -600	10.90	-	3.30	3.30
PT -800	16.10	-	14.60	1.10
PT -1000	16.76	-	16.27	1.03
PT -1200	0.30	12.3	10.10	1.25

^a The re-oxidation coefficient (PdO+PdO₂)/Pd⁰ of catalysts is defined as the area of the decomposition peaks divided by that of the re-oxidation peak.

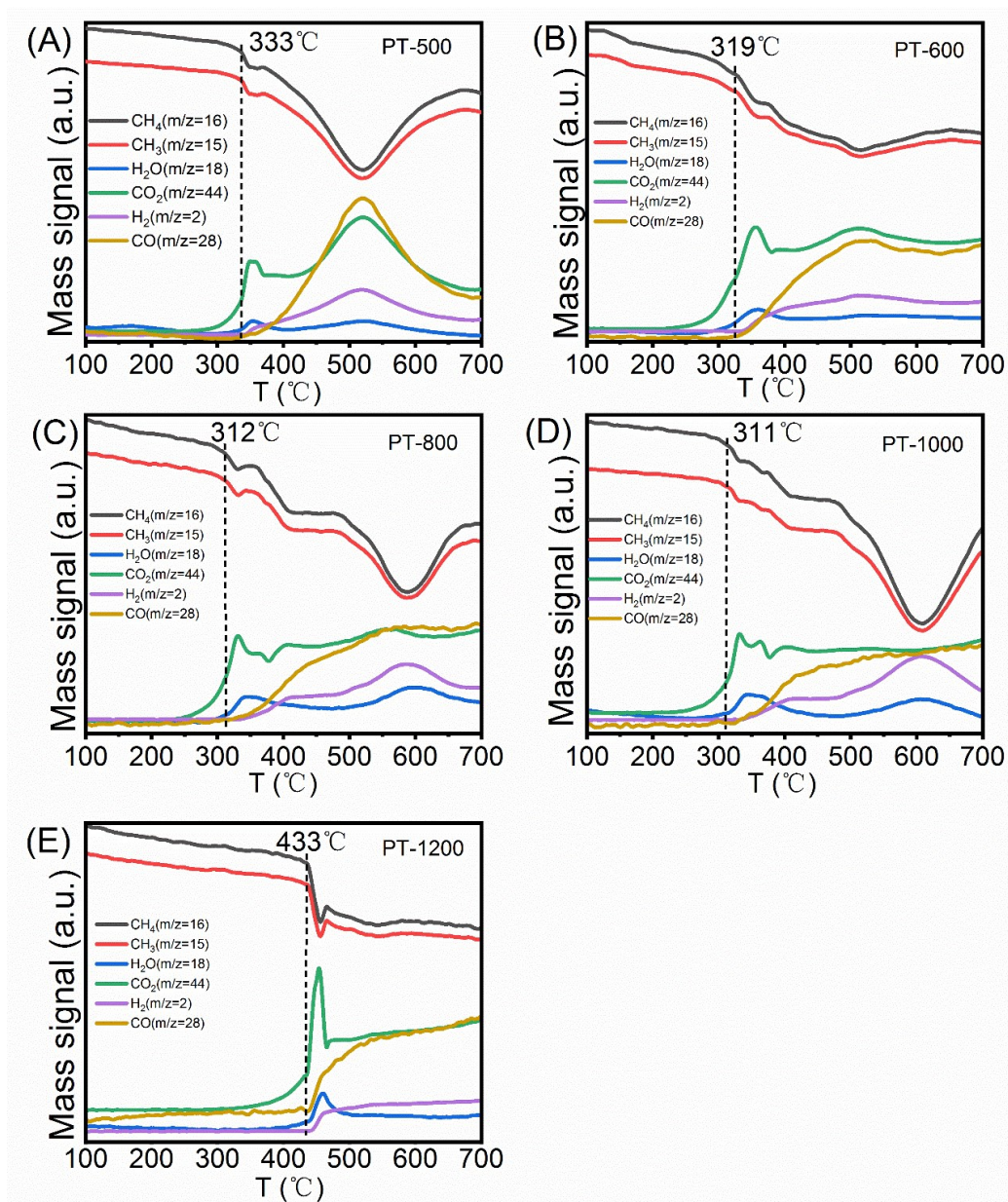


Fig. S8 CH₄-TPR profiles of the PT-x catalysts.

Table S8. XPS analyses of Pd 3d_{5/2} for PT-1000-fresh and PT-1000-used catalysts.

sample	Pd ⁴⁺	Pd ²⁺	Pd ⁰	n(Pd)/n(Ti) ratio (×10 ²)
	BE (eV)/%	BE (eV)/%	BE (eV)/%	
PT-1000-fresh	337.5/15.1	336.5/81.1	335.1/3.8	11.4
P T-1000-used	337.5/18.4	336.6/75.2	335.2/6.3	10.1

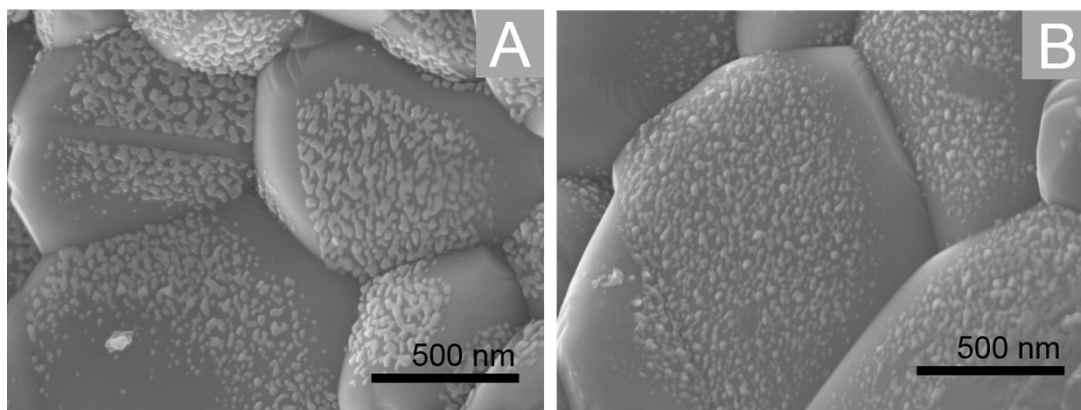


Fig. S9 SEM images of PT-1000-fresh (A) and PT-1000-used (B) catalysts.

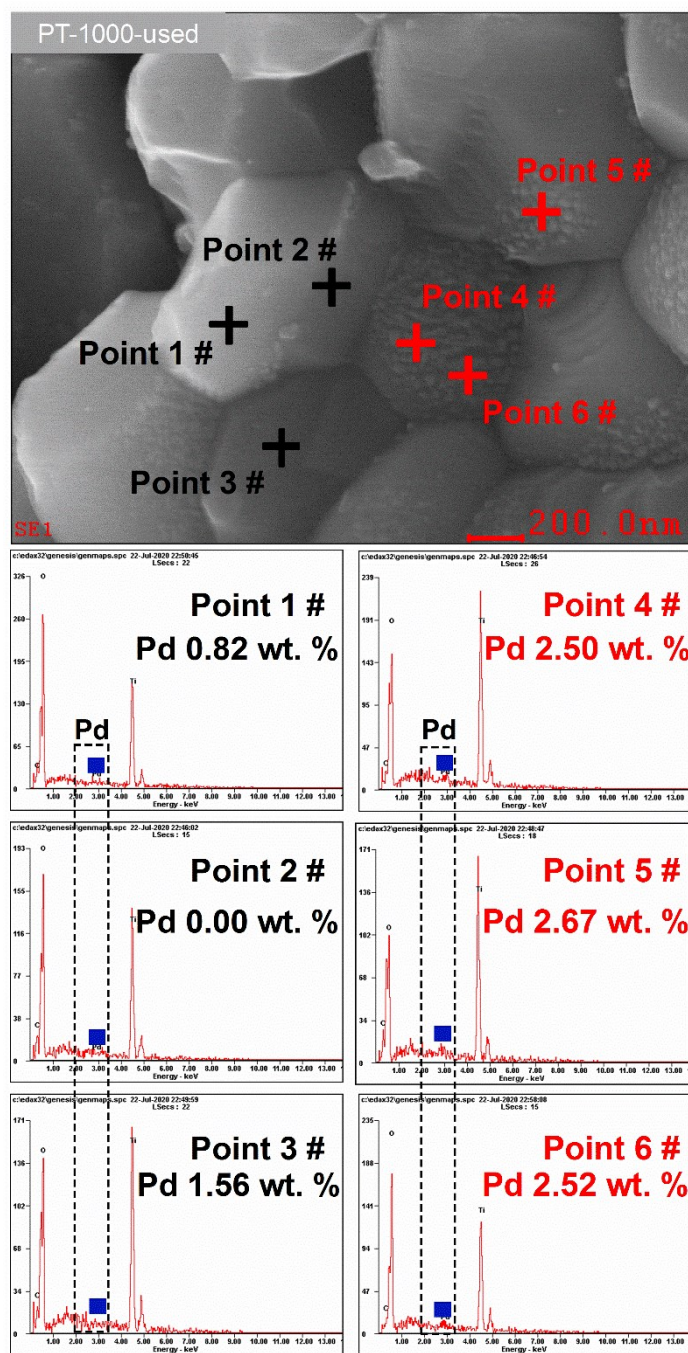


Fig. S10 EDS analysis performed on the individual particles in PT-1000-used catalyst.

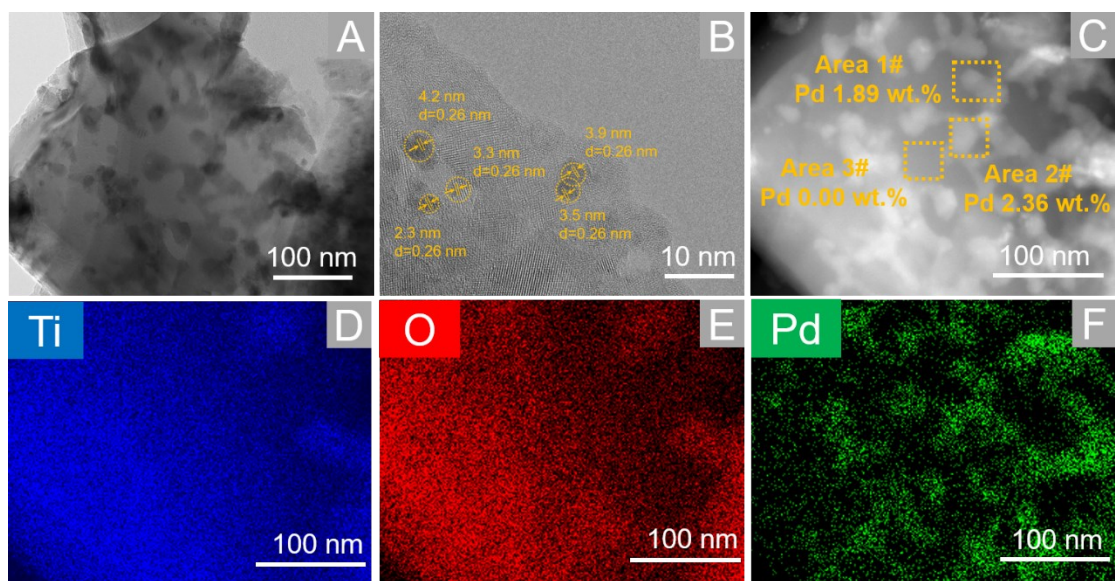


Fig. S11 HRTEM images (A, B), HAADF-STEM images (C) and EDS elemental maps (D, E, F) of the PT-1000-used catalyst.

Table S9. O₂-TPO profiles of PT-1000-fresh and PT-1000-used catalysts.

sample	Decomposition peak area of PdO	Decomposition peak area of PdO ₂	Re-oxidation peak area of Pd ⁰	(PdO+PdO ₂)/ Pd ⁰
PT-1000-fresh	16.76	-	16.27	1.03
PT-1000-used	13.44	2.81	13.30	1.22

References

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