Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

DFT investigations for the reaction mechanism of methane oxidation to formaldehyde occurring Pd(II)/Al-MCM-41

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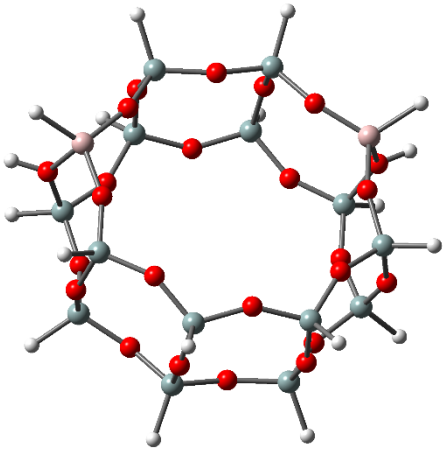


$H_{18}Al_2Si_{14}O_{24}$
$[H_2]$•[8–MR]

Figure S1: OPBE/TZVP-optimized structure of the 8 ($H_{18}Al_2Si_{14}O_{24}$) clusters (MS) .

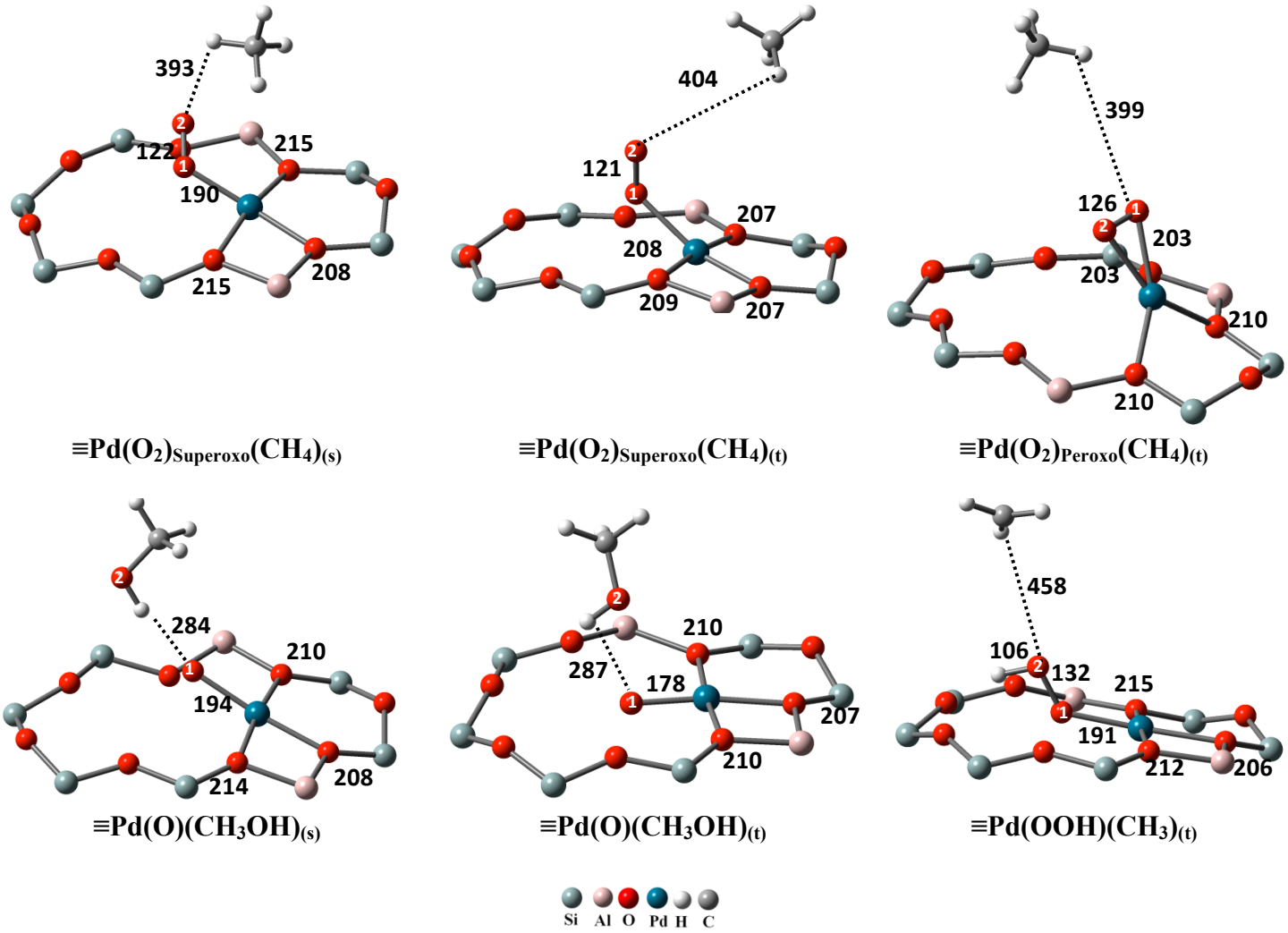
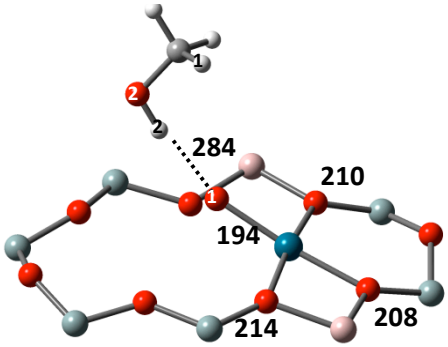
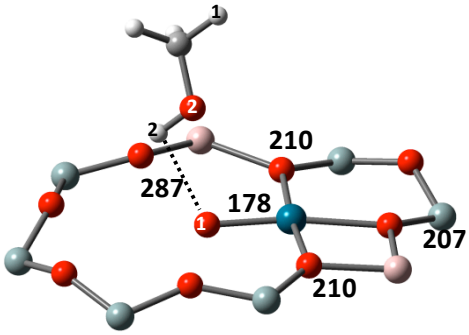


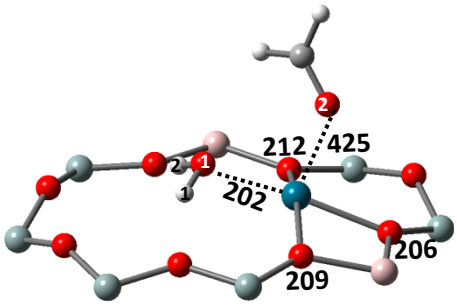
Figure S2: UOPBE/TZVP-optimized structures of CH_4 adsorption on ≡Pd(O_2) cluster, of CH_3OH adsorption on ≡Pd(O) cluster and geometries of ≡Pd(OOH)(CH_3). The bond lengths are given in pm, and s and t in the parentheses indicate singlet and triplet respectively. Pictures restricted to rings containing $[PdO_2]^{2+}$ species.



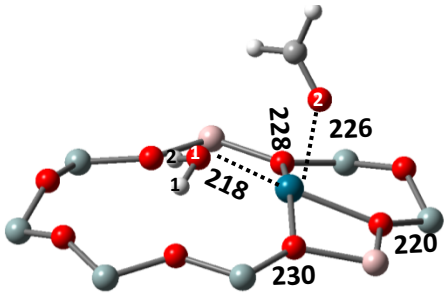
≡Pd(O)(CH$_3$OH)$_{(s)}$



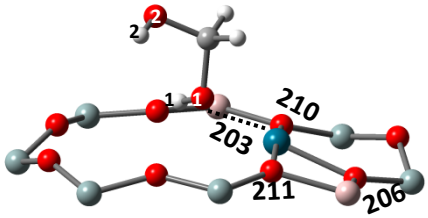
≡Pd(O)(CH$_3$OH)$_{(t)}$



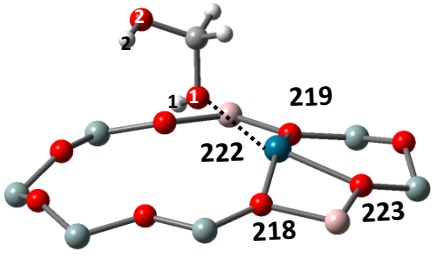
≡Pd(H$_2$O)(CH$_2$O)$_{(s)}$



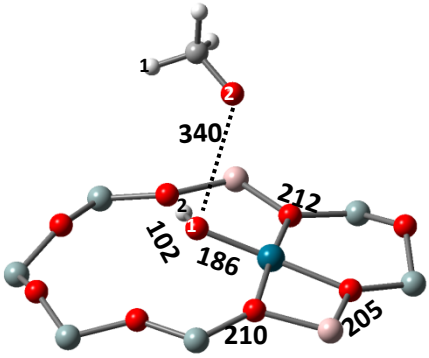
≡Pd(H$_2$O)(CH$_2$O)$_{(t)}$



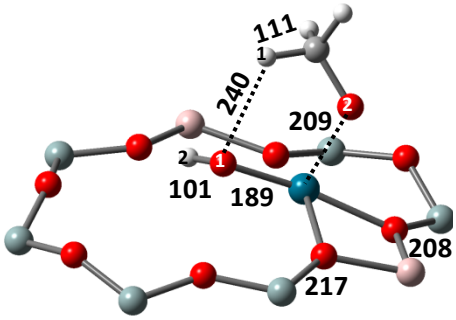
≡Pd(CH$_2$(OH)$_2$)$_{(s)}$



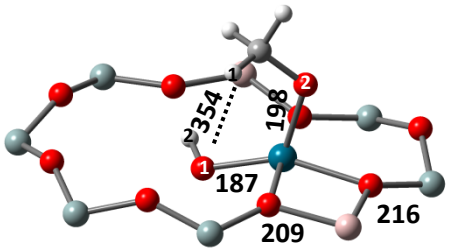
≡Pd(CH$_2$(OH)$_2$)$_{(t)}$



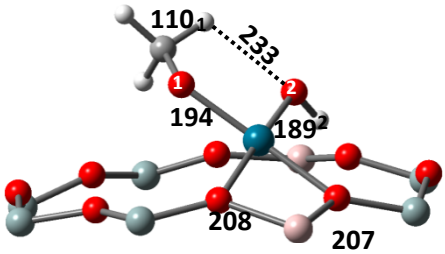
≡Pd(OH)(CH$_3$O)^{I} $_{(t)}$



≡Pd(OH)(CH$_3$O)^{II}$_{(t)}$



≡Pd(OH)(CH$_3$O)^{II}$_{(s)}$



≡Pd(OH)(CH$_3$O)^{III}$_{(t)}$

Figure S3: UOPBE/TZVP-optimized structures of CH_3OH adsorption on ≡Pd(O) cluster ; of formaldehyde and water adsorption on ≡Pd cluster ; of methanediol adsorption on ≡Pd cluster and geometries of ≡Pd(OH)(CH$_3$O)^{I} , ≡Pd(OH)(CH$_3$O)^{II} and ≡Pd(OH)(CH$_3$O)^{III}. The bond lengths are given in pm, and s and t in the parentheses indicate singlet and triplet respectively.

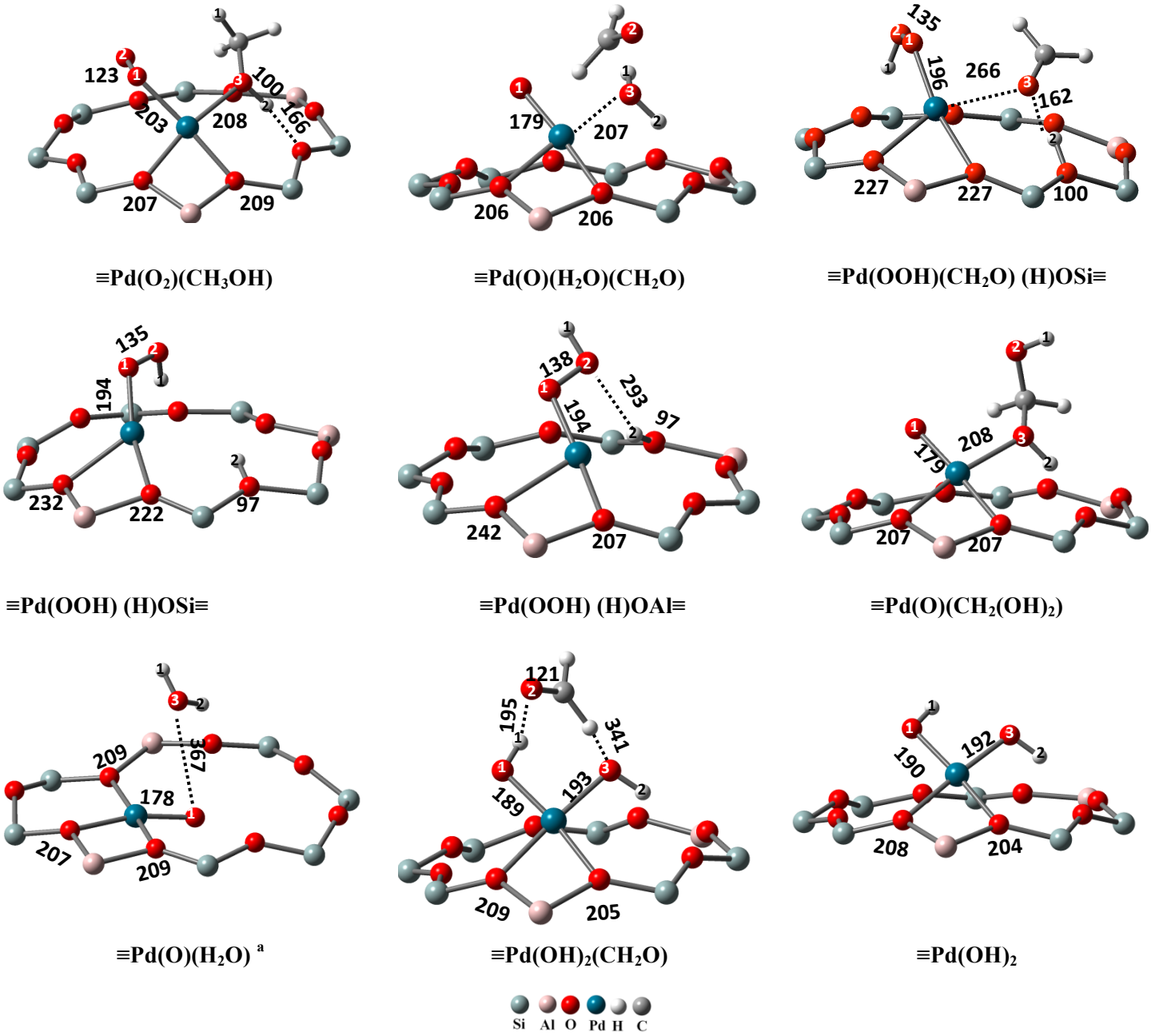


Figure S4: UOPBE/TZVP-optimized structures of CH_3OH adsorption on ≡Pd(O_2) cluster ; of formaldehyde and water adsorption on ≡Pd(O) cluster ; of methanediol adsorption on ≡Pd(O) cluster ; of water adsorption on ≡Pd(O) cluster and geometries of ≡Pd(OOH)(CH_2O)(H)OSi≡ , ≡Pd(OOH) (H)OSi≡ , ≡Pd(OOH) (H)OAl≡ , ≡Pd(OH)$_2$(CH_2O) and ≡Pd(OH)$_2$. The bond lengths are given in pm, and s and t in the parentheses indicate singlet and triplet respectively. Pictures restricted to rings containing $[PdO_2]^{2+}$ species.

[a] the intermediate **Pd(O)(H_2O)** comes from **≡Pd(OOH) (H)OAl≡** so the water oxygen is number 2 if it comes from **≡Pd (OH)$_2$** so oxygen number 3

Table S1. Standard free energies ΔG (kJ/mol) and activation free energy barriers $\Delta G^{\ddagger}$ (kJ/mol) for each transition state for direct oxidation of methane to formaldehyde on ≡Pd(O_2) and on ≡Pd(O) clusters at 773K. All species are in their triplet ground state except ≡Pd(s) that is in its singlet ground sate.

Reaction	**Steps**	**≡Pd(O_2)**	**≡Pd(O)**
		ΔG /$\Delta G^{\ddagger}$	**ΔG /$\Delta G^{\ddagger}$**
≡Pd(s) → ≡Pd(t)	Spin flip	100	
≡Pd + O_2 → ≡Pd(O_2) ≡Pd(O) + ½ O_2 → ≡Pd(O_2) ≡Pd + ½ O_2 → ≡Pd(O)	Adsorption of molecular O_2	75 8 67	
≡Pd(O_2) + CH_4 → ≡Pd(O_2) (CH_4) ≡Pd(O) + CH_4 → ≡Pd(O) (CH_4)	Methane adsorption	64	109
≡Pd(O_2) (CH_4) → ≡Pd(OOH)(CH_3) ≡Pd(O) (CH_4) → ≡Pd(OH) (CH_3)	**TS1:** Proton transfer from the CH_4 to form radical methyl	191 / 222	28 / 118
≡Pd(OOH)(CH_3) → ≡Pd(O)(CH_3OH) ≡Pd(OH)(CH_3) → ≡Pd (CH_3OH)	**TS2:** Hydroxyl transfer from the active species to form methanol	-191 / 110	-159 / 20
≡Pd(O)(CH_3OH) → ≡Pd(O) +CH_3OH ≡Pd(CH_3OH) → ≡Pd +CH_3OH	Desorption of methanol	-95	-69[a]
≡Pd(O_2) + CH_3OH → ≡Pd(O_2)(CH_3OH) ≡Pd(O) + (CH_3OH) → ≡Pd(O)(CH_3OH)	Adsorption of methanol	11	95
≡Pd(O)(CH_3OH) → ≡Pd(OH)(CH_3O)	**TS3**: Proton transfer from the OH to form methoxy		54 / 72
≡Pd(OH)(CH_3O) → ≡Pd(H_2O)(CH_2O)	**TS4**: Proton transfer from the methoxy to form formaldehyde and water		-226 / 18
≡Pd(O_2) (CH_3OH) → ≡Pd(OOH)(CH_2O) (H)OSi≡	**TS5**: Proton transfer from the carbon atom to form active species	-1 / 83	
≡Pd(OOH)(CH_2O) (H)OSi≡ → ≡Pd(O)($CH_2(OH)_2$)	**TS7:** Proton transfer from O_{MS} and OH transfer from PdOOH to form methanediol	-97 / 111	
≡Pd(O)($CH_2(OH)_2$) → ≡Pd($OH)_2$(CH_2O)	**TS9:** Formation of formaldehyde	-38 / 100	
≡Pd($OH)_2$(CH_2O) → ≡Pd($OH)_2$ + CH_2O ≡Pd(H_2O)(CH_2O) → ≡Pd(H_2O) + CH_2O	Desorption of formaldehyde	-75	-72
≡Pd($OH)_2$ → ≡Pd(O)(H_2O)	**TS10:** Formation of water	-23 / 102	
≡Pd(O)(H_2O) → ≡Pd(O)+(H_2O) ≡Pd(H_2O) → ≡Pd + H_2O	Desorption of water	-77	-90

[a] Gannouni et al. [22] The Pd^{2+} oxo species supported on a 8-membered ring

Table S2: Formation electronic energy ΔE_{Rel}^{elec} (kJ/mol) (Eq. (1)), Bond Distances (Pd-O_{MS}), (Pd-O1**)**, (Pd-O1**)** and (O1-O2**)** (pm) for ≡Pd$(O_2)_{Dioxo}$; ≡Pd$(O_2)_{Peroxo}$; ≡Pd$(O_2)_{Superoxo}$(t) and ≡Pd$(O_2)_{Superoxo}$(s).

	ΔE_{Rel}^{elec}	d(Pd-O_{MS}**)**	d(Pd-O1**)**	d(Pd-O2**)**	d(O1-O2**)**
≡Pd$(O_2)_{Dioxo}$(t)	231	212/212	181	181	275
≡Pd$(O_2)_{Peroxo}$(t)	37	210/210	203	203	126
≡Pd$(O_2)_{Superoxo}$(t)	-10	207/208/208	208	288	121
≡Pd$(O_2)_{Superoxo}$(s)	14	216/206/216	190	274	122

Table S3: Mulliken charge analysis for **≡Pd(O)(t)** ; ≡Pd$(O_2)_{Dioxo}$**(t)** ; ≡Pd$(O_2)_{Peroxo}$**(t)** ; ≡Pd$(O_2)_{Superoxo}$(t) and ≡Pd$(O_2)_{Superoxo}$(s).

	Pd	O_{MS}	O1/ O2	Al1/Al2
≡Pd(O)(t)	0.645	-0.587/-0.583/-0.606	-0.120	0.796/0.742
≡Pd$(O_2)_{Dioxo}$(t)	0.665	-0.612/-0.612	-0.179/ -0.179	0.737/0.738
≡Pd$(O_2)_{Peroxo}$(t)	0.526	-0.615/-0.615	-0.005/ 0.004	0.738/0.738
≡Pd$(O_2)_{Superoxo}$(t)	0.547	-0.591/-0.583/-0.603	0.019/0.070	0.741/0.809
≡Pd$(O_2)_{Superoxo}$(s)	0.590	-0.599/-0.595/-0.613	0.046/0.025	0.743/0.799

Table S4: Optimized geometrical parameters of all Species involved in the oxidation of methane to methanol on the ≡$Pd(O_2)$ cluster. Bond Distances (pm) and Angles (degree).

	≡$Pd(O_2)_{Superoxo(t)}$					**≡$Pd(O_2)_{Superoxo}$(s)**			**≡$Pd(O_2)_{Peroxo(t)}$**		
	$Pd(O_2)$ $(CH_4)_{(t)}$	**$TS_{1(t)}$**	**Pd(OOH) $(CH_3)_{(t)}$**	**$TS_{2(t)}$**	**Pd(O) $(CH_3OH)_{(t)}$**	**$Pd(O_2)$ $(CH_4)_{(s)}$**	**$TS_{1(s)}$**	**Pd(O) (CH_3OH) (s)**	**$Pd(O_2)$ $(CH_4)_{(t)}$**	**$TS1_{(t)}$**	**Pd(O) $(CH_3OH)_{(t)}$**
Pd-O^{MS}	207	209	215	212	210	215	212	210	210	206	210
Pd-O^{MS}	207	205	206	207	207	208	207	208	210	207	207
Pd-O^{MS}	209	211	212	211	210	215	212	214	---------	------	210
Pd-O1	208	193	191	185	178	190	194	194	203	181	178
Pd-O2	287	273	274	285	392	274	276	525	203	209	392
O1-O2	121	132	132	153	332	122	133	367	126	180	332
Pd-C	549	522	642	467	487	491	431	562	648	386	487
Pd-H	491	367	361	356	389	487	359	434	591	286	389
O1-H	478	190	183	187	287	416	191	284	399	285	287
O2-H	404	107	106	98	96	393	104	96	416	115	96
O2-C	426	270	458	215	141	450	222	141	460	220	141
C-H	109	162	465	241	193	109	163	193	109	129	193
Pd– O1 – O2	119	112	115	114	95	121	114	135	71	70	95
O1 – O2 –H	120	104	99	93	54	93	107	25	88	149	54
Pd– O2–H	98	144	138	129	81	92	136	17	160	121	81
O2 –H–C	94	174	80	62	43	114	111	44	177	129	43
H–C–Pd	53	15	33	48	49	81	53	40	55	33	49
C– O2 – O1	124	107	140	173	127	78	121	107	153	175	127

Table S5a: Optimized geometrical parameters of all Species involved in the oxidation of methanol to formaldehyde on the ≡Pd(O) cluster. Bond Distances (pm) and Angles (degree).

	≡Pd(O) (CH_3OH) (t)	TS_3							TS_4			≡ Pd(H_2 (CH_2O (t)
		TS_{3A} (t)	TS_{3B} (t)	TS_{3C} (t)	Pd ($CH_2(OH)_2$) (t)	Pd(OH) $(CH_3O)^I$ (t)	Pd(OH) $(CH_3O)^{III}$ (t)	Pd(OH) $(CH_3O)^{II}$ (t)	TS_{4A} (t)	TS_{4B} (t)	TS_{4C} (t)	
Pd-O^{MS}	210	210	209	223	219	212	--------	216	219	215	------	228
Pd-O^{MS}	207	208	206	210	223	205	207	208	223	207	205	220
Pd-O^{MS}	210	213	210	218	218	210	208	217	217	217	210	230
Pd-O1	178	183	185	182	222	186	194	189	223	194	193	218
Pd-O2	392	489	363	204	444	406	189	209	416	216	195	226
O1-O2	332	312	247	242	232	340	268	285	220	267	259	304
Pd-C	487	407	479	311	323	513	294	297	363	289	281	312
Pd-H1	520	283	504	335	269	527	311	306	269	260	261	263
Pd-H2	389	506	248	245	457	245	250	245	312	249	251	270
O1-H1	499	129	333	222	100	394	233	240	103	149	199	97
O1-H2	287	330	105	248	253	102	356	101	118	101	325	101
O2-H1	202	214	208	254	261	205	207	203	281	198	151	368
O2-H2	96	97	142	97	96	356	103	356	129	344	104	374
O2-C	141	135	135	203	143	134	283	136	129	133	249	122
C-H1	109	127	110	109	201	110	110	111	235	122	119	397
C-H2	193	191	237	241	191	589	362	350	163	309	299	376
– O1 – O2	95	161	113	55	154	96	45	47	139	60	48	48
– O1 – H1	87	130	151	112	107	127	94	90	104	97	50	108
– O1 – H2	112	161	114	59	147	113	115	111	129	111	48	109
– O2 –H1	136	18	94	53	22	89	57	56	19	33	50	13
– O2 –H2	54	92	2	105	91	17	143	13	26	13	121	12
d– O2–H1	118	12	122	93	34	115	102	95	40	77	97	45
d– O2–H2	81	94	28	103	92	37	115	42	30	46	110	45
O2 –H1–C	42	37	36	51	31	37	38	39	27	41	133	17
O2 –H2–C	43	42	30	56	43	19	34	22	52	23	52	19
H1–C–Pd	101	11	97	93	55	91	88	84	47	64	68	41
H2–C–Pd	49	110	9	51	123	28	43	44	60	49	51	45
– O2 – O1	127	52	118	52	35	114	29	83	53	70	31	86
– H1 – O1	47	166	81	87	41	94	105	113	44	138	41	35
– H2 – O1	126	50	152	43	34	88	34	53	75	17	24	50

Table S5b: Optimized geometrical parameters of all Species involved in the oxidation of methanol to formaldehyde on the ≡Pd(O) cluster. Bond Distances (pm) and Angles (degree).

	≡Pd(O) (CH_3OH)(s)	TS_3(s)				TS_4(s)		≡ Pd(H_2O) (CH_2O) (s)
		TS_{3A} (s)	TS_{3B} (s)	Pd ($CH_2(OH)_2$) (s)	Pd(OH) (CH_3O)^{II} (s)	TS_{4A} (s)	TS_{4B} (s)	
Pd-O^{MS}	214	208	209	210	209	211	207	212
Pd-O^{MS}	210	209	212	211	209	210	212	206
Pd-O^{MS}	208	210	214	206	216	206	208	209
Pd-O1	194	198	187	203	187	202	197	202
Pd-O2	525	466	240	418	198	396	209	425
O1-O2	367	312	233	231	331	220	268	437
Pd-C	563	371	351	295	286	338	296	507
Pd-H1	524	245	407	259	316	261	267	250
Pd-H2	434	520	208	435	243	293	251	260
O1-H1	402	102	312	105	354	111	160	97
O1-H2	284	358	120	251	100	120	99	100
O2-H1	210	224	20	260	209	280	195	507
O2-H2	97	97	120	97	358	127	353	486
O2-C	141	130	139	138	138	129	134	120
C-H1	110	154	110	206	110	242	118	561
C-H2	193	189	205	192	365	165	160	517
Pd– O1 – O2	136	135	69	148	31	140	50	73
Pd– O1 – H1	118	111	106	110	63	110	91	108
Pd– O1 – H2	129	141	82	145	112	130	112	113
O1 – O2 –H1	83	11	98	24	78	22	36	8
O1 – O2 –H2	26	111	14	90	16	26	10	11
Pd– O2–H1	78	8	130	37	101	41	83	29
Pd– O2–H2	18	118	60	94	40	31	44	32
O2 –H1–C	38	34	38	32	36	27	42	12
O2 –H2–C	44	40	41	43	22	50	22	14
H1–C–Pd	64	28	112	59	95	50	64	26
H2–C–Pd	41	134	32	125	42	60	45	29
C– O2 – O1	107	53	110	36	23	55	71	107
C– H1– O1	98	175	79	41	79	44	138	34
C– H2– O1	128	43	144	34	74	76	25	36

Table S6: Optimized geometrical parameters of ≡Pd(O_2)(CH_3OH) and ≡Pd(OOH)(CH_2O)(H)OSi≡ clusters and of the transition states TS_5. Bond Distances (pm) and Angles (degree).

	≡Pd(O_2)(CH_3OH)	**TS_5**	**≡Pd(OOH)(CH_2O) (H)OSi≡**
Pd-O_{MS}	207	213	227
Pd-O_{MS}	209	214	227
Pd-O_{MS}	-----	-----	-----
Pd-O1	203	200	196
Pd-O2	288	289	296
O1-O2	123	129	135
Pd-O3	208	203	266
H2- O3	100	161	162
H2- O_{MS}	**166**	101	100
H2- O**1**	-----	-----	449
O3 -C	143	130	122
C-H1	109	141	417
O2-H1	292	117	99
O2-C	323	254	382
O1-C	329	304	362
Pd– O1 – O2	122	121	125
H1 – C – O3	107	103	120
Pd– O3 –C	125	121	134
O1 – O2 –H1	81	108	107
O1 – Pd– O3	94	95	89
Pd– O3 –H2	102	102	95
O3 –H2– O_{MS}	162	162	172
O3 –H2– O**1**	-----	-----	32
H1 –O1– H2	-----	-----	98
Pd –O1– H1	-----	-----	98

Table S7: Optimized geometrical parameters of ≡Pd(OOH)(CH_2O) (H)OSi≡ ; ≡Pd(OOH) (H)OSi≡ ; ≡Pd(OOH) (H)OAl≡ and ≡Pd(O)(H_2O)clusters and of the transition states TS_6. Bond Distances (pm) and Angles (degree).

	≡Pd(OOH) (CH_2O) (H)OSi≡	**≡Pd(OOH) (H)OSi≡**	**≡Pd(OOH) (H)OAl≡**	**TS_6**	**≡Pd(O)(H2O)**
Pd-O_{MS}	227	227	207	216	207
Pd-O_{MS}	227	227	242	226	209
Pd-O_{MS}	-----	-------	------	----	209
Pd-O1	196	193	193	192	178
Pd-O2	296	290	283	290	353
O1-O2	135	135	138	144	370
Pd-O3	266	----------	------	---------	---------
H2- O3	162	------	------	----------	----------
H2- O_{MS}	100	97	97	163	278
H2- O**1**	449	405	293	265	329
O3 -C	122	----	------	------	----
C-H1	417	----	----------	-------	----
O2-H1	99	100	97	98	96
O2-H2	---------	------	293	144	96
O2-C	382	-----	-----	-----	------
O1-C	362	-----	------	----------	----------
Pd– O1 – O2	125	124	115	119	70
H1 – C – O3	120	----	----	---	---
Pd– O3 –C	134	-----	-----	---	---
O1 – O2 –H1	107	109	101	105	135
O1 – Pd– O3	89	----	------	---------	--------
Pd– O3 –H2	95	----------	--------	----------	---------
O3 –H2– O_{MS}	172	---------	----------	------	----------
O3 –H2– O**1**	32	-------	----------	-------	----------
H1 –O1– H2	98	81	70	49	15
Pd –O1– H1	98	101	146	140	70
O2–H2– O_{MS}	-----	------	155	176	140

Table S8: Optimized geometrical parameters of ≡Pd(OOH)(CH_2O) (H)OSi≡ ; ≡Pd($CH_2(OH)_2$) ; ≡Pd$(OH)_2$(CH_2O) ; ≡Pd$(OH)_2$ and ≡Pd(O)(H_2O) clusters and of the transition states TS_7; TS_9 and TS_{10} Bond Distances (pm) and Angles (degree).

	≡Pd(OOH) (CH_2O) (H)OSi≡	**TS_7**	**≡Pd(O) ($CH_2(OH)_2$)**	**TS_9**	**≡Pd$(OH)_2$ (CH_2O)**	**≡Pd$(OH)_2$**	**TS_{10}**	**≡Pd(O)(H2O)**
Pd-O_{MS}	227	216	207	205	205	204	205	207
Pd-O_{MS}	227	224	207	209	209	208	209	209
Pd-O_{MS}	-----	-------	-------	-------	-------	-------	-------	209
Pd-O1	196	194	179	185	189	190	186	178
Pd-O2	296	298	380	200	422	-------	-------	-----
O1-O2	135	159	334	335	290	-------	-----	------
Pd-O3	266	221	208	200	193	192	204	353
H2- O3	162	138	99	98	98	98	98	96
H2- O_{MS}	100	107	172	193	204	197	188	96
H2- O**1**	449	-------	358	353	352	349	117	443
O3 -C	122	132	147	174	381	-----	-------	----
C-H1	417	206	192	216	284	-----	----	----
O2-H1	99	97	97	127	195	-----	----	---
O2-C	382	155	137	129	121	-----	----	----
O1-C	362	251	310	310	377	-----	----	----
Pd– O1 – O2	125	115	90	101	121	----	-------	------
H1 – C – O3	120	92	95	78	40	-----	----	----
Pd– O3 –C	134	104	126	121	107	----	-----	----
O1 – O2 –H1	107	97	137	8	6	-----	----	-----
O1 – Pd– O3	89	78	91	90	89	87	70	70
Pd– O3 –H2	95	101	105	104	106	106	110	84
O3 –H2– O_{MS}	172	168	157	152	158	158	168	94
O3 –H2– O**1**	32	-------	32	28	26	17	40	107
H1 –O1– H2	98	-------	49	69	72	66	26	34
Pd –O1– H1	98	-------	83	109	112	106	81	70

Table S9: Optimized geometrical parameters of ≡Pd($CH_2(OH)_2$) and ≡Pd(O)(H_2O)(CH_2O) clusters and of the transition states TS_8 Bond Distances (pm) and Angles (degree).

	≡Pd(O) ($CH_2(OH)_2$)	**TS_8**	**≡Pd(O)(H_2O)(CH_2O)**
Pd-O_{MS}	207	207	206
Pd-O_{MS}	207	209	206
Pd-O_{MS}	-------	-------	------
Pd-O1	179	180	179
Pd-O2	380	332	411
O1-O2	334	256	359
Pd-O3	208	205	207
H2- O3	99	162	98
H2- O_{MS}	172	101	180
H2- O**1**	358	246	351
O3 -C	147	150	356
C-H1	192	161	258
O2-H1	97	136	168
O2-C	137	134	121
O1-C	310	286	381
Pd– O1 – O2	90	98	93
H1 – C – O3	95	44	412
Pd– O3 –C	126	114	106
O1 – O2 –H1	137	70	47
O1 – Pd– O3	91	88	90
Pd– O3 –H2	105	102	105
O3 –H2– O_{MS}	157	157	157
O3 –H2– O**1**	32	23	36
H1 –O1– H2	49	36	25
Pd –O1– H1	83	71	68