

Supporting Information

Cooperative Catalysis of Methane Oxidation through Modulating the Stabilization of PdO and Electronic Properties over Ti-Doped Alumina-Supported Palladium Catalysts

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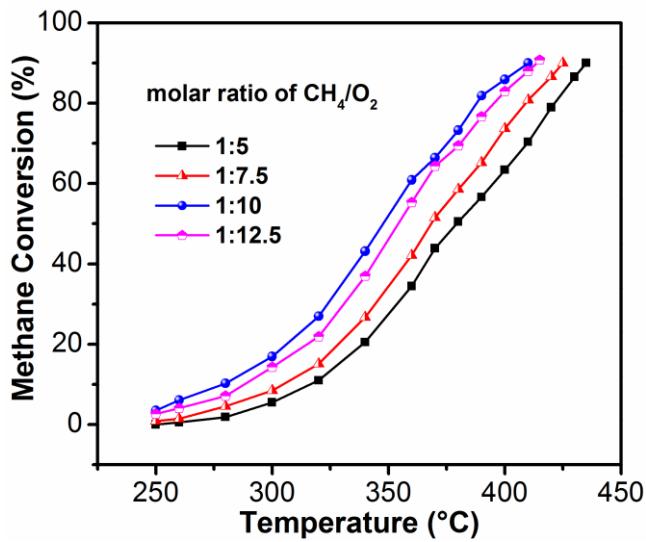


Figure S1. Effect of the CH_4/O_2 molar ratio on catalytic activity for Pd/15TA catalyst.

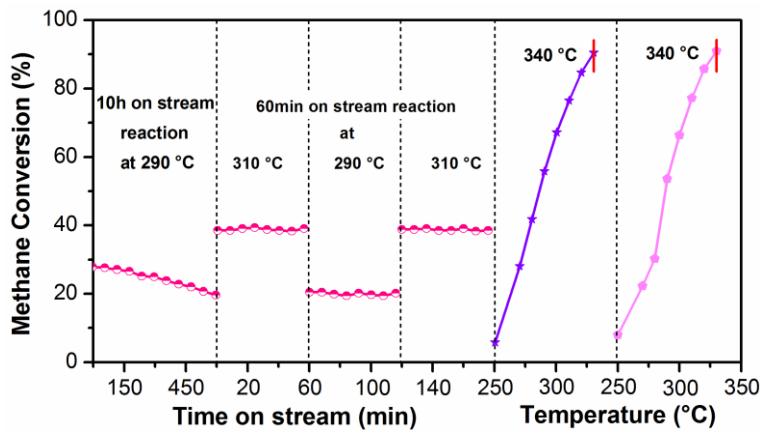


Figure S2. Low-temperature stability and cyclic test of Pd/15TA catalyst.

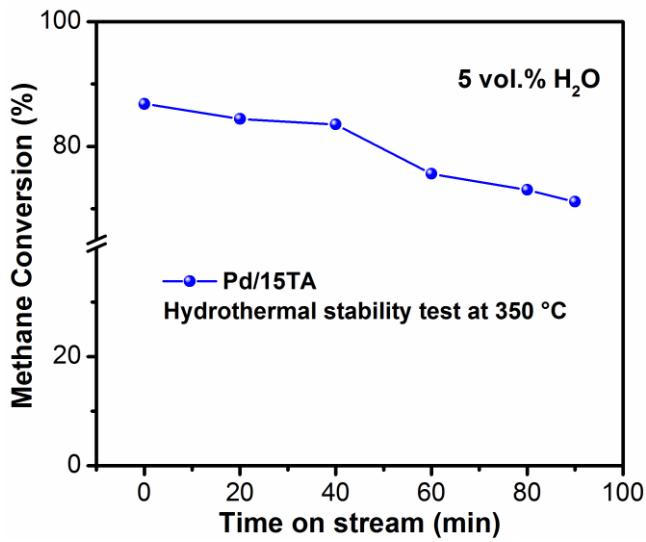


Figure S3. Hydrothermal stability test of Pd/15TA catalyst at 350 °C. Reaction condition: 1 vol % CH₄, 10 vol % O₂ and 5 vol % H₂O in N₂ as balance gas, GHSV = 50 000 mL h⁻¹ g⁻¹.

Table S1 Performance Comparison of Some Palladium-Based Catalysts.

catalysts	Pd loading amount (wt %)	T_{50} (°C)	T_{90} (°C)	reaction condition	from
Pd/15TA	0.5	345	410	1 vol % CH ₄ , 10 vol % O ₂ and N ₂ equilibrium gas GHSV=50 000 mL g ⁻¹ h ⁻¹	This work
PdNiAl	1	~340	410	0.4 vol % CH ₄ and balancing air GHSV=80 000 mL g ⁻¹ h ⁻¹	(1)
Pd/Ti-Al ₂ O ₃	2	377	~440	CH ₄ /O ₂ /He = 1/10/89 vol GHSV=18 750 mL h ⁻¹ g ⁻¹	(2)
Pd/FLAO	0.5	370	430	1.0 vol % CH ₄ , 20 vol % O ₂ and 79 vol % N ₂ GHSV=16 000 mL h ⁻¹ g ⁻¹	(3)
Pd/ZA-M	1.5	360	>400	750 ppm CH ₄ , 0.1 vol % CO, 5.0 vol % O ₂ , 12 vol % CO ₂ , 12 vol % H ₂ O and N ₂ balance GHSV=50 000 mL h ⁻¹ g ⁻¹	(4)
0.2% Pd/Si(5.2)–Al–O(800) –550	0.2	492	520	4 vol % CH ₄ , 86 vol % N ₂ and 10 vol % O ₂ GHSV=42 000 mL g ⁻¹ h ⁻¹	(5)
PdCFPdSBA-15(M)	1	>350	~410	1000 ppm CH ₄ and 10% (v/v) O ₂ , balanced by Ar and He GHSV=180 000 mL g ⁻¹ h ⁻¹	(6)
Pd/ZrO ₂ (30)	1	~440	~490	0.1 vol % CH ₄ , 3.15 vol % O ₂ /N ₂ with 10 vol % water vapor GHSV=240 000 cm ³ g ⁻¹ h ⁻¹	(7)
H-Pd@CeO ₂ -600(24)	1	406	465	2 vol % CH ₄ , 4 vol % O ₂ , 20 vol % CO ₂ and N ₂ as balancing gas GHSV=100 000 mL h ⁻¹ g ⁻¹	(8)

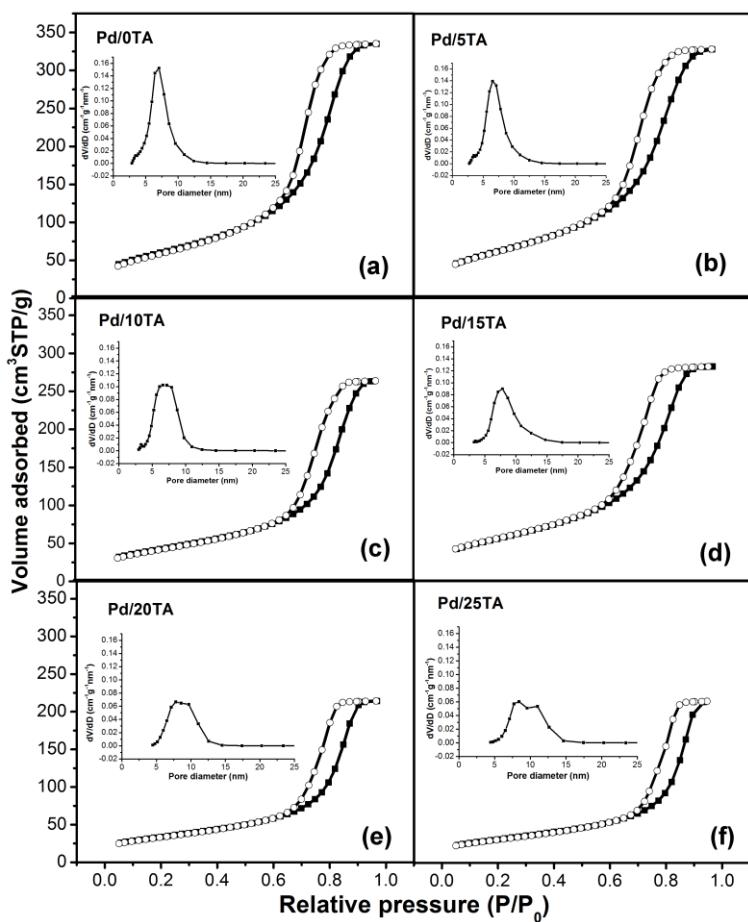


Figure S4. Nitrogen adsorption-desorption isotherms and corresponding pore size distributions (inset) of Pd/xTA catalysts ((a) Pd/0TA, (b) Pd/5TA, (c) Pd/10TA, (d) Pd/15TA, (e) Pd/20TA, and (f) Pd/25TA).

Table S2 Specific Surface Area, Pore Volume and Average Pore Diameter of Pd/xTA Catalysts.

sample	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	pore volume ($\text{cm}^3 \text{ g}^{-1}$)	average pore diameter (nm)
Pd/0TA	218	0.52	6.7
Pd/5TA	225	0.51	6.8
Pd/10TA	202	0.44	6.8
Pd/15TA	154	0.41	8.2
Pd/20TA	122	0.33	8.5
Pd/25TA	113	0.33	9.3

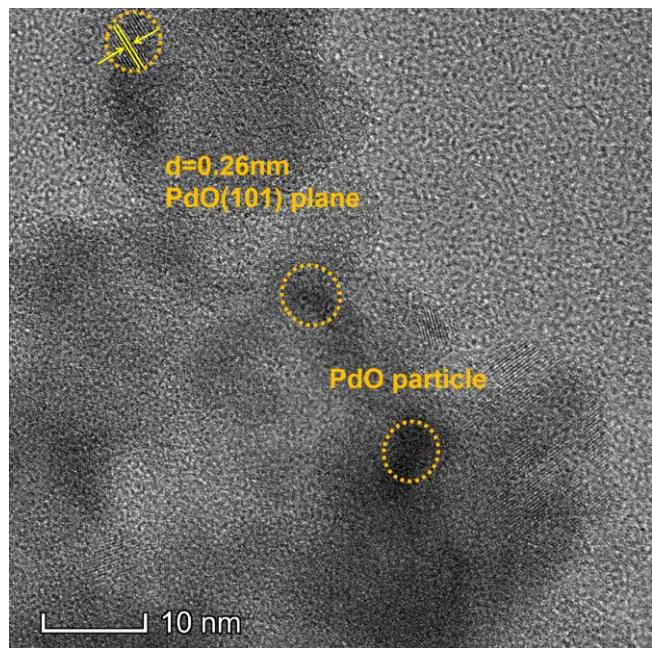


Figure S5. HRTEM image of Pd/15TA catalyst.

Table S3 O₂-TPO Profiles of Pd/xTA Catalysts

catalysts	decomposition temperature of PdO (T/ °C)	reoxidation temperature of PdO (T/ °C)	decomposition peak area of PdO
Pd/0TA	706.5	534.2	34.33
Pd/5TA	716.6	525.2	34.15
Pd/10TA	706.6	639.9	37.57
Pd/15TA	721.6	640.9	38.65
Pd/20TA	673.8 / 737.1	647.8	27.45
Pd/25TA	683.7 / 741.8	651.8	24.83

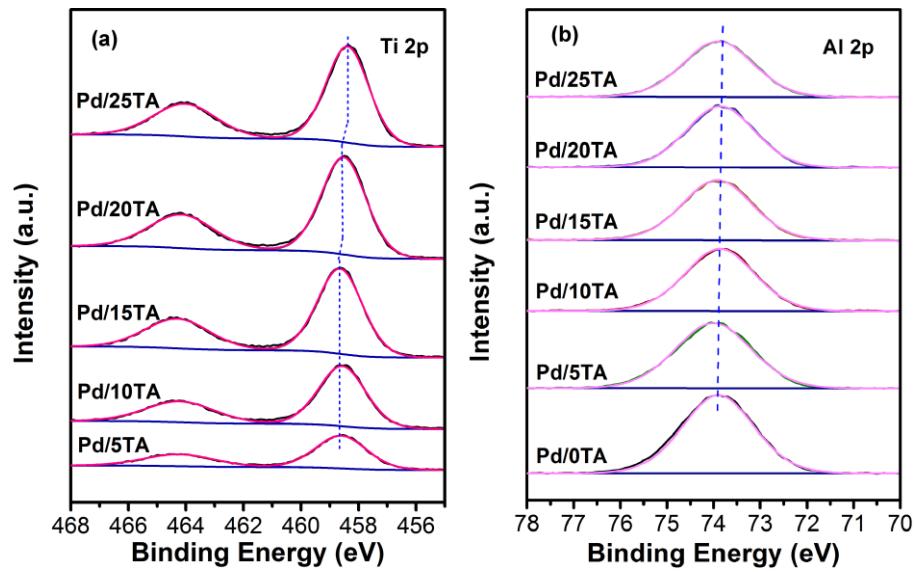


Figure S6. (a) Ti 2p and (b) Al 2p XPS spectra of Pd/xTA catalysts.

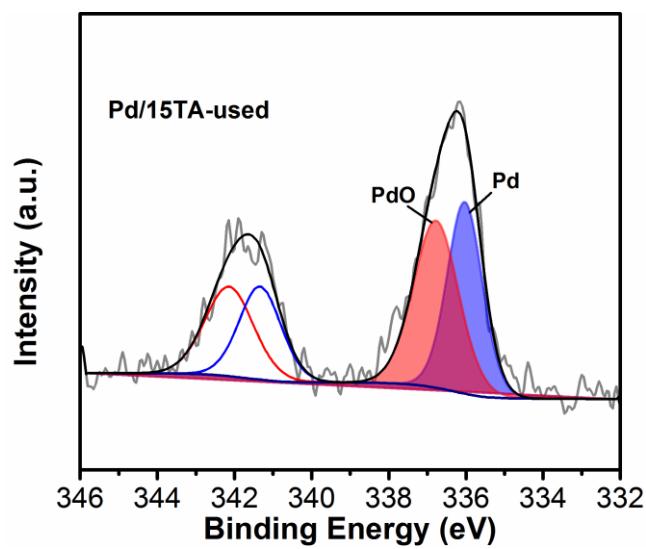


Figure S7. Pd 3d XPS spectra of Pd/15TA catalyst after activity evaluation test.

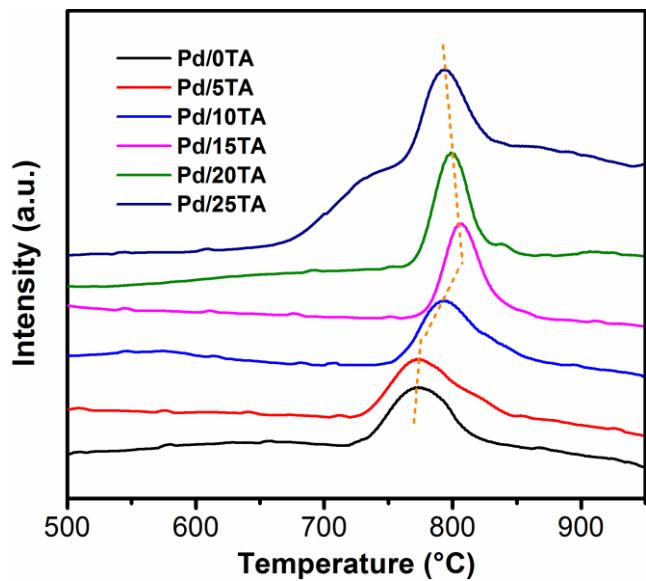


Figure S8. O₂-TPD profiles of Pd/xTA catalysts.

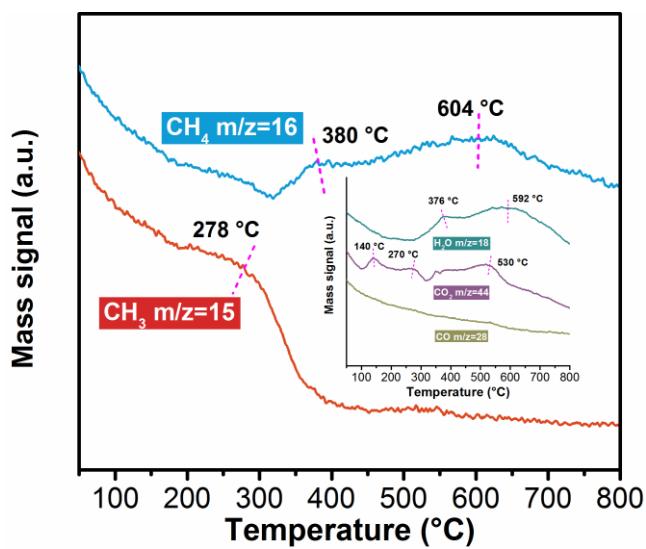


Figure S9. CH_4 -TPD profiles of Pd/15TA catalyst.

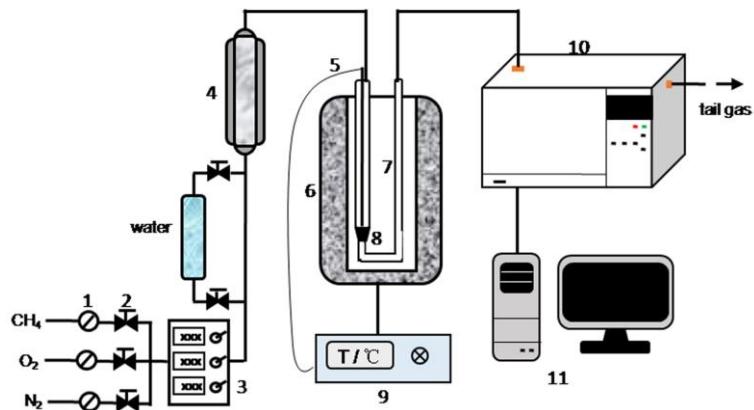


Figure S10. Experimental apparatus diagram of fixed-bed quartz flow reactor for methane combustion. 1-Pressure gauges; 2-Relief valves; 3-Mass-flow controllers; 4-Gas mixer; 5-Thermocouple; 6-Electric furnaces; 7-U-shaped quartz tube; 8-Catalyst; 9-Programmed temperature controller; 10-Gas cromatograph (GC); 11-Computer.

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