Supporting Information

The Effect of Steps on the Decomposition of CH_3O at PdZn Alloy Surfaces

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Table 1S. Unit cell parameters of PdZn(221)

a, Å	7.378
b, Å	5.866
c, Å	21.531
$\alpha = \beta = \gamma$, degree	90

Table 2S. Total energy (eV) of atoms and molecules in the gas phase

Species	O	H	CH_3	CH_2O	CH_3O
Total energy	-1.810	-1.119	-18.183	-22.228	-24.477

Table 3S. Cartesian coordinates (Å) of substrate atoms and the resulting total energy (eV)

	$(221)^{Pd}$			$(221)^{Zn}$			Bulk Truncated [a]		
	x	y	z	x	y	z	x	y	z
Pd	0.061	0.000	8.775	2.119	1.467	9.397	0.000	0.000	8.612
Pd	4.165	0.000	10.028	6.319	1.467	10.568	4.272	0.000	9.958
Pd	0.061	2.933	8.775	2.119	4.400	9.397	0.000	2.933	8.612
Pd	4.165	2.933	10.028	6.319	4.400	10.568	4.272	2.933	9.958
Pd	1.148	0.000	11.326	3.334	1.467	11.978	1.166	0.000	11.304
Pd	5.470	0.000	12.662	0.188	1.467	13.326	5.438	0.000	12.649
Pd	1.148	2.933	11.326	3.334	4.400	11.978	1.166	2.933	11.304
Pd	5.470	2.933	12.662	0.188	4.400	13.326	5.438	2.933	12.649
Pd	2.332	0.000	13.995	4.468	1.467	14.668	2.332	0.000	13.995
Pd	6.604	0.000	15.341	1.362	1.467	16.014	6.604	0.000	15.341
Pd	2.332	2.933	13.995	4.468	4.400	14.668	2.332	2.933	13.995
Pd	6.604	2.933	15.341	1.362	4.400	16.014	6.604	2.933	15.341
Pd	3.498	0.000	16.686	5.634	1.467	17.359	3.498	0.000	16.686
Pd	0.392	0.000	18.032	2.528	1.467	18.705	0.392	0.000	18.032
Pd	3.498	2.933	16.686	5.634	4.400	17.359	3.498	2.933	16.686
Pd	0.392	2.933	18.032	2.528	4.400	18.705	0.392	2.933	18.032
Zn	2.158	1.467	9.226	0.105	0.000	8.728	2.136	1.467	9.285
Zn	6.298	1.467	10.567	4.244	0.000	9.860	6.408	1.467	10.631
Zn	2.158	4.400	9.226	0.105	2.933	8.728	2.136	4.400	9.285
Zn	6.298	4.400	10.567	4.244	2.933	9.860	6.408	4.400	10.631
Zn	3.294	1.467	12.008	1.149	0.000	11.351	3.302	1.467	11.977
Zn	0.202	1.467	13.329	5.448	0.000	12.645	0.196	1.467	13.322
Zn	3.294	4.400	12.008	1.149	2.933	11.351	3.302	4.400	11.977
Zn	0.202	4.397	13.329	5.448	2.933	12.645	0.196	4.400	13.322
Zn	4.468	1.467	14.668	2.332	0.000	13.995	4.468	1.467	14.668
Zn	1.362	1.467	16.014	6.604	0.000	15.341	1.362	1.467	16.014
Zn	4.468	4.400	14.668	2.332	2.933	13.995	4.468	4.400	14.668
Zn	1.362	4.400	16.014	6.604	2.933	15.341	1.362	4.400	16.014
Zn	5.634	1.467	17.359	3.498	0.000	16.686	5.634	1.467	17.360
Zn	2.528	1.467	18.705	0.392	0.000	18.032	2.528	1.467	18.705
Zn	5.634	4.400	17.359	3.498	2.933	16.686	5.634	4.400	17.359
Zn	2.528	4.400	18.705	0.392	2.933	18.032	2.528	4.400	18.705
Total Energy			-112.095			-112.118			-111.846

[a] Coordinates of unrelaxed $(221)^{Pd}$; for unrelaxed $(221)^{Zn}$, interchange Pd and Zn atoms.

In Tables 4S to 9S, we provide the Cartesian coordinates (Å) of various adsorbed species on PdZn(221) slabs (see Table 3S) and the corresponding total energies (eV).

Table 4S. Most favorable adsorption site of H, O, CH_3, CH_3O, and CH_2O on PdZn(221)

		$(221)^{Pd}$			$(221)^{Zn}$		
		x	y	z	x	y	z
H		7.077	1.467	7.867	2.799	2.933	8.523
Total energy				-115.832			-115.613
O		2.326	0.000	8.018	0.667	1.467	7.668
Total energy				-118.125			-118.817
CH_3	H	0.104	2.956	6.100	1.658	2.355	6.709
	H	5.985	3.765	6.709	1.658	0.578	6.709
	H	6.087	1.972	6.688	3.178	1.467	6.949
	C	6.656	2.902	6.820	2.105	1.467	7.172
Total energy				-131.992			-131.522
CH_3O	H	5.637	0.717	6.062	6.321	2.352	5.636
	H	6.973	1.451	5.086	6.321	0.581	5.636
	H	5.817	2.492	6.012	7.874	1.467	5.498
	C	6.384	1.539	6.036	6.882	1.467	5.976
	O	7.314	1.495	7.149	6.988	1.467	7.409
Total energy				-138.690			-139.312
CH_2O	H	4.415	5.730	7.196	2.086	3.310	6.858
	H	4.331	1.736	6.918	2.267	5.115	6.810
	C	4.946	0.828	7.071	1.731	4.270	7.250
	O	6.188	0.901	7.072	0.339	4.379	7.260
Total energy				-134.770			-134.809

Table 5S. Transition states of $CH_3O \rightarrow CH_2O + H$ on $(221)^{Pd}$ and $(221)^{Zn}$

		$(221)^{Pd}$ terrace			$(221)^{Pd}$ edge			$(221)^{Zn}$		
		x	y	z	x	y	z	x	y	z
	H	4.528	0.564	8.473	6.320	5.173	7.739	2.000	3.427	7.968
	H	4.777	0.421	6.513	5.722	0.142	6.078	1.605	3.292	6.229
	H	4.485	2.182	7.192	4.912	0.837	7.624	2.051	5.016	6.684
	C	5.140	1.281	7.119	5.817	0.773	6.982	1.356	4.181	6.815
	O	6.429	1.441	7.245	6.632	1.760	6.943	0.101	4.438	7.080
Total energy				-137.987			-137.969			-138.037

Table 6S. Transition states of $CH_3O \rightarrow CH_3 + O$ on $(221)^{Pd}$

	$(221)^{Pd}$ terrace			$(221)^{Pd}$ terrace_2			$(221)^{Pd}$ edge		
	x	y	z	x	y	z	x	y	z
H	5.783	1.308	6.697	3.567	4.492	8.027	6.342	2.163	5.841
H	7.009	2.320	5.807	4.821	5.239	7.122	0.786	2.540	5.936
H	5.563	3.102	6.657	3.301	0.391	7.425	6.888	3.859	6.301
C	6.301	2.282	6.658	4.038	5.531	7.837	7.138	2.775	6.295
O	0.675	1.480	7.478	5.594	0.990	8.505	6.430	1.499	7.750
Total energy			-136.460			-135.712			-136.536

Table 7S. Transition state and final states of $CH_3O \rightarrow CH_3 + O$ on $(221)^{Zn}$

	Transition state			Final state		
	x	y	z	x	y	z
H	1.839	2.372	6.508	1.721	2.357	6.782
H	1.839	0.561	6.508	1.721	0.576	6.782
H	3.262	1.467	7.200	3.262	1.467	6.990
C	2.175	1.467	7.045	2.188	1.467	7.219
O	0.336	1.467	7.500	6.360	1.467	8.212
Total energy			-136.948			-138.198

Table 8S. Final states of $CH_3O \rightarrow CH_2O + H$ on $(221)^{Pd}$ and $(221)^{Zn}$

	$(221)^{Pd}$ terrace			$(221)^{Pd}$ edge			$(221)^{Zn}$		
	x	y	z	x	y	Z	x	y	z
H	4.077	4.398	8.936	7.339	4.377	7.805	2.800	2.901	8.612
H	4.416	5.731	7.195	4.588	5.772	7.181	2.179	3.633	6.968
H	4.332	1.735	6.917	4.266	1.716	6.747	2.090	5.448	6.795
C	4.948	0.828	7.070	4.992	0.924	7.018	1.695	4.497	7.162
O	6.186	0.900	7.071	6.203	1.166	7.094	0.322	4.410	7.229
Total energy			-138.159			-138.198			-138.140

Table 9S. Final states of $CH_3O \rightarrow CH_3 + O$ on $(221)^{Pd}$

	$(221)^{Pd}$ terrace			$(221)^{Pd}$ terrace_2			$(221)^{Pd}$ edge		
	x	y	z	x	y	z	x	y	z
H	6.328	2.468	6.459	4.531	0.301	7.610	0.535	3.351	6.144
H	0.538	3.331	6.249	3.062	1.191	7.246	6.434	4.267	6.629
H	6.410	4.258	6.627	2.989	5.291	7.241	6.362	2.465	6.514
C	6.948	3.316	6.773	3.443	0.282	7.754	6.994	3.336	6.743
O	2.354	0.003	8.031	6.009	1.511	8.484	5.642	1.248	8.711
Total energy			-137.976			-137.132			-137.318

Table 10S. Vibrational frequencies (cm^{-1}) of adsorbed CH_2O and the initial state (IS) of CH_3O on $(221)^{Pd}$ and $(221)^{Zn}$.

	CH_2O		IS	
	$(221)^{Pd}$	$(221)^{Zn}$	$(221)^{Pd}$	$(221)^{Zn}$
ν_1	2973	3080	2916	3004
ν_2	2892	3008	2878	2992
ν_3	1578	1453	2783	2928
ν_4	1444	1142	1453	1455
ν_5	1201	1089	1446	1453
ν_6	1006	883	1420	1420
ν_7	293	609	1124	1138
ν_8	230	423	1119	1119
ν_9	178	295	925	1138
ν_{10}	140	236	295	993
ν_{11}	93	169	281	317
ν_{12}	31	136	267	260
ν_{13}			201	149
ν_{14}			118	134
ν_{15}			64	86

Table 11S. Vibrational frequencies (cm^{-1}) of transition states for C-H and C-O bond breaking of adsorbed CH3O on $(221)^{Pd}$ and $(221)^{Zn}$.

	C-H bond breaking			C-O bond breaking			
	terrace	edge	$(221)^{Zn}$	terrace	Terrace_2	edge	$(221)^{Zn}$
ν_1	2896	2958	3082	3041	3032	3034	3019
ν_2	2795	2849	3014	3021	2859	2983	2988
ν_3	1482	1605	1543	2909	2364	2865	2912
ν_4	1429	1465	1478	1428	1493	1429	1429
ν_5	1244	1281	1287	1382	1322	1392	1385
ν_6	1200	1185	1173	1150	1084	1117	1215
ν_7	883	1065	1070	824	750	850	938
ν_8	725	780	977	690	713	746	771
ν_9	540	475	608	421	350	425	400
ν_{10}	321	334	328	342	332	378	384
ν_{11}	251	217	209	306	282	286	320
ν_{12}	241	198	146	190	193	206	273
ν_{13}	129	82	82	107	114	102	101
ν_{14}	9	25	66	45	45	39	46
ν_{15}	510*i*	699*i*	845*i*	513*i*	432*i*	488*i*	627*i*