Supplementary material for:

Experimental and theoretical investigation of oxidative methane activation on Pt-Pt catalysts

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1. XRD and metal cluster dispersion [1]

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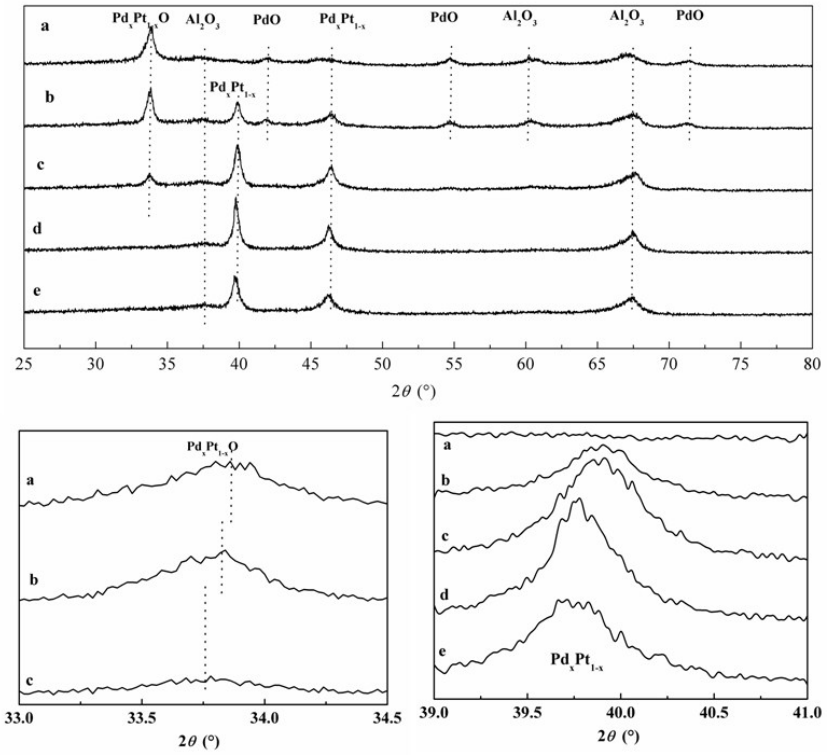


Fig. S1 XRD patterns of the catalysts samples (a) $Pd_{1.0}Pt_0$, (b) $Pd_{0.75}Pt_{0.25}$, (c) $Pd_{0.5}Pt_{0.5}$,(d) $Pd_{0.25}Pt_{0.75}$,(e) $Pd_0Pt_{1.0}$.

Table S1 Metal loading, CO uptake and metal cluster dispersion of the different catalysts

Sample	Composition	Pd loading (wt%)	Pt loading (wt%)	CO uptake (μmol (g^{-1} catalysts))	Pd-Pt dispersion (%) from CO uptake
$Pd_{1.0}Pt_0$	1:0	2.1	0	9.5	9.6
$Pd_{0.75}Pt_{0.25}$	0.75:0.25	1.6	0.9	11.3	9.3
$Pd_{0.50}Pt_{0.50}$	0.5:0.5	1.0	1.7	9.8	7.3
$Pd_{0.25}Pt_{0.75}$	0.25:0.75	0.6	2.6	10.0	6.2
$Pd_0Pt_{1.0}$	0:1	0	3.4	15.0	8.8

2. Kinetically relevant steps in CH_4-O_2 reactions on surfaces of these catalysts. Reaction orders for methane and oxygen can be calculated by fitting experimental data.

(1) On Pd catalyst.

$$r_{II-III,Pd} = k_{II-III,app}\left(O_2\right)^{-0.15}(CH_4)^1 \qquad P_{O2} \le 1.7kPa \qquad (1)$$

$$r_{IV,Pd} = k_{IV,app}\left(O_2\right)^{0}(CH_4)^1 \qquad 1.7kPa < P_{O2} < 11kPa \qquad (2)$$

$$r_{V,Pd} = k_{V,app}\left(O_2\right)^{0}(CH_4)^1 \qquad P_{O2} \ge 11kPa \qquad (3)$$

(2) On $Pd_{0.75}Pt_{0.25}$ catalyst

$$r_{I,Pd_{0.75}} = k_{I,app}\left(O_2\right)^{1.1}(CH_4)^{0.1} \qquad 0 < (O_2 / CH_4) < 0.08 \qquad (4)$$

$$r_{II,Pd_{0.75}} = k_{II,app}\left(O_2\right)^{-0.82}(CH_4)^{1.82} \qquad 0.08 < (O_2 / CH_4) < 1 \qquad (5)$$

$$r_{IV,Pd_{0.75}} = k_{IV,app}\left(O_2\right)^{0}(CH_4)^1 \qquad P_{O2} > 3 \sim 5kPa \qquad (6)$$

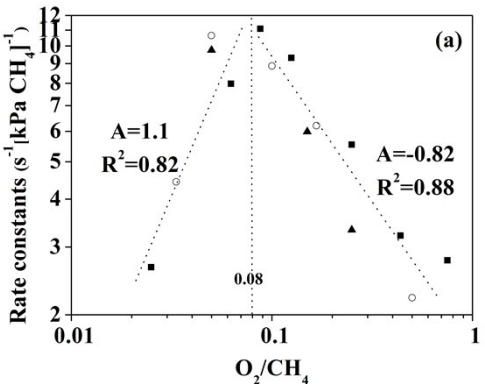


Fig. S2 First-order constant ($r_{CH4}(CH_4)^{-1}$) for methane oxidation as a single valued function of O_2/CH_4 ratio on $Pd_{0.75}Pt_{0.25}$

(3) On $Pd_{0.5}Pt_{0.5}$ catalyst

$$r_{I,Pd_{0.5}} = k_{I,app}\left(O_2\right)^{1.0} \qquad 0 < (O_2 / CH_4) < 0.1 \qquad (7)$$

$$r_{II,Pd_{0.5}} = k_{II,app}\left(O_2\right)^{-0.72}(CH_4)^{1.72} \qquad 0.1 < (O_2 / CH_4) < 1 \qquad (8)$$

$$r_{IV,Pd_{0.5}} = k_{IV,app}\left(O_2\right)^{0}(CH_4)^1 \qquad P_{O2} > 4 \sim 6kPa \qquad (9)$$

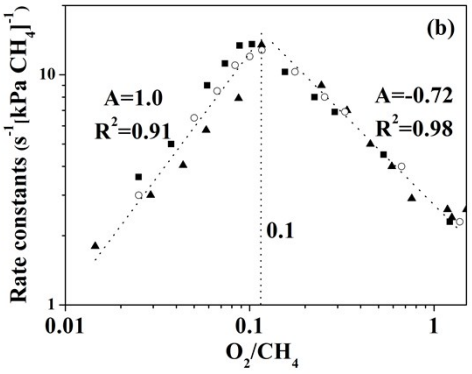


Fig. S3 First-order constant ($r_{CH4}(CH_4)^{-1}$) for methane oxidation as a single valued function of O_2/CH_4 ratio on $Pd_{0.5}Pt_{0.5}$

(4) On $Pd_{0.25}Pt_{0.75}$ catalyst

$$r_{I,Pd_{0.25}} = k_{I,app}\left(O_2\right)^{1.0} \qquad 0 < (O_2 / CH_4) < 0.1 \qquad (10)$$

$$r_{II,Pd_{0.25}} = k_{II,app}\left(O_2\right)^{-0.72}(CH_4)^{1.72} \qquad 0.1 < (O_2 / CH_4) < 1.1 \qquad (11)$$

$$r_{IV,Pd_{0.25}} = k_{IV,app}\left(O_2\right)^{0.1}(CH_4)^{1} \qquad P_{O2} > 5 \sim 7kPa \qquad (12)$$

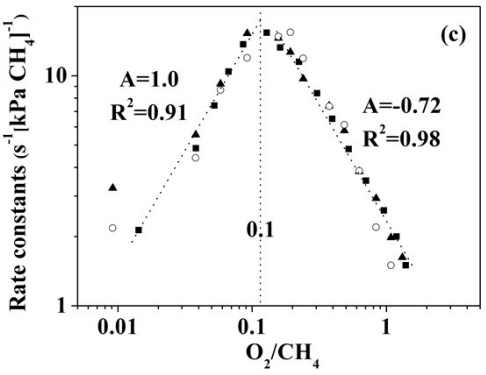


Fig. S4 First-order constant ($r_{CH4}(CH_4)^{-1}$) for methane oxidation as a single valued function of O_2/CH_4 ratio on $Pd_{0.25}Pt_{0.75}$

(5) On Pt catalyst

$$r_{I,Pt} = k_{I,app}\left(O_2\right)^{1.1}(CH_4)^{-0.1} \qquad 0 < (O_2 / CH_4) < 0.12 \qquad (13)$$

$$r_{II,Pt} = k_{II,app}\left(O_2\right)^{2.38}(CH_4)^{-1.38} \qquad 0.1 < (O_2 / CH_4) < 2 \sim 3 \qquad (14)$$

$$r_{III,Pt} = k_{III,app}(CH_4)^{1} \qquad 2 \sim 3 < (O_2 / CH_4) \qquad (15)$$

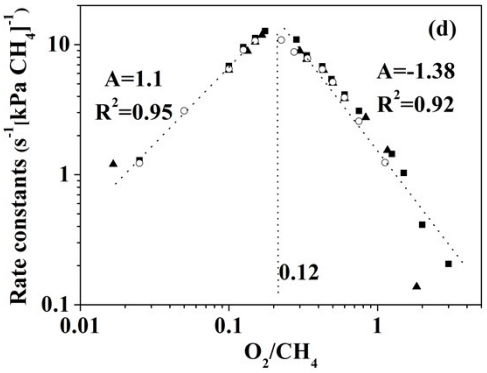


Fig. S5 First-order constant ($r_{CH4}(CH_4)^{-1}$) for methane oxidation as a single valued function of O_2/CH_4 ratio on Pt

3. Arrhenius plots of first order rate constants for methane combustion on Pd, Pt and Pd-Pt catalysts

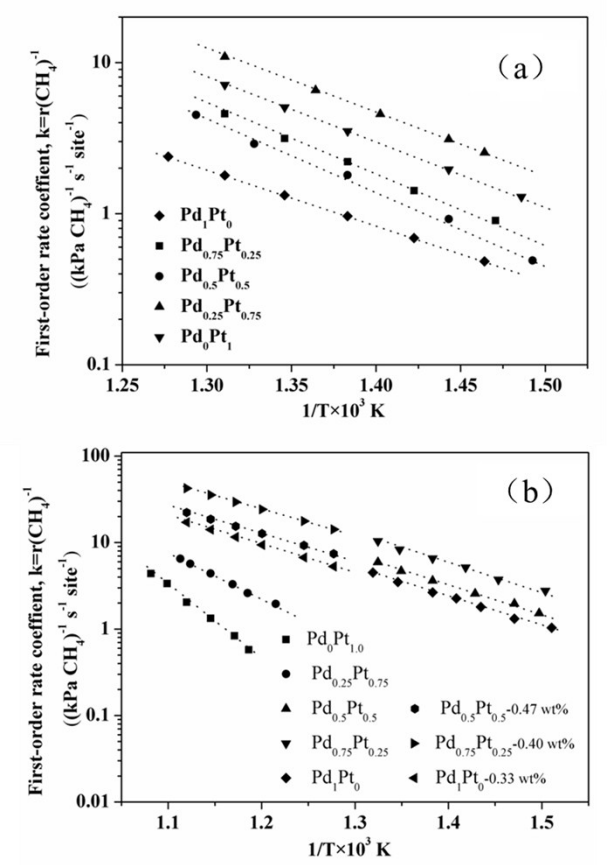


Fig.S6. Arrhenius plots of the methane first oder rate coeffient versus 1000/T for methane combustion on different catalysts. (a) Oxygen pressure at 2 kPa for $Pd_{0.75}Pt_{0.25}$,$Pd_{0.5}Pt_{0.5}$, $Pd_{0.25}Pt_{0.75}$ and $Pt_{1.0}$., and 0.5 kPa for $Pd_{1.0}$; (b) Oxygen preesure at 20 kPa for all catalysts. R-square for these experimental data are larger than 0.93.

4. Binding energies of the adsorption O on different metal surface with different O coverage

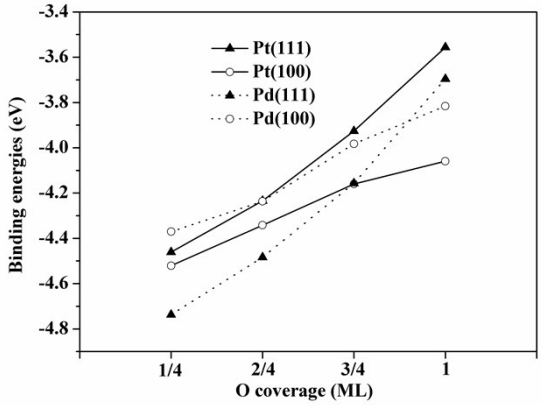
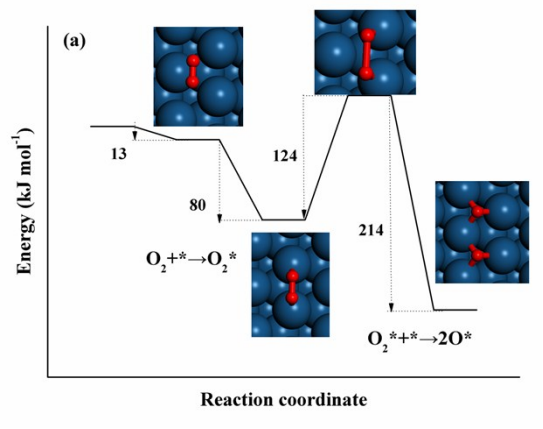


Fig. S7 Binding energies of the adsorption O on different metal surface with different O coverage

5. Structures of reactant, transition states and product for O_2 dissociation on the Pt(111) and Pd(111) covered with different O coverage.[2]



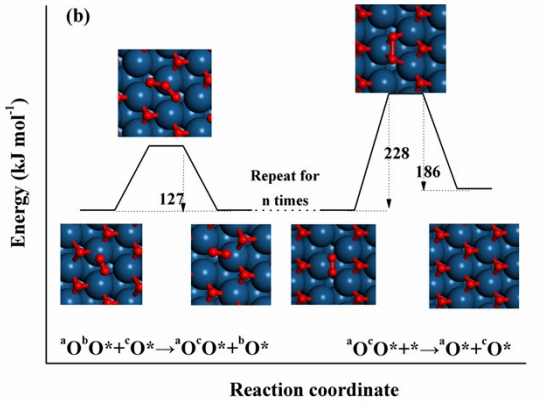
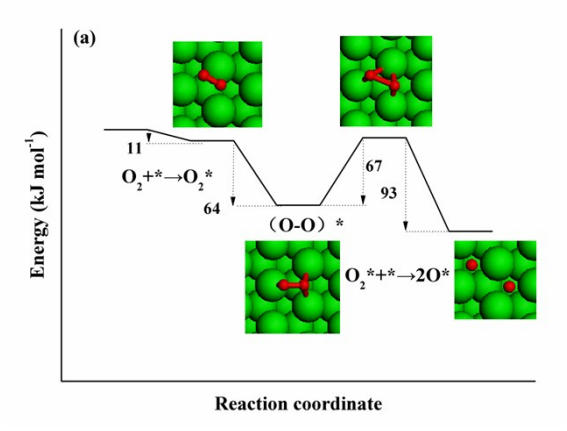


Fig. S8 (a) Reaction coordinate and structures of reactant, transition state, and product for O_2 dissociation on a bare Pt (111) facet. (b) Reaction coordinate and structures of reactant, transition state, intermediate, and product for O_2 dissociation on the (111) facet of Pt nearly saturated with chemisorbed oxygen atoms. a,b, and c are used to differentiate the O atoms involved in the steps



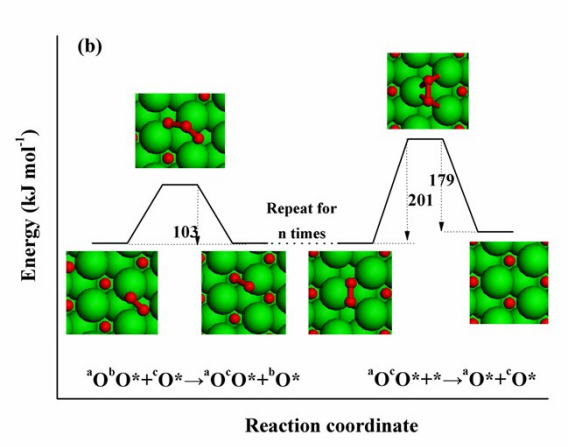


Fig. S9 (a) Reaction coordinate and structures of reactant, transition state, and product for O_2 dissociation on a bare Pd (111) facet. (b) Reaction coordinate and structures of reactant, transition state, intermediate, and product for O_2 dissociation on the (111) facet of Pd nearly saturated with chemisorbed oxygen atoms. a,b, and c are used to differentiate the O atoms involved in the steps

6. Structures of reactant, transition states and product for CH_4 dissociation on (a) MeO(111), (b) 1/4 ML O, (c)3/4 ML O and (d) 1 ML O coverage on Me(111) surfaces, (e) PdO(101)/Pt(100) and (f) PdO(101).

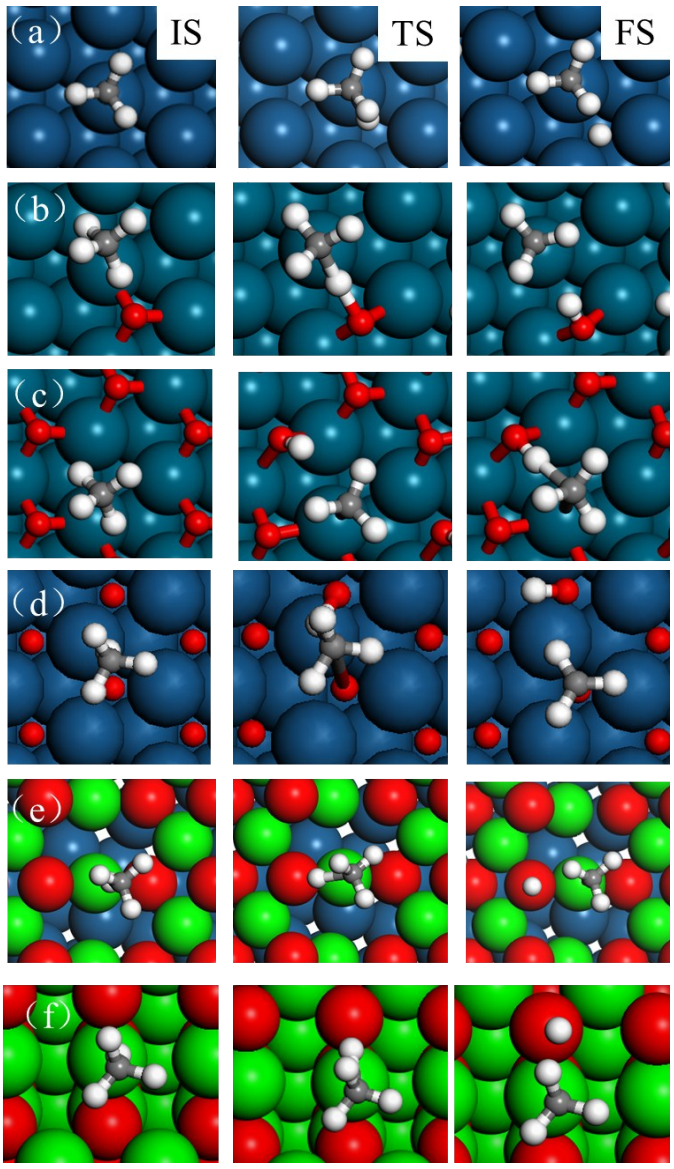


Fig. S10 Structures of reactant, transition states and product for CH_4 dissociation on (a) MeO(111), (b) 1/4 ML O, (c)3/4 ML O and (d) 1 ML O coverage on Me(111) surfaces, (e) PdO(101)/Pt(100) and (f) PdO(101).(a),(d), (e), (f) were from our previous study[2].

7. **Parameters include bond length of transition states, activation energies and binding energies for CH_4 dissociation on the different oxygen potential surfaces.**

	Catalyst	Bond length (Å) Transition states				Activation energies (kJ mol^{-1})	Binding energies (eV) [Site]	
		C-H（O）	Me（H）-C	Me-H	H-O		CH_3	H
0 ML O	Pd(111)	1.607	2.233	1.665		83	-2.253	-3.812
	Pt(111)	1.634	2.336	1.670		78	-2.435	-3.720
	Pd/PtPd(111)	1.598	2.231	1.673		79	-2.319	-3.805
	Pt/PtPd(111)	1.582	2.343	1.667		75	-2.513	-3.744
1/4 ML O	Pd(111)	1.401	2.430	2.153	1.385	105	-2.314	-4.022
	Pt(111))	1.350	2.333	2.086	1.424	118	-2.586	-3.981
3/4 ML O	Pd(111)	1.601	2.730	2.553	1.029	135	-1.640	-4.381
	Pt(111)	1.312	2.352	2.123	1.521	147	-2.197	-4.628
	Pd/PtPd(111)	1.623	2.803	2.532	1.123	139	-1.562	-4.210
	Pt/PtPd(111)	1.289	2.413	2.231	1.483	152	-2.180	-4.395
1 ML O	Pd(111)	2.925	1.478		1.135	163	-1.164	-4.730
	Pt(111)	3.251	1.574		1.423	175	-0.921	-4.656
	Pd/PtPd(111)	2.932	1.468		1.186	159	-1.212	-4.742
	Pt/PtPd(111)	3.158	1.564		1.398	178	-0.889	-4.642
PdO（101）/Pt(100)		1.338	2.311	1.926	1.336	110	-2.451	-2.252
2 layer PdO（101）/Pt(100)		1.320	2.155	1.913	1.276	67	-2.688	-1.956
PdO(101)		1.331	2.241	1.852	1.284	61	-2.704	-1.942

8. Derivation of methane combustion rates limited by O_2 pressure on *-* site pairs

$$2r_1 = k_{1.2f}\theta_{O_2}\theta_* = 2k_{2.1}P_m\theta_*^2 \quad (16)$$

$$2r_1 = k_{1.2f}K_{1.1}P_O\theta_*^2 = 2k_{2.1f}P_m\theta_*^2 \quad (17)$$

$$\theta_* = 1 \quad (18)$$

$$r_1 = 0.5k_{1.2f}K_{1.1}P_O \quad (19)$$

9. Derivation of methane combustion rates limited by C-H bond activation on

O*-* site pairs

$$2r_2 = k_{1.2f}K_{1.1}P_O\theta_*^2 = 2k_{2.2f}P_m\theta_*\theta_O \quad (20)$$

$$\frac{\theta_*}{\theta_O} = \frac{2k_{2.2f}P_m}{k_{1.2f}K_{1.1}P_O} \quad (21)$$

$$\theta_* = \frac{1}{1+\frac{\theta_O}{\theta_*}} = \frac{1}{1+\frac{k_{1.2f}K_{1.1}P_O}{2k_{2.2f}P_m}} \quad (22)$$

$$r_2 = \frac{2k_{2.2f}^{\ 2}}{k_{1.2f}K_{1.1}}\frac{P_m^{\ 2}}{P_O} \quad (23)$$

10. Derivation of methane combustion rates limited by C-H bond activation on O*-O* site pairs

$$r_3 = k_{2.3f}P_m\theta_*^2 \quad (24)$$

$$\theta_O = 1 \quad (25)$$

$$r_3 = k_{2.3f}P_m \quad (26)$$

11. Derivation of methane combustion rates limited by C-H bond activation on Pd-O site pairs

$$r_4 = k_{2.4f}P_m\theta_{V_O}\theta_* \quad \textbf{(27)}$$

$$\theta_* \approx \theta_{V_O} = 1 \quad \textbf{(28)}$$

$$r_4 = k_{2.4f}P_m \quad \textbf{(29)}$$

References:

[1] W. Qi, J. Ran, X. Du, R. Wang, J. Shi, J. Niu, P. Zhang, M. Ran, Kinetics Consequences of Methane Combustion on Pd, Pt and Pd-Pt Catalysts, Rsc Advances, 6 (2016) 109834-109845.

[2] W. Qi, J. Ran, Z. Zhang, J. Niu, P. Zhang, L. Fu, B. Hu, Q. Li, Methane combustion reactivity during the metal→metallic oxide transformation of Pd-Pt catalysts: Effect of oxygen pressure, Applied Surface Science, 435 (2017) 776-785.