

Supplementary Materials: Oxygen Atom Function: The Case of Methane Oxidation Mechanism to Synthesis Gas over a Pd Cluster

Yuanyuan Meng ¹, Yuyuan Xue ¹, Chuanmin Ding ¹, Xiaofeng Gao ², Kan Zhang ³, Ping Liu ³, Junwen Wang ^{1,*} and Zhe Li ^{1,*}

Table S1. Gibbs free energies (G), energy barriers (E_b), enthalpies (H), and reaction energies (E_r) in the process of methane activation by Pd₂.

Pd ₂	G (a.u.)	G (eV)	E _b (eV)	H (a.u.)	E _r (eV)
CH ₄	-367.1245	0.00		-366.9792	
TS1	-367.1012	0.61	0.61	-366.9629	
CH ₃ + H	-367.1327	-0.22		-366.9916	-0.33
TS2	-367.0933	0.82	1.03	-366.9585	
CH ₂ + 2H	-367.1117	0.33		-366.9685	0.61
TS3	-367.0287	2.52	2.18	-366.8915	
CH + 3H	-367.0457	2.07		-366.9069	1.62
TS4	-366.9857	3.65	1.58	-366.8521	
C + 4H	-367.0411	2.19		-366.9020	0.13

Table S2. Gibbs free energies (G), energy barriers (E_b), enthalpies (H) and reaction energies (E_r) in the process of methane activation by Pd₂O.

Pd ₂ O	G (a.u.)	G (eV)	E _b (eV)	H (a.u.)	E _r (eV)
CH ₄	-442.3237	0.00		-442.1631	
TS1 [']	-442.2821	1.09	1.09	-442.1319	
CH ₃ + H	-442.2961	0.73		-442.1328	0.79
TS2 [']	-442.2475	2.00	1.28	-442.0990	
CH ₂ + 2H	-442.2589	1.70		-442.1032	0.78
TS3 [']	-442.1936	3.42	1.71	-442.1016	
CH + 3H	-442.2103	2.89		-442.1001	0.08
TS4 [']	-442.1599	4.30	1.33	-442.0958	
C + 4H	-442.1849	3.65		-442.1270	-0.71

Table S3. Gibbs free energies (G), energy barriers (E_b), enthalpies (H), and reaction energies (E_r) in the process of hydrogen generation by Pd₂.

Pd ₂	G (a.u.)	G (eV)	E _b (eV)	H (a.u.)	E _r (eV)
CH ₂ + 2H	-367.1117	0.00		-366.9685	
TS5	-367.1062	0.14	0.14	-366.9703	
CH ₂ + 2HS	-367.1081	0.09		-366.9664	0.06
TS6	-367.0970	0.39	0.29	-366.9573	
CH ₂ + 2HN	-367.1127	-0.03		-366.9750	-0.22
TS7	-367.0937	0.47	0.50	-366.9583	
CH ₂ + H ₂	-367.1195	-0.20		-366.9740	0.03

Table S4. Gibbs free energies (G), energy barriers (E_b), enthalpies (H), and reaction energies (E_r) in the process of hydrogen generation by Pd₂O.

Pd ₂ O	G (a.u.)	G (eV)	E _b (eV)	H (a.u.)	E _r (eV)
CH ₂ + 2H	-442.2589	0.00		-442.1032	
TS5 [†]	-442.2554	0.09	0.09	-442.1016	
CH ₂ + 2HS	-442.2507	0.21		-442.1001	0.08
TS6 [†]	-442.2495	0.25	0.03	-442.0958	
CH ₂ + 2HN	-442.2846	-0.67		-442.1270	-0.71
TS7 [†]	-442.2635	-0.12	0.55	-442.1088	
CH ₂ + H ₂	-442.2652	-0.16		-442.1081	0.50

Table S5. Gibbs free energies (G), energy barriers (E_b), enthalpies (H), and reaction energies (E_r) in the process of carbon monoxide formation by Pd₂.

Pd ₂	G (a.u.)	G (eV)	E _b (eV)	H (a.u.)	E _r (eV)
CH	-365.3203	0.00		-365.1963	
TS8	-365.2724	1.26	1.26	-365.1483	
C + H	-365.2857	0.91		-365.1624	0.89
C + O	-439.8384	0.39		-439.7045	
TS9	-439.8062	0.85	0.46	-439.6789	
CO	-440.0329	-5.10		-439.9013	-5.17
CH + O	-440.4671	0.00		-440.3284	
TS10	-440.4406	0.70	0.70	-440.3008	
CHO	-440.5792	-2.94		-440.4362	-2.83
TS11	-440.5665	-2.61	0.33	-440.4297	
CO + H	-440.5902	-3.23		-440.4538	-0.46
CH + O	-440.4671	0.00		-440.3284	
TS12	-440.4351	0.84	0.84	-440.3002	
COH	-440.5448	-2.04		-440.4051	-2.01
TS13	-440.5191	-1.36	0.68	-440.3777	
CO + H	-440.5902	-3.23		-440.4538	-1.28

Table S6. Gibbs free energies (G), energy barriers (E_b), enthalpies (H), and reaction energies (E_r) in the process of carbon monoxide formation by Pd₂.

Pd ₂	G (a.u.)	G (eV)	E _b (eV)	H (a.u.)	E _r (eV)
CH	-440.4571	0.00		-440.3215	
TS8 [†]	-440.4217	0.93	0.93	-440.2886	
C + H	-440.4299	0.72		-440.2957	0.68
C + O	-514.9918	0.45		-514.8450	
TS9 [†]	-514.9596	0.84	0.39	-514.8238	
CO	-515.1696	-4.67		-515.0246	-4.71
CH + O	-515.6080	0.00		-515.4564	
TS10 [†]	-515.5959	0.32	0.32	-515.4481	
CHO	-515.7350	-3.33		-515.5825	-3.31
TS11 [†]	-515.7176	-2.88	0.46	-515.5640	

CO + H	-515.7446	-3.58		-515.5945	-0.31
CH + O	-515.6080	0.00		-515.4564	
TS12 '	-515.5940	0.37	0.37	-515.4475	
COH	-515.6847	-2.01		-515.5313	-1.97
TS13 '	-515.6640	-1.47	0.54	-515.5142	
CO + H	-515.7446	-3.58		-515.4564	1.97