

## Supporting Information

### CO<sub>2</sub> Coverage Accelerates Oxygen Removal in Oxy-Combustion Systems

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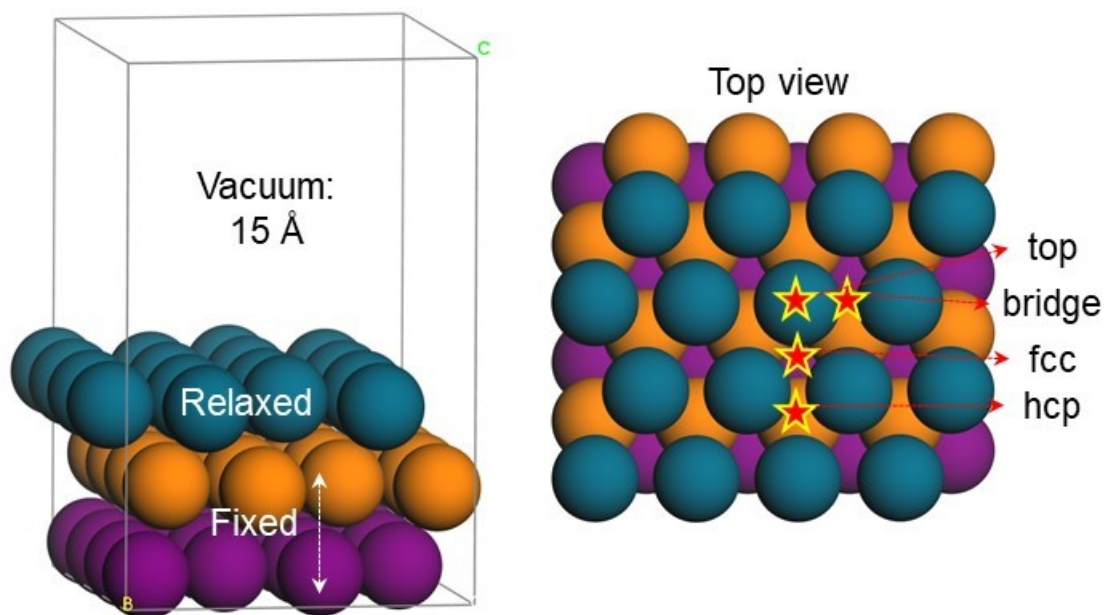


Figure S1. Structure of Pd (111) and adsorption sites on it.

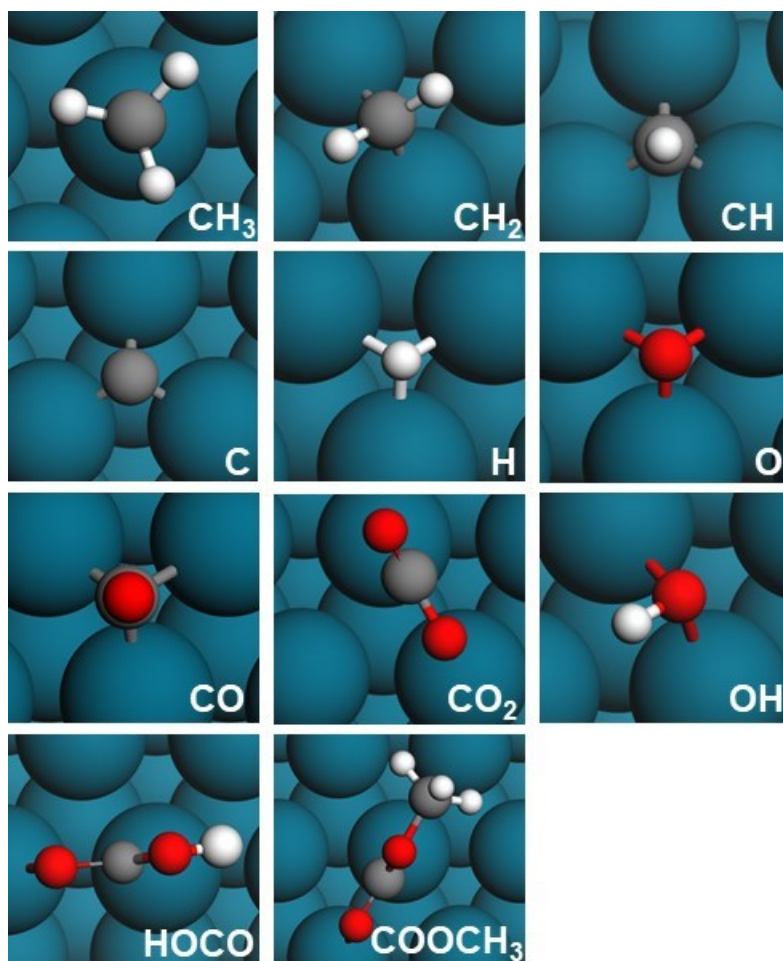


Figure S2. Optimized adsorbate structure on Pd (111) surface. Blue, red, grey, and white atoms represent Pd, O, C, and H atoms, respectively.

Table S1. Reaction rates of CH<sub>4</sub> and 1/2O<sub>2</sub> with Pd-TiO<sub>2</sub> under different feed gas composition (CO<sub>2</sub> concentration).

CO <sub>2</sub> conc. (mol m <sup>3</sup> )	$R_{CH_4}$ (mmol/g <sub>cat</sub> /hr)		$1/2R_{O_2}$ (mmol/g <sub>cat</sub> /hr)		$\left  \frac{R_{CH_4} - 1/2R_{O_2}}{R_{CH_4}} \right  \times 100$ (%) <sup>a</sup>	
	723 K	773 K	723 K	773 K	723 K	773 K
0	-0.0637	-0.0689	-0.0604	-0.0653	5.28	5.35
12.7	-0.0723	-0.0759	-0.0719	-0.0757	0.46	0.34
23.9	-0.0827	-0.0873	-0.0811	-0.0855	1.88	2.03
38.6	-0.0891	-0.0909	-0.0891	-0.0927	0.00	2.02

<sup>a</sup> Via complete CH<sub>4</sub> oxidation reaction ( $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ ):

$$\frac{R_{CH_4}}{-1} = \frac{R_{O_2}}{-2}$$

Table S2. Reaction energy ( $\Delta E$ ) and activation energy ( $E_a$ ) for CH<sub>4</sub> dissociation reaction with and without zero-point energy (ZPE) correction.

Adsorbate	Configuration	Without ZPE correction		With ZPE correction	
		$E_a$ (eV)	$\Delta E$ (eV)	$E_a$ (eV)	$\Delta E$ (eV)
1CO <sub>2</sub>	St5	1.16	0.010	1.19	0.164
2CO <sub>2</sub>	St1+St5	1.12	0.026	1.10	0.168
3CO <sub>2</sub>	St1+St3+St5	1.10	0.021	1.08	0.155
1HOCO	St2	1.22	0.083	1.21	0.256
2HOCO	St2+St3	1.12	0.181	1.10	0.320
3HOCO	St1+St2+St3	1.25	0.304	1.23	0.482

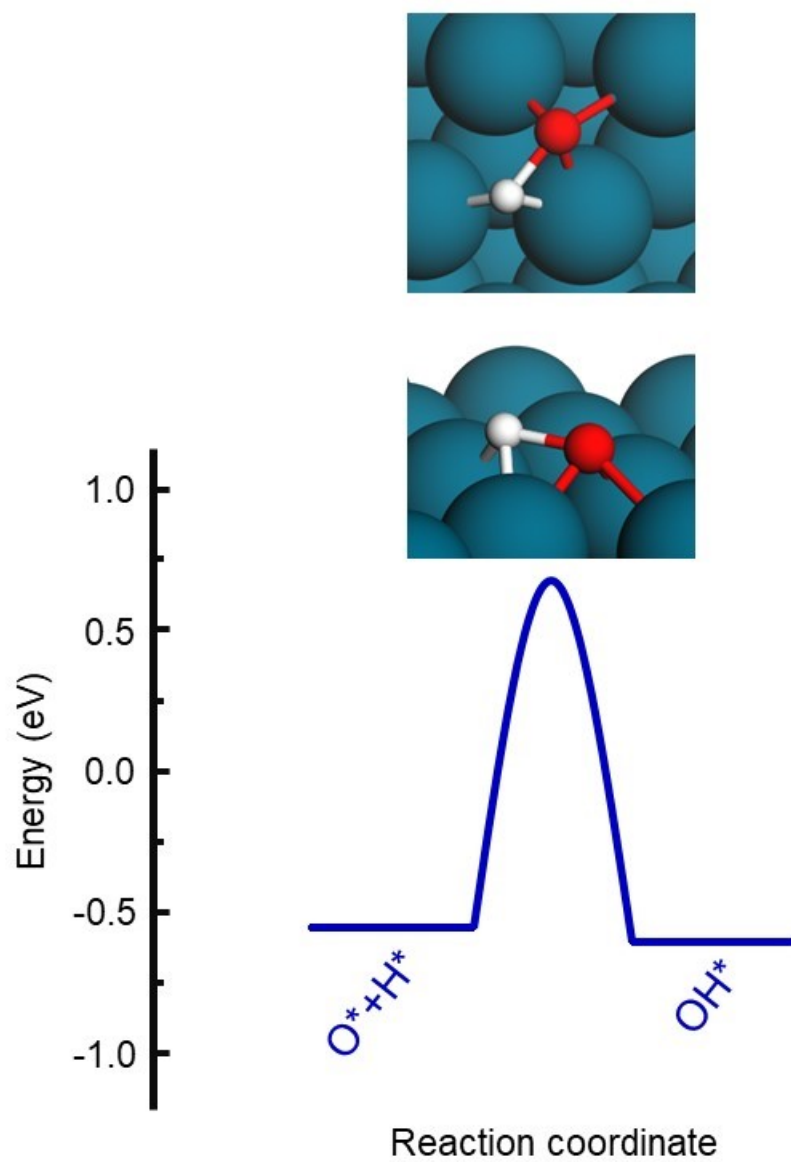


Figure S3. Energy diagram of the reaction of OH\* formation on Pd (111) surface. Blue, red, grey, and white atoms represent Pd, O, C, and H atoms, respectively.

Table S3. Reaction energy ( $\Delta E$ ) and activation energy ( $E_a$ ) for elementary reaction steps on Pd (111).

No.	Elementary step	$\Delta E$ (eV)	$E_a$ (eV)
1	$\text{CH}_4+2^* \rightarrow \text{CH}_3^*+\text{H}^*$	-0.09	1.29
	$\text{CH}_4+3\text{CO}_2^*+2^* \rightarrow \text{CH}_3^*+\text{H}^*+3\text{CO}_2^*$	0.02	1.10
2	$\text{CH}_3^*+^* \rightarrow \text{CH}_2^*+\text{H}^*$	0.01	1.73
	$\text{CH}_3^*+3\text{CO}_2^*+^* \rightarrow \text{CH}_2^*+\text{H}^*+3\text{CO}_2^*$	0.22	1.64
3	$\text{CH}_2^*+^* \rightarrow \text{CH}^*+\text{H}^*$	-0.54	0.39
	$\text{CH}_2^*+3\text{CO}_2^*+^* \rightarrow \text{CH}^*+\text{H}^*+3\text{CO}_2^*$	-0.43	0.35
4	$\text{CH}^*+^* \rightarrow \text{C}^*+\text{H}^*$	0.34	1.86
	$\text{CH}^*+3\text{CO}_2^*+^* \rightarrow \text{C}^*+\text{H}^*+3\text{CO}_2^*$	-0.31	1.48
5	$\text{C}^*+\text{O}^* \rightarrow \text{CO}^*+^*$	-2.11	2.48
	$\text{C}^*+\text{O}^*+3\text{CO}_2^* \rightarrow \text{CO}^*+^*+3\text{CO}_2^*$	-2.25	2.43
6	$\text{CO}^*+\text{O}^* \rightarrow \text{CO}_2^*+^*$	0.12	2.34
	$\text{CO}^*+\text{O}^*+3\text{CO}_2^* \rightarrow \text{CO}_2^*+^*+3\text{CO}_2^*$	-0.03	2.39