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 \cite{1}
Fig. S1 XRD patterns of the catalysts samples (a) Pd\textsubscript{1.0}Pt\textsubscript{0}, (b) Pd\textsubscript{0.75}Pt\textsubscript{0.25}, (c) Pd\textsubscript{0.5}Pt\textsubscript{0.5}, (d) Pd\textsubscript{0.25}Pt\textsubscript{0.75}, (e) Pd\textsubscript{0}Pt\textsubscript{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\textsuperscript{-1} catalysts)) | Pd-Pt dispersion (%) from CO uptake |
|--------------|---------------|------------------|------------------|--------------------------------------------------|-------------------------------------|
| Pd\textsubscript{1.0}Pt\textsubscript{0} | 1:0           | 2.1              | 0                | 9.5                                              | 9.6                                 |
| Pd\textsubscript{0.75}Pt\textsubscript{0.25} | 0.75:0.25     | 1.6              | 0.9              | 11.3                                             | 9.3                                 |
| Pd\textsubscript{0.5}Pt\textsubscript{0.5} | 0.5:0.5       | 1.0              | 1.7              | 9.8                                              | 7.3                                 |
| Pd\textsubscript{0.25}Pt\textsubscript{0.75} | 0.25:0.75     | 0.6              | 2.6              | 10.0                                             | 6.2                                 |
| Pd\textsubscript{0}Pt\textsubscript{1.0} | 0:1           | 0                | 3.4              | 15.0                                             | 8.8                                 |

2. Kinetically relevant steps in CH\textsubscript{4}-O\textsubscript{2} reactions on surfaces of these catalysts.

Reaction orders for methane and oxygen can be calculated by fitting experimental data.
(1) On Pd catalyst.

\[ r_{\text{II}, \text{Pd}} = k_{\text{II}, \text{app}} (O_2)^{0.15} (CH_4)^1 \quad P_{O_2} \leq 1.7 \text{kPa} \]  

(2) On Pd\(_{0.75}\)Pt\(_{0.25}\) catalyst

\[ r_{\text{I}, \text{Pd}_{0.75}} = k_{\text{I}, \text{app}} (O_2)^{0.1} (CH_4)^{0.1} \quad 0 < (O_2 / CH_4) < 0.08 \]  

\[ r_{\text{II}, \text{Pd}_{0.75}} = k_{\text{II}, \text{app}} (O_2)^{-0.82} (CH_4)^{1.82} \quad 0.08 < (O_2 / CH_4) < 1 \]  

\[ r_{\text{IV}, \text{Pd}_{0.75}} = k_{\text{IV}, \text{app}} (O_2)^{0} (CH_4)^1 \quad P_{O_2} > 3 \sim 5 \text{kPa} \]  

Fig. S2 First-order constant (\(r_{\text{CH}_4}(\text{CH}_4)^{-1}\)) for methane oxidation as a single valued function of

\[ \text{O}_2/\text{CH}_4 \text{ ratio on Pd}_{0.75}\text{Pt}_{0.25} \]

(3) On Pd\(_{0.5}\)Pt\(_{0.5}\) catalyst

\[ r_{\text{I}, \text{Pd}_{0.5}} = k_{\text{I}, \text{app}} (O_2)^{1.0} \quad 0 < (O_2 / CH_4) < 0.1 \]  

\[ r_{\text{II}, \text{Pd}_{0.5}} = k_{\text{II}, \text{app}} (O_2)^{-0.72} (CH_4)^{1.72} \quad 0.1 < (O_2 / CH_4) < 1 \]  

\[ r_{\text{IV}, \text{Pd}_{0.5}} = k_{\text{IV}, \text{app}} (O_2)^{0} (CH_4)^1 \quad P_{O_2} > 4 \sim 6 \text{kPa} \]
Fig. S3 First-order constant \( r_{\text{CH}_4(\text{CH}_4)^{-1}} \) for methane oxidation as a single valued function of

\[ \frac{\text{O}_2}{\text{CH}_4} \] on Pd\(_{0.5}\)Pt\(_{0.5}\)

(4) On Pd\(_{0.25}\)Pt\(_{0.75}\) catalyst

\[ r_{\text{I,Pd}_{0.25}} = k_{\text{I,app}} \left( \frac{\text{O}_2}{\text{CH}_4} \right)^{1.0} \quad 0 < \left( \frac{\text{O}_2}{\text{CH}_4} \right) < 0.1 \] (10)

\[ r_{\text{II,Pd}_{0.25}} = k_{\text{II,app}} \left( \frac{\text{O}_2}{\text{CH}_4} \right)^{0.72} \left( \text{CH}_4 \right)^{1.72} \quad 0.1 < \left( \frac{\text{O}_2}{\text{CH}_4} \right) < 1.1 \] (11)

\[ r_{\text{IV,Pd}_{0.25}} = k_{\text{IV,app}} \left( \frac{\text{O}_2}{\text{CH}_4} \right)^{0.1} \left( \text{CH}_4 \right)^{1} \quad P_{\text{O}_2} > 5 \sim 7 \text{kPa} \] (12)

Fig. S4 First-order constant \( r_{\text{CH}_4(\text{CH}_4)^{-1}} \) for methane oxidation as a single valued function of

\[ \frac{\text{O}_2}{\text{CH}_4} \] on Pd\(_{0.25}\)Pt\(_{0.75}\)

(5) On Pt catalyst
\[ r_{1,\text{Pt}} = k_{1,\text{app}} \left( O_2 \right)^{1.1} \left( CH_4 \right)^{-0.1} \quad 0 < \left( O_2 / CH_4 \right) < 0.12 \quad (13) \]

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

\[ r_{III,\text{Pt}} = k_{III,\text{app}} \left( CH_4 \right)^1 \quad 2 \sim 3 < \left( O_2 / CH_4 \right) \quad (15) \]

Fig. S5 First-order constant \((r_{\text{CH}_4(\text{CH}_4)^{-1}})\) for methane oxidation as a single valued function of \(O_2/\text{CH}_4\) 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 order rate coefficient 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\(_{1.0}\); (b) Oxygen pressure 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].

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-                | Me (H)                                | Me-H                       | H-O                       | CH₃       | H       |
|                           |                | H (O) -C          |                                       |                            |                          |         |         |
|                           |                |                   |                                       |                            |                          |         |         |
| 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  |
|                           | Pd/PtPd(111)   | 1.289             | 2.413                                 | 2.231                      | 1.483                    | 152      | -2.180  | -4.395  |
|                           | Pt/PtPd(111)   | 1.293             | 2.413                                 | 2.231                      | 1.483                    | 152      | -2.180  | -4.395  |
| 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  |

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8. Derivation of methane combustion rates limited by O₂ pressure on *-* site pairs

\[ 2r_i = k_{1,2} \theta_{O_2} \theta_* = 2k_{2,1} P_m \theta_*^2 \]  \hspace{1cm} (16)

\[ 2r_i = k_{1,2} K_{1,1} P_0 \theta_*^2 = 2k_{2,1} P_m \theta_*^2 \]  \hspace{1cm} (17)

\[ \theta_* = 1 \]  \hspace{1cm} (18)

\[ r_i = 0.5 k_{1,2} K_{1,1} P_0 \]  \hspace{1cm} (19)

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

\[ 2r_z = k_{12f} K_{11} P_O \theta_*^2 = 2k_{22f} P_m \theta \theta_O \]  \hspace{1cm} (20)

\[ \frac{\theta_*}{\theta_O} = \frac{2k_{22f} P_m}{k_{12f} K_{11} P_O} \]  \hspace{1cm} (21)

\[ \theta_* = \frac{1}{1 + \frac{\theta_O}{\theta_*}} = \frac{1}{1 + \frac{k_{12f} K_{11} P_O}{2k_{22f} P_m}} \]  \hspace{1cm} (22)

\[ r_z = \frac{2k_{22f}^2 P_m^2}{k_{12f} K_{11} P_O} \]  \hspace{1cm} (23)

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

\[ r_z = k_{23f} P_m \theta_*^2 \]  \hspace{1cm} (24)

\[ \theta_O = 1 \]  \hspace{1cm} (25)

\[ r_z = k_{23f} P_m \]  \hspace{1cm} (26)

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

\[ r_4 = k_{24f} P_m \theta \theta_O \theta_* \]  \hspace{1cm} (27)

\[ \theta_* \approx \theta_{\theta_O} = 1 \]  \hspace{1cm} (28)

\[ r_4 = k_{24f} P_m \]  \hspace{1cm} (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.
