Supplementary material for:

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

Wenjie Qi\textsuperscript{a, b}, Jingyu Ran\textsuperscript{a, b, *}, Ruirui Wang\textsuperscript{a, b}, Xuesen Du\textsuperscript{a, b}, Jun Shi\textsuperscript{a, b}, Juntian Niu\textsuperscript{a, b}, Peng Zhang\textsuperscript{a, b} Mingchu Ran\textsuperscript{b}

\textsuperscript{a} Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Ministry of Education of PRC, Chongqing University, 174 Shazheng Street, Shapingba District, Chongqing, 400044, China

\textsuperscript{b} College of Power Engineering, Chongqing University, Chongqing 400030, China

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

1.1 Derivation of CH\textsubscript{4} 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:

\[ r_a = k_{4\text{Ia}}[CH_4][O] \]  \hspace{1cm} (1a)

or

\[ r_a = k_{2\text{a}}[O_2][*] \]  \hspace{1cm} (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 [*]

\[ [O_2] = K_1 P_{O_2}[*] \]  \hspace{1cm} (3a)

* Corresponding Author
Telephone: +86- 18996085138; Fax: +61- 23-65111832. E-mail: Ranjy@cqu.edu.cn (Jingyu Ran).
[CH₄] = K_{3a} P_{CH₄} [\ast] \quad (4a)

[O] is given by eq1, eq2 and eq3

\[ [O] = \frac{k_{2a} K_{1a} P_{O_2}}{2k_{4.1a} K_{3a} P_{CH₄}} [\ast] \quad (5a) \]

and

\[ [CO_2] = \frac{P_{CO_2}}{K_{6.1a}} [\ast] \quad (6a) \]

When the concentration of CO₂ is high enough, the surfaces are covered by CO₃\ast

\[ [CO_3] = \frac{k_{a.2a} K_{1a} P_{O_2} P_{CO_2}}{2k_{4.1a} k_{3a} P_{CH₄}} [\ast] \quad (7a) \]

In addition, CO\ast and C\ast are given by

\[ [CO] = \frac{2k_{4.1a} k_{3a} P_{CH₄} P_{CO_2}}{K_{5} K_{6.1a} k_{2a} K_{1a} P_{O_2}} [\ast] \quad (8a) \]

\[ [C] = \frac{4k_{4.1a}^2 k_{3a}^2 P_{CH₄}^2 P_{CO_2}}{k_{2a}^2 K_{1a}^2 K_{4.2a} K_{6.1a} K_{5} P_{O_2}} [\ast] \quad (9a) \]

H₂O\ast are described by an equation

\[ [H_2O] = \frac{P_{H_2O}}{K_{8a}} [\ast] \quad (10a) \]

The quasi-equilibrium between OH\ast and H₂O\ast can be expressed by

\[ K_{7a} K_{8a} [OH] [H_2O] = [H_2O] [O] [\ast] P_{H_2O} \quad (11a) \]
In this paper, the surface species of C*, CO were not taken into consideration. The relationship of all species can be given by:

\[ [\text{C}^*]+[O_2]+[O]+[\text{CH}_4]+[\text{CO}]+[\text{OH}]+[\text{H}_2\text{O}]+[\text{CO}_2]+[\text{CO}_3] = 1 \]  

(13a)

It also can be written as follow:

\[ [\text{C}^*] = \frac{1}{[\text{C}^*]+[O_2]+[O]+[\text{CH}_4]+[\text{CO}]+[\text{OH}]+[\text{H}_2\text{O}]+[\text{CO}_2]+[\text{CO}_3]} \]  

(14a)

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

\[
\frac{1}{[\text{C}^*]} = 1 + K_{1a} P_{O_2} + \frac{k_{1a} K_{1a} P_{O_2}}{2k_{4,1a} k_{3a} P_{\text{CH}_4}} + K_{3a} P_{\text{CH}_4} + \frac{4k_{4,1a}^2 k_{3a}^2 P_{\text{CH}_4}^2 P_{\text{CO}_2}}{k_{2a}^2 K_{1a}^2 K_{4,2a} K_{6,1a} K_{5} P_{O_2}^2} + \frac{2k_{4,1a} k_{3a} P_{\text{CH}_4} P_{\text{CO}_2}}{K_{5} K_{6,1a} k_{2a} K_{1a} P_{O_2}} \]

(15a)

In this paper, the surface species of C*, CO were not taken into consideration owing to the high O₂ concentration. Hence, the rate equation can be simplified as follows:

\[
r_a = \frac{k_{2a} K_{1a} P_{O_2}}{2 \left( 1 + K_{1a} P_{O_2} + \frac{k_{2a} K_{1a} P_{O_2}}{2k_{4,1a} k_{3a} P_{\text{CH}_4}} + K_{3a} P_{\text{CH}_4} + \frac{\sqrt{k_{2a} K_{1a} P_{O_2} P_{\text{H}_2\text{O}}}}{2k_{7a} K_{8a} k_{4,1a} k_{3a} P_{\text{CH}_4}} + \frac{1}{K_{6a}} + \frac{k_{6,2a} k_{2a} K_{1a} P_{O_2}}{2k_{4,1a} k_{3a} P_{\text{CH}_4}} \right)^2} \]

(16a)
1.2 Derivation of CH$_4$ reaction rates are limited by C-H bond activation on O*-site pairs on Pt-like surfaces. Suppose all but step 2b (reversible) and step 3b (irreversible) are quasi-equilibrated, and the overall rate for methane oxidation rate can be written as follows:

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

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

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

Equation 1b can be simplified to

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

Some other species can be given by

$$[CO_2] = \frac{P_{CO_2}}{K_{6,1b}}[^*] \quad (4b)$$

$$[CO] = \frac{P_{CO_2}}{k_{ib}K_{6,1b}} \sqrt{\frac{k_{2br}K_{1b}P_{O_2}[^*]}{2k_{3b}P_{CH_4} + k_{2br}}} \quad (5b)$$

$$[H_2O] = \frac{P_{H_2O}}{K_{4b}}[^*] \quad (6b)$$

$$[OH] = \sqrt{\frac{P_{H_2O}}{k_{7b}K_{6b}}} \sqrt{\frac{k_{2br}K_{1b}P_{O_2}[^*]}{2k_{3b}P_{CH_4} + k_{2br}}} \quad (7b)$$

$$[CO_2] = K_{6,2b} \sqrt{\frac{k_{2br}K_{1b}P_{O_2}[^*]}{2k_{3b}P_{CH_4} + k_{2br}}}P_{CO_2} \quad (8b)$$
The relationship of all species can be given by the Langmuir adsorption equation,

\[ [*] + [O_2] + [O] + [*] + [CO] + [OH] + [H_2O] + [CO_2] + [CO_3] = 1 \]  

(9b)

Here, the intermediates CH_4* were not taken into consideration due to the rare vacancy sites (*) for methane adsorption. Besides, equation (9b) also can be written as follow

\[ [*] = \frac{1}{1 + [O_2] + [O] + [OH] + [CO] + [CO_2] + [CO_3] + [H_2O]} \]  

(10b)

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

\[ [*] = \frac{1}{1 + K_{1b} P_{O_2} + \frac{k_{2b} K_{1b} P_{O_2}}{2k_{3b} P_{CH_4} + k_{2br}} + \frac{P_{H_2O}}{K_{7b} K_{ab}} \frac{k_{2b} K_{1b} P_{O_2}}{2k_{3b} P_{CH_4} + k_{2br}} + \left( \frac{1}{K_{6,1b}} + K_{6,2b} \right) \frac{k_{2b} K_{1b} P_{O_2}}{2k_{3b} P_{CH_4} + k_{2br}}} \]  

(11b)

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

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

\[ \left( 1 + K_{1b} P_{O_2} + \frac{k_{2b} K_{1b} P_{O_2}}{2k_{3b} P_{CH_4} + k_{2br}} + \frac{P_{H_2O}}{K_{7b} K_{ab}} \frac{k_{2b} K_{1b} P_{O_2}}{2k_{3b} P_{CH_4} + k_{2br}} + \left( \frac{1}{K_{6,1b}} + K_{6,2b} \right) \frac{k_{2b} K_{1b} P_{O_2}}{2k_{3b} P_{CH_4} + k_{2br}} \right)^2 P_{CO_2} + \frac{P_{H_2O}}{K_{ab}} \]
2. Optimized structure of the oxide (101) layers on (100) metallic substrates.

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

(a) PdO(101)/Pd/Pt(100), (b) PdO(101)/PdPt(100), (c) 2 layers PdO(101)/Pt(100), (d) Pd$_{0.75}$Pt$_{0.25}$ on αO(101)/Pt(100), (e) Pd$_{0.75}$Pt$_{0.25}$ on βO(101)/Pt(100). In the case of Pd$_{0.75}$Pt$_{0.25}$ on αO(101)/Pt(100), one surface Pd atom coordinated to four O atoms (α site) is replaced by one Pt atom. For Pd$_{0.75}$Pt$_{0.25}$
on β-O(101)/Pt(100), one surface Pd atom coordinated to three O atoms (α site) is replaced by one Pt atom.