

Supplementary material for:

**Kinetics Consequences of Methane Combustion on Pd, Pt and Pd-Pt
Catalysts**

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1. Derivation of methane combustion rates on oxide Pd-like and Pt-like surfaces

1.1 Derivation of CH₄ reaction rates are limited by C-H bond activation on Pd-O

site pairs for Pd-like surfaces. Suppose all but step 2a and step 4a are quasi-

equilibrated, and the overall rate for methane oxidation rate can be written as

follows:

$$r_a = k_{4.1a} [CH_4][O] \quad (1a)$$

or

$$r_a = k_{2a} [O_2][*] \quad (2a)$$

From the expressions for the equilibrium constant it is possible to get the coverage

density of the main intermediates which can be expressed by [*]

$$[O_2] = K_{1a} P_{O_2} [*] \quad (3a)$$

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23 $[CH_4] = K_{3a} P_{CH_4} [^*]$ (4a)

24 [O] is given by eq1, eq2 and eq3

25 $[O] = \frac{k_{2a} K_{1a} P_{O_2}}{2k_{4.1a} k_{3a} P_{CH_4}} [^*]$ (5a)

26 and

27 $[CO_2] = \frac{P_{CO_2}}{K_{6.1a}} [^*]$ (6a)

28 When the concentration of CO₂ is high enough, the surfaces are covered by

29 CO₃*

30

31 $[CO_3] = \frac{k_{6.2a} k_{2a} K_{1a} P_{O_2} P_{CO_2}}{2k_{4.1a} k_{3a} P_{CH_4}} [^*]$ (7a)

32 In addition, CO* and C* are given by

33 $[CO] = \frac{2k_{4.1a} k_{3a} P_{CH_4} P_{CO_2}}{K_5 K_{6.1a} k_{2a} K_{1a} P_{O_2}} [^*]$ (8a)

34 $[C] = \frac{4k_{4.1a}^2 k_{3a}^2 P_{CH_4}^2 P_{CO_2}}{k_{2a}^2 K_{1a}^2 K_{4.2a} K_{6.1a} K_5 P_{O_2}^2} [^*]$ (9a)

35

36 H₂O* are described by a equation

37

38

39 $[H_2O] = \frac{P_{H_2O}}{K_{8a}} [^*]$ (10a)

40 The quasi-equilibrium between OH* and H₂O* can be expressed by

41 $K_{7a} K_{8a} [OH]^2 [H_2O] = [H_2O][O][^*] P_{H_2O}$ (11a)

42 Then, OH* can be written as follow

$$43 \quad [OH] = \sqrt{\frac{k_{2a}K_{1a}P_{O_2}}{2K_{7a}K_{8a}k_{4.1a}k_{3a}P_{CH_4}} P_{H_2O}[*]} \quad (12a)$$

44

45 The relationship of all species can be given by

$$46 \quad [*] + [O_2] + [O] + [CH_4] + [*] + [CO] + [OH] + [H_2O] + [CO_2] + [CO_3] = 1 \quad (13a)$$

47 It also can be written as follow

$$48 \quad [*] = \frac{1}{\frac{[*]}{[*]} + \frac{[O_2]}{[*]} + \frac{[O]}{[*]} + \frac{[CH_4]}{[*]} + \frac{[C]}{[*]} + \frac{[OH]}{[*]} + \frac{[H_2O]}{[*]} + \frac{[CO_2]}{[*]} + \frac{[CO_3]}{[*]}} \quad (14a)$$

49 Taken together with all the equations (eq 1a to eq 12a), eq 14a can be

50 written as

51

$$52 \quad \frac{1}{[*]} = 1 + K_{1a}P_{O_2} + \frac{k_{2a}K_{1a}P_{O_2}}{2k_{4.1a}k_{3a}P_{CH_4}} + K_{3a}P_{CH_4} + \frac{4k_{4.1a}^2k_{3a}^2P_{CH_4}^2P_{CO_2}}{k_{2a}^2K_{1a}^2K_{4.2a}K_{6.1a}K_5P_{O_2}^2} + \frac{2k_{4.1a}k_{3a}P_{CH_4}P_{CO_2}}{K_5K_{6.1a}k_{2a}K_{1a}P_{O_2}} +$$

$$53 \quad \sqrt{\frac{k_{2a}K_{1a}P_{O_2}}{2K_{7a}K_{8a}k_{4.1a}k_{3a}P_{CH_4}} P_{H_2O}} + \frac{P_{H_2O}}{K_{8a}} + \left(\frac{1}{K_{6a}} + \frac{k_{6.2a}k_{2a}K_{1a}P_{O_2}}{2k_{4.1a}k_{3a}P_{CH_4}} \right) P_{CO_2} \quad (15a)$$

54 In this paper, the surface species of C*, CO were not taken into consideration

55 owing to the high O₂ concentration. Hence, the rate equation can be simplified as

56 follows:

$$r_a =$$

$$57 \quad \frac{k_{2a}K_{1a}P_{O_2}}{2 \left(1 + K_{1a}P_{O_2} + \frac{k_{2a}K_{1a}}{2k_{4.1a}k_{3a}} \frac{P_{O_2}}{P_{CH_4}} + K_{3a}P_{CH_4} + \sqrt{\frac{k_{2a}K_{1a}}{2K_{7a}K_{8a}k_{4.1a}k_{3a}} \frac{P_{O_2}P_{H_2O}}{P_{CH_4}}} + \frac{P_{H_2O}}{K_{8a}} + \left(\frac{1}{K_{6a}} + \frac{k_{6.2a}k_{2a}K_{1a}P_{O_2}}{2k_{4.1a}k_{3a}P_{CH_4}} \right) P_{CO_2} \right)^2} \quad (16a)$$

58

60 **1.2 Derivation of CH₄ reaction rates are limited by C-H bond activation on O*-**

61 **O* site pairs on Pt-like surfaces.** Suppose all but step 2b (reversible) and step 3b
 62 (irreversible) are quasi-equilibrated, and the overall rate for methane oxidation
 63 rate can be written as follows:

$$64 \quad r_b = k_{3b}[O]^2 P_{CH_4} = \frac{k_{2bf}K_{1b}P_{O_2}[*]^2 - k_{2br}[O]^2}{2} \quad (1b)$$

65 Besides, from the expression for the equilibrium constants it is possible to get the
 66 coverage density of the main intermediates which can be expressed by [*]

67

$$68 \quad [O_2] = K_{1b}P_{O_2}[*] \quad (2b)$$

69 Equation 1b can be simplified to

$$70 \quad [O] = \sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}}[*] \quad (3b)$$

71 Some other species can be given by

$$72 \quad [CO_2] = \frac{P_{CO_2}}{K_{6.1b}}[*] \quad (4b)$$

$$73 \quad [CO] = \frac{P_{CO_2}}{K_{5b}K_{6.1b}\sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}}}[*] \quad (5b)$$

$$74 \quad [H_2O] = \frac{P_{H_2O}}{K_{8b}}[*] \quad (6b)$$

$$75 \quad [OH] = \sqrt{\frac{P_{H_2O}}{K_{7b}K_{8b}}\sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}}}[*] \quad (7b)$$

$$76 \quad [CO_3] = K_{6.2b}\sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}}[*]P_{CO_2} \quad (8b)$$

77 The relationship of all species can be given by the Langmuir adsorption

78 equation,

79

$$80 \quad [*] + [O_2] + [O] + [*] + [CO] + [OH] + [H_2O] + [CO_2] + [CO_3] = 1 \quad (9b)$$

81 Here, the intermediates CH_4^* were not taken into consideration due to the

82 rare vacancy sites (*) for methane adsorption. Besides, equation (9b) also can be

83 written as follow

84

$$85 \quad [*] = \frac{[*]}{1} = \frac{1}{1 + \frac{[O_2]}{[*]} + \frac{[O]}{[*]} + \frac{[OH]}{[*]} + \frac{[CO_2]}{[*]} + \frac{[CO_3]}{[*]} + \frac{[H_2O]}{[*]}} \quad (10b)$$

86 Taken together with all the equations (eq 2b to eq 8b), eq 10b can be written

87 as

88

$$[*] =$$

$$89 \quad \frac{1}{1 + K_{1b}P_{O_2} + \sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}} + \sqrt{\frac{P_{H_2O}}{K_{7b}K_{8b}} \sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}} + \left(\frac{1}{K_{6.1b}} + K_{6.2b} \sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}} \right) P_{CO_2} + \frac{P_{H_2O}}{K_{8b}}}$$

90 (11b)

91 Hence, the overall rate for methane oxidation on Pt-like catalysts can be given by:

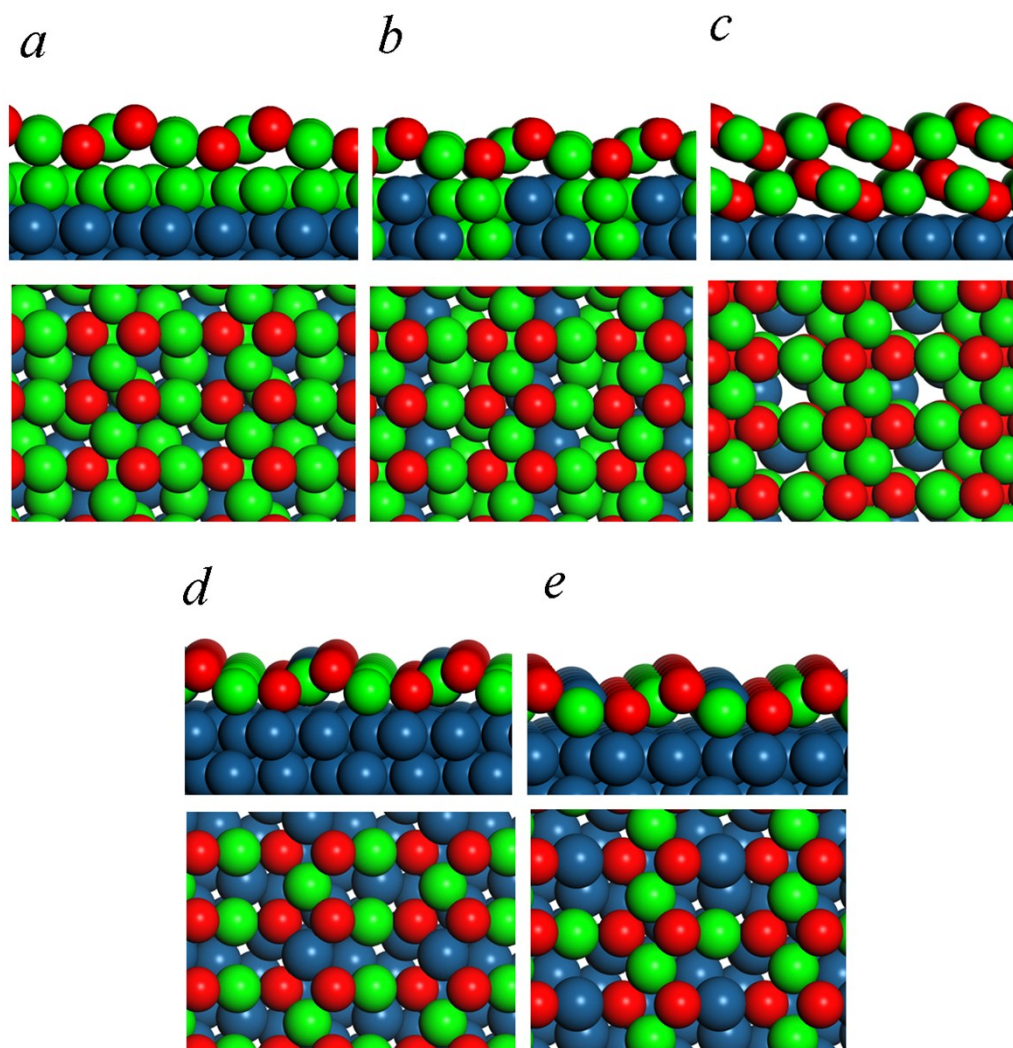
92

$$r_b = \frac{k_{3b}k_{2bf}K_{1b}}{2k_{3b}P_{CH_4} + k_{2br}} P_{O_2} P_{CH_4} \times$$

93

$$\frac{1}{\left(1 + K_{1b}P_{O_2} + \sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}} + \sqrt{\frac{P_{H_2O}}{K_{7b}K_{8b}} \sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}} + \left(\frac{1}{K_{6.1b}} + K_{6.2b} \sqrt{\frac{k_{2bf}K_{1b}P_{O_2}}{2k_{3b}P_{CH_4} + k_{2br}}} \right) P_{CO_2} + \frac{P_{H_2O}}{K_{8b}} \right)^2}$$

95 **2. Optimized structure of the oxide (101) layers on (100) metallic**
 96 **substrates.**



97

98 Figure S1. Side- and top-views of the optimized structure of oxide (101) layers on (100) sublayer.

99 (a) PdO(101)/Pd/Pt(100), (b) PdO(101)/PdPt(100), (c) 2 layers PdO(101)/Pt(100), (d) Pd_{0.75}Pt_{0.25}

100 on α -O(101)/Pt(100), (e) Pd_{0.75}Pt_{0.25} on β -O(101)/Pt(100). In the case of Pd_{0.75}Pt_{0.25} on α -O(101)/Pt(100),

101 one surface Pd atom coordinated to four O atoms (α site) is replaced by one Pt atom. For Pd_{0.75}Pt_{0.25}

102 on β -O(101)/Pt(100), one surface Pd atom coordinated to three O atoms (α site) is replaced by one Pt

103 atom.