SUPPORTING INFORMATION

DFT Study of Water Adsorption and Decomposition on the Ga-rich GaP(001)(2×4) Surface

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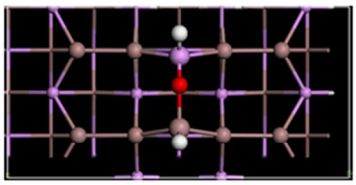
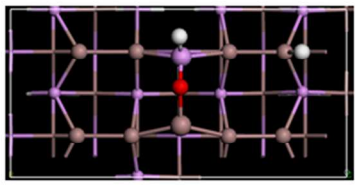


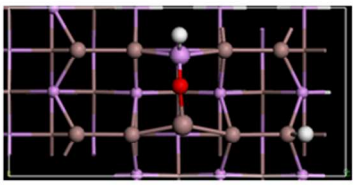
E_{ads} = −0.448

(a1) 1P-O-2G_H-1P_H-2G



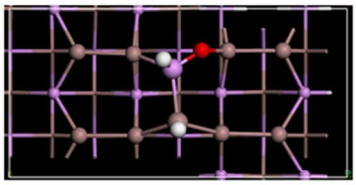
E_{ads} = −0.570

(a2) 1P-O-2G_H-1P_H-3G



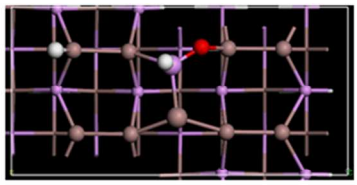
E_{ads} = −0.580

(a3) 1P-O-2G_H-1P_H-4G



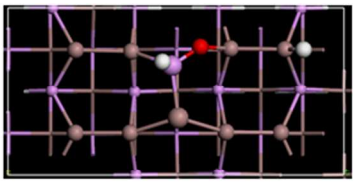
E_{ads} = −0.586

(b1) 1P-O-5G_H-1P_H-2G



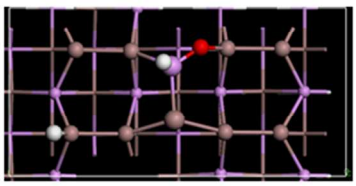
E_{ads} = −0.594

(b2) 1P-O-5G_H-1P_H-3G'



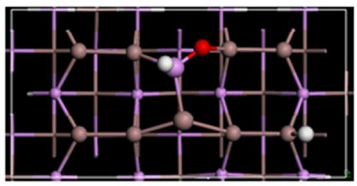
E_{ads} = −0.631

(b3) 1P-O-5G_H-1P_H-3G



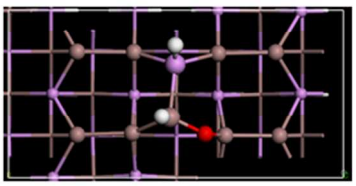
E_{ads} = −0.575

(b4) 1P-O-5G_H-1P_H-4G'



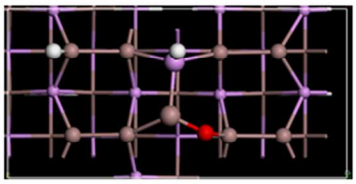
E_{ads} = −0.616

(b5) 1P-O-5G_H-1P_H-4G



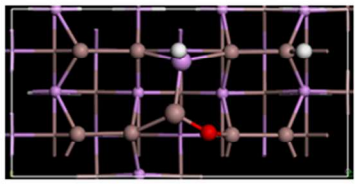
E_{ads} = −0.557

(c1) 2G-O-6G_H-1P_H-2G



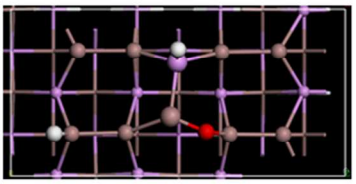
E_{ads} = −0.769

(c2) 2G-O-6G_H-1P_H-3G'



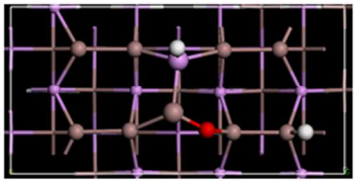
E_{ads} = −0.740

(c3) 2G-O-6G_H-1P_H-3G



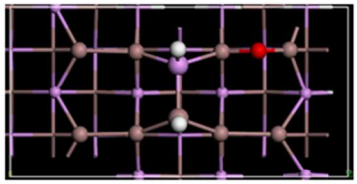
E_{ads} = −0.764

(c4) 2G-O-6G_H-1P_H-4G'



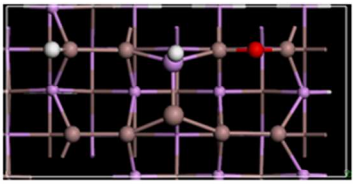
E_{ads} = −0.704

(c5) 2G-O-6G_H-1P_H-4G



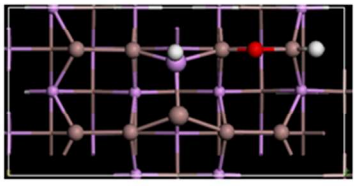
E_{ads} = −0.994

(d1) 3G-O-5G_H-1P_H-2G



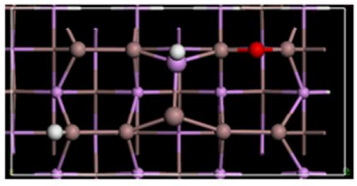
E_{ads} = −0.956

(d2) 3G-O-5G_H-1P_H-3G'



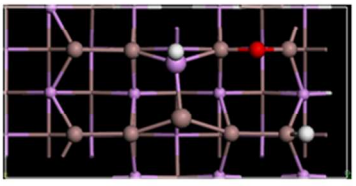
E_{ads} = −0.877

(d3) 3G-O-5G_H-1P_H-3G



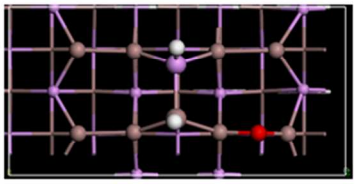
E_{ads} = −0.944

(d4) 3G-O-5G_H-1P_H-4G'



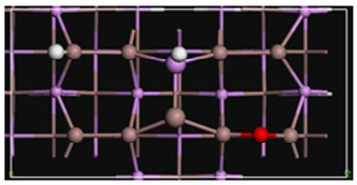
E_{ads} = −0.986

(d5) 3G-O-5G_H-1P_H-4G



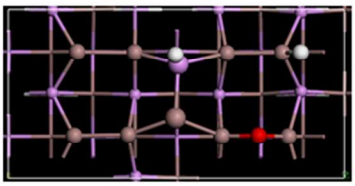
E_{ads} = −0.743

(e1) 4G-O-6G_H-1P_H-2G



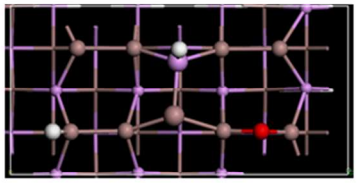
E_{ads} = −0.751

(e2) 4G-O-6G_H-1P_H-3G'



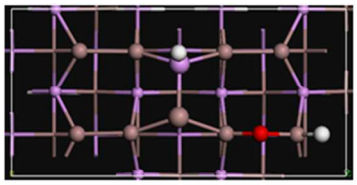
E_{ads} = −0.749

(e3) 4G-O-6G_H-1P_H-3G



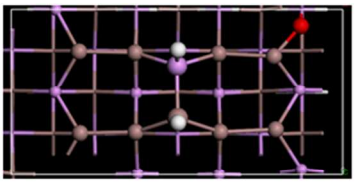
E_{ads} = −0.727

(e4) 4G-O-6G_H-1P_H-4G'



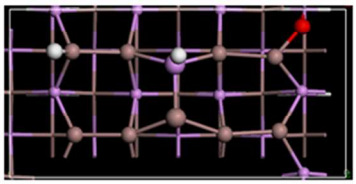
E_{ads} = −0.585

(e5) 4G-O-6G_H-1P_H-4G



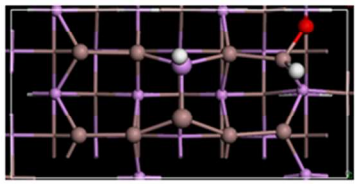
E_{ads} = −0.066

(f1) 3G-O-7P_H-1P_H-2G



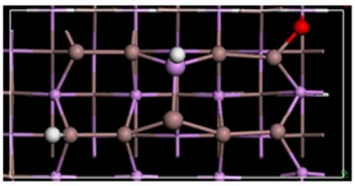
E_{ads} = −0.024

(f2) 3G-O-7P_H-1P_H-3G'



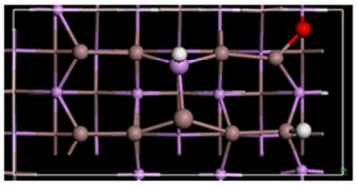
E_{ads} = +0.025

(f3) 3G-O-7P_H-1P_H-3G



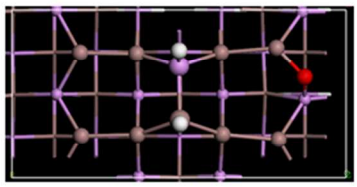
E_{ads} = −0.014

(f4) 3G-O-7P_H-1P_H-4G'



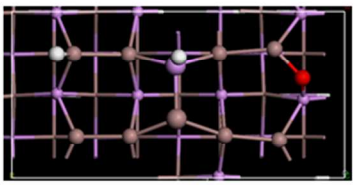
E_{ads} = −0.018

(f5) 3G-O-7P_H-1P_H-4G



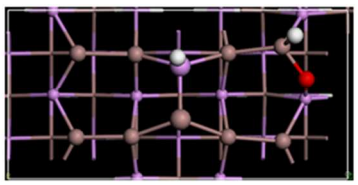
E_{ads} = −0.022

(g1) 3G-O-8P_H-1P_H-2G



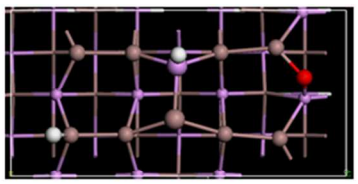
E_{ads} = +0.028

(g2) 3G-O-8P_H-1P_H-3G'



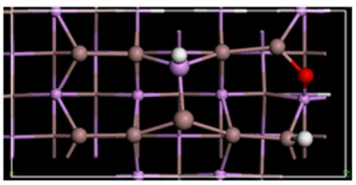
E_{ads} = +0.091

(g3) 3G-O-8P_H-1P_H-3G



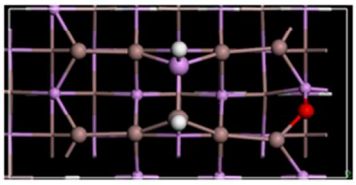
E_{ads} = +0.034

(g4) 3G-O-8P_H-1P_H-4G'



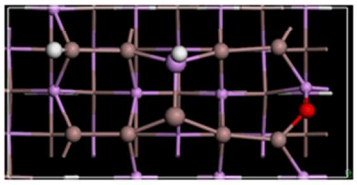
E_{ads} = +0.036

(g5) 3G-O-8P_H-1P_H-4G



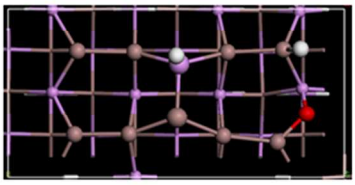
E_{ads} = +0.007

(h1) 4G-O-8P_H-1P_H-2G



E_{ads} = +0.084

(h2) 4G-O-8P_H-1P_H-3G'



E_{ads} = +0.089

(h3) 4G-O-8P_H-1P_H-3G

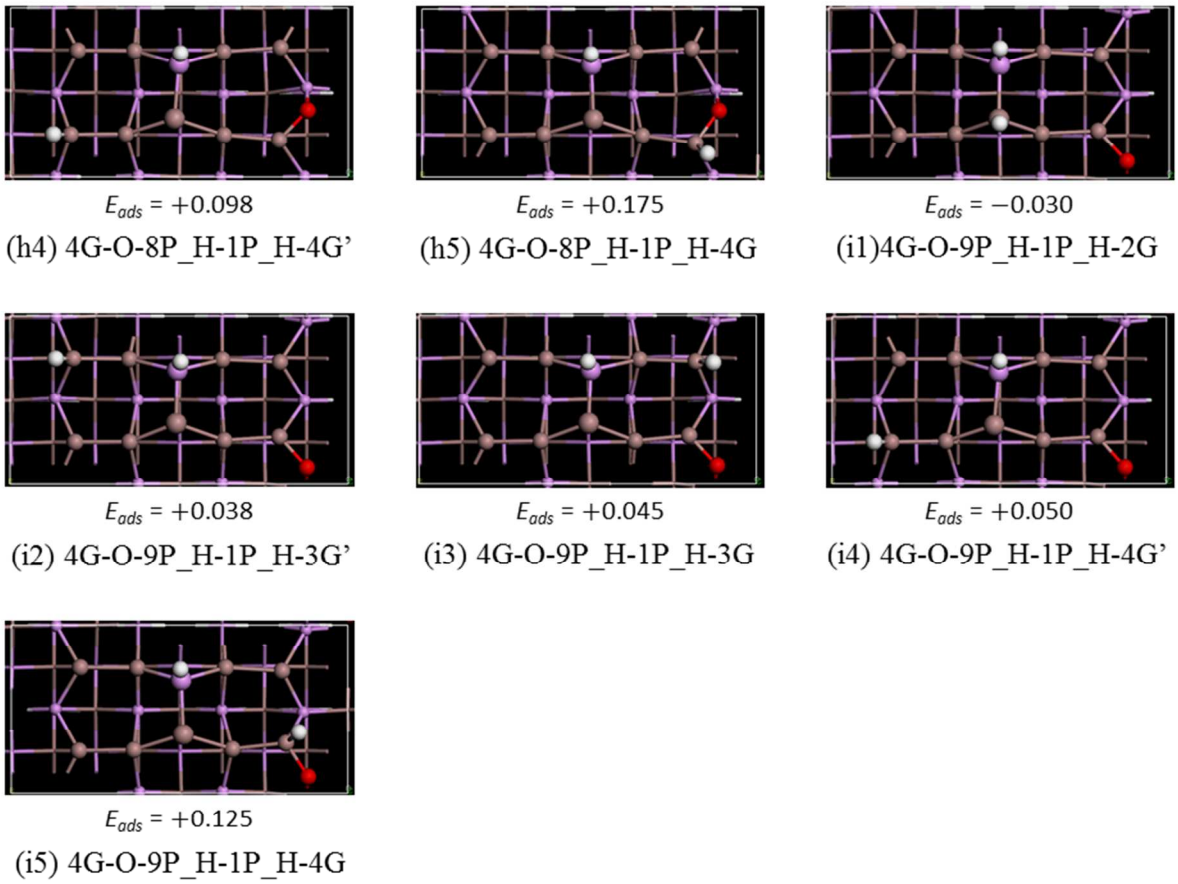


Figure S1. The optimized geometry and the corresponding adsorption energy for the 43 test structures in the O/2H decomposition state. Colorful spheres indicate atoms (purple-phosphorous, tan-gallium, red-oxygen, and white-hydrogen).

	1P-O-2G_H2			1P-O-2G			Variation (%)		
	X1(Å)	Y1(Å)	Z1(Å)	X2(Å)	Y2(Å)	Z2(Å)	X2-X1	Y2-Y2	Z2-Z3
1P	5.832	3.858	6.378	5.835	3.859	6.380	0.042	0.011	0.036
2G	5.831	3.233	10.359	5.832	3.231	10.362	0.021	-0.062	0.030
3G’	1.943	12.516	10.170	1.947	12.515	10.177	0.207	-0.010	0.072
5G’	1.922	9.987	10.569	1.932	9.985	10.577	0.514	-0.021	0.076
5G	2.440	7.760	11.643	2.453	7.760	11.654	0.539	0.004	0.094
3G	5.831	12.287	10.359	5.832	12.288	10.363	0.025	0.010	0.038
4G’	1.923	5.532	10.569	1.931	5.535	10.577	0.411	0.053	0.076
6G’	1.943	3.002	10.170	1.946	3.004	10.177	0.186	0.069	0.075
6G	5.826	9.539	10.425	5.831	9.541	10.437	0.082	0.020	0.121
4G	5.828	5.982	10.425	5.831	5.977	10.437	0.055	-0.081	0.118
O	4.113	7.758	12.501	4.122	7.758	12.523	0.217	-0.007	0.177
Eads	0.238 eV			0.239 eV			0.001 %		

	1P-O-5G_H2			1P-O-5G			Variation (%)		
	X1(Å)	Y1(Å)	Z1(Å)	X2(Å)	Y2(Å)	Z2(Å)	X2-X1	Y2-Y2	Z2-Z3
1P	5.207	8.022	12.278	5.207	8.025	12.279	0.000	0.037	0.009
2G	2.906	7.812	11.585	2.905	7.814	11.585	-0.002	0.035	0.006
3G’	5.792	12.331	10.296	5.791	12.331	10.296	-0.016	0.000	0.004
5G’	5.666	9.679	10.509	5.666	9.680	10.511	0.004	0.012	0.013
5G	5.874	5.527	10.366	5.875	5.527	10.367	0.003	0.004	0.010
3G	5.863	2.980	10.206	5.862	2.980	10.206	-0.005	-0.023	-0.001
4G’	1.943	12.433	10.181	1.942	12.435	10.182	-0.046	0.009	0.007
6G’	1.904	9.900	10.578	1.904	9.902	10.580	0.004	0.016	0.011
6G	2.000	5.618	10.663	2.000	5.620	10.663	-0.004	0.030	0.001
4G	1.982	3.059	10.235	1.982	3.059	10.237	0.000	0.029	0.021
O	5.957	6.631	11.886	5.956	6.628	11.887	-0.012	-0.042	0.004
Eads	0.207 eV			0.207 eV			0.000 %		

	2G-O-6G_H2			2G-O-6G			Variation (%)		
	X1(Å)	Y1(Å)	Z1(Å)	X2(Å)	Y2(Å)	Z2(Å)	X2-X1	Y2-Y2	Z2-Z3
1P	5.820	3.857	6.380	5.820	3.857	6.380	0.002	0.003	0.000
2G	5.718	6.014	10.437	5.719	6.012	10.436	0.007	-0.028	-0.010
3G’	5.795	3.217	10.389	5.796	3.215	10.388	0.013	-0.040	-0.012
5G’	1.974	12.491	10.166	1.974	12.491	10.166	0.004	0.002	-0.005
5G	1.925	2.909	10.151	1.925	2.908	10.151	0.022	-0.035	0.003
3G	3.075	7.998	11.772	3.074	7.997	11.771	-0.031	-0.012	-0.007
4G’	2.032	9.983	10.624	2.032	9.984	10.624	-0.012	0.002	-0.003
6G’	1.933	5.403	10.518	1.932	5.402	10.519	-0.015	-0.014	0.017
6G	5.826	12.311	10.344	5.827	12.312	10.344	0.004	0.003	-0.001
4G	5.792	9.593	10.400	5.791	9.593	10.398	-0.009	-0.007	-0.013

O	2.115	6.470	11.981	2.114	6.470	11.982	-0.059	-0.003	0.006
Eads	-0.288 eV			-0.288 eV			0.000 %		

	3G-O-5G_H2			3G-O-5G			Variation (%)		
	X1(Å)	Y1(Å)	Z1(Å)	X2(Å)	Y2(Å)	Z2(Å)	X2-X1	Y2-Y2	Z2-Z3
1P	5.348	7.825	11.987	5.368	7.832	11.987	0.379	0.088	0.002
2G	3.003	7.834	11.588	3.023	7.840	11.587	0.696	0.079	-0.010
3G’	5.800	12.306	10.345	5.816	12.315	10.345	0.270	0.072	-0.002
5G’	5.719	9.583	10.421	5.741	9.585	10.416	0.389	0.023	-0.044
5G	5.728	5.914	10.534	5.755	5.921	10.540	0.475	0.119	0.052
3G	5.820	2.768	10.192	5.830	2.782	10.197	0.166	0.491	0.045
4G’	1.946	12.466	10.184	1.962	12.472	10.187	0.843	0.051	0.023
6G’	1.954	9.932	10.616	1.978	9.936	10.613	1.215	0.035	-0.026
6G	1.963	5.733	10.597	1.995	5.740	10.592	1.588	0.116	-0.043
4G	1.962	3.149	10.334	1.972	3.161	10.330	0.509	0.373	-0.039
O	5.768	4.180	11.276	5.786	4.188	11.287	0.306	0.204	0.098
Eads	-0.443 eV			-0.443 eV			0.000 %		

	4G-O-6G_H2			4G-O-6G			Variation (%)		
	X1(Å)	Y1(Å)	Z1(Å)	X2(Å)	Y2(Å)	Z2(Å)	X2-X1	Y2-Y2	Z2-Z3
1P	5.332	7.863	11.972	5.363	7.842	11.968	0.575	-0.261	-0.030
2G	2.956	7.876	11.602	2.987	7.879	11.597	1.072	0.043	-0.047
3G’	5.801	12.332	10.329	5.821	12.320	10.344	0.347	-0.100	0.145
5G’	5.733	9.636	10.407	5.765	9.608	10.399	0.564	-0.294	-0.078
5G	5.720	6.125	10.380	5.744	6.092	10.383	0.427	-0.551	0.025
3G	5.789	3.246	10.509	5.806	3.246	10.486	0.302	0.015	-0.216
4G’	1.945	12.490	10.165	1.966	12.500	10.159	1.044	0.075	-0.054
6G’	1.970	9.985	10.646	2.005	9.997	10.652	1.772	0.119	0.056
6G	1.969	5.740	10.698	1.993	5.751	10.686	1.225	0.198	-0.113
4G	1.925	2.622	10.148	1.940	2.636	10.154	0.806	0.527	0.060
O	1.950	3.986	11.309	1.970	4.000	11.312	0.994	0.359	0.025
Eads	-0.324 eV			-0.323 eV			-0.309 %		

	3G-O-7P_H2			3G-O-7P			Variation (%)		
	X1(Å)	Y1(Å)	Z1(Å)	X2(Å)	Y2(Å)	Z2(Å)	X2-X1	Y2-Y2	Z2-Z3
1P	5.341	7.751	11.954	5.341	7.752	11.955	-0.009	0.008	0.004
2G	2.980	7.757	11.545	2.979	7.757	11.546	-0.018	0.004	0.003
3G’	5.817	12.283	10.366	5.816	12.282	10.366	-0.005	-0.001	0.000
5G’	5.751	9.536	10.399	5.751	9.536	10.400	-0.008	0.007	0.005
5G	5.698	5.940	10.417	5.698	5.941	10.419	-0.005	0.027	0.016
3G	5.568	3.290	10.579	5.568	3.291	10.581	0.003	0.051	0.020

4G’	1.970	12.453	10.186	1.969	12.453	10.187	-0.007	-0.001	0.002
6G’	1.994	9.914	10.619	1.993	9.914	10.619	-0.021	-0.002	-0.001
6G	1.979	5.604	10.613	1.979	5.604	10.613	0.004	0.003	0.005
4G	2.117	3.063	10.187	2.117	3.064	10.187	0.029	0.007	0.003
O	6.956	1.974	10.564	6.959	1.976	10.563	0.043	0.077	-0.006
Eads	0.388 eV			0.388 eV			0.000 %		

	3G-O-8P_H2			3G-O-8P			Variation (%)		
	X1(Å)	Y1(Å)	Z1(Å)	X2(Å)	Y2(Å)	Z2(Å)	X2-X1	Y2-Y2	Z2-Z3
1P	5.365	7.778	11.963	5.364	7.776	11.961	-0.003	-0.023	-0.017
2G	2.997	7.765	11.553	2.996	7.764	11.554	-0.020	-0.013	0.005
3G’	5.822	12.291	10.362	5.823	12.288	10.363	0.012	-0.020	0.002
5G’	5.756	9.561	10.405	5.757	9.557	10.404	0.014	-0.033	-0.008
5G	5.806	5.978	10.436	5.805	5.975	10.435	-0.016	-0.053	-0.010
3G	6.035	3.319	10.625	6.035	3.317	10.624	-0.001	-0.066	-0.012
4G’	1.959	12.454	10.191	1.960	12.454	10.190	0.047	-0.002	-0.007
6G’	1.993	9.916	10.622	1.994	9.915	10.622	0.053	-0.004	0.001
6G	2.004	5.609	10.614	2.003	5.609	10.612	-0.036	0.006	-0.019
4G	1.784	3.072	10.195	1.784	3.071	10.195	0.014	-0.027	0.004
O	4.679	1.972	10.554	4.681	1.967	10.553	0.045	-0.246	-0.012
Eads	0.435 eV			0.435 eV			0.000 %		

	4G-O-8P_H2			4G-O-8P			Variation (%)		
	X1(Å)	Y1(Å)	Z1(Å)	X2(Å)	Y2(Å)	Z2(Å)	X2-X1	Y2-Y2	Z2-Z3
1P	5.350	7.724	11.941	5.350	7.724	11.941	-0.004	0.004	-0.001
2G	2.985	7.799	11.555	2.985	7.800	11.556	-0.016	0.011	0.005
3G’	5.822	12.269	10.375	5.822	12.270	10.375	0.002	0.002	-0.002
5G’	5.762	9.507	10.385	5.761	9.508	10.386	-0.005	0.014	0.008
5G	5.736	5.912	10.397	5.735	5.913	10.398	-0.004	0.023	0.005
3G	5.944	3.201	10.319	5.944	3.201	10.321	0.002	0.000	0.014
4G’	1.967	12.479	10.176	1.967	12.479	10.176	0.006	0.002	0.001
6G’	2.001	9.951	10.634	2.001	9.951	10.634	-0.013	0.002	-0.002
6G	1.936	5.693	10.602	1.936	5.694	10.602	-0.006	0.006	0.004
4G	1.716	3.160	10.466	1.716	3.161	10.466	-0.024	0.013	0.006
O	3.071	1.847	10.522	3.073	1.847	10.521	0.065	-0.010	-0.011
Eads	0.499 eV			0.499 eV			0.000 %		

	4G-O-9P_H2			4G-O-9P			Variation (%)		
	X1(Å)	Y1(Å)	Z1(Å)	X2(Å)	Y2(Å)	Z2(Å)	X2-X1	Y2-Y2	Z2-Z3
1P	5.378	7.747	11.957	5.378	7.747	11.956	0.000	0.003	-0.001
2G	3.017	7.815	11.562	3.018	7.816	11.561	0.009	0.009	-0.001

3G′	5.818	12.269	10.373	5.818	12.270	10.372	-0.004	0.005	-0.002
5G′	5.769	9.523	10.391	5.769	9.524	10.392	-0.001	0.011	0.006
5G	5.743	5.930	10.410	5.744	5.931	10.411	0.004	0.015	0.002
3G	5.653	3.202	10.338	5.653	3.203	10.339	0.003	0.007	0.008
4G′	1.966	12.477	10.177	1.965	12.477	10.178	-0.008	0.000	0.005
6G′	2.008	9.950	10.634	2.008	9.950	10.634	-0.013	-0.001	-0.002
6G	2.023	5.695	10.610	2.024	5.696	10.611	0.012	0.012	0.001
4G	2.189	3.162	10.470	2.190	3.162	10.470	0.029	0.001	0.003
O	0.783	1.902	10.580	0.784	1.902	10.582	0.216	-0.007	0.014
Eads	0.454 eV			0.454 eV			0.000 %		

Table S2. Each table shows X, Y, and Z coordinates of the eleven surface atoms (1P, 2~6G, 3~6G', and O in the 1st column) in two optimized structures; surface bridge oxide structures with (2nd, 3rd, and 4th column) and without (5th, 6th, and 7th column) a hydrogen molecule in vacuum. The values in the 8th, 9th, and 10th columns of the table indicate percent variations of X, Y, and Z coordinates between the two structures for the given surface atoms. In the 14th row of the table, the adsorption energies of the two structures and the percent variation between the two values are displayed in the 2nd, 3rd, and 4th columns, respectively.

S3. Details of black, red, and blue mechanisms in Figure 6

a. Black mechanism

In Figure 6, the black lines in each step indicate the adsorption energies for the mechanism; H2O-2G-WB, H2O-2G-SB ➔ HO-2G_H-1P ➔ 2G-O-6G_H-1P_H-XG ➔ 2G-O-6G_H2 (XG=2G, 3G, 3G', 4G and 4G'). Here Gray lines indicate the adsorption energies for 1P-O-2G_H-1P_H-XG (XG=2G, 3G, 3G', 4G and 4G') states in the 3rd step and 1P-O-2G_H2 state in the 4th step. We see that, adsorption of a water molecule onto the 2G atom is thermodynamically favored (1st step to 2nd step in Figure 6). Then, the molecular water adsorbate on 2G decomposes to form the HO-2G_H-1P state with a small transition energy, because such hydrogen dissociation-and-transportation within one dimer is frequently observed in surface decomposition reactions [12-15, 31-33]. When energy is further supplied to the HO-2G_H-1P state, two competitive decomposition pathways are followed (black and gray in the 3rd step, Figure 6). The hydroxyl group (HO-2G) may transform to either 2G-O-6G bridge states (black lines in the 3rd step, Figure 6) or 1P-O-2G bridge states (grey lines in the 3rd step, Figure 6). Of the two surface oxide states, 2G-O-6G bridge state has lower adsorption energy and be more favored than its counter pathway.

b. Red mechanism

Red lines represent the adsorption energies for the mechanism; H2O-3G ➔ HO-3G_H-1P ➔ 3G-O-5G_H-1P_H-XG ➔ 3G-O-5G_H2 (XG=2G, 3G, 3G', 4G and 4G'). Here dark red lines display the adsorption energies of 3G-O-7P_H-1P_H-XG (XG=2G, 3G, 3G', 4G and 4G') state in the 3rd step and 3Ga-O-7P_H2 state in the 4th step. The light red lines represent the adsorption energies of 3G-O-8P_H-1P_H-XG (XG=2G, 3G, 3G', 4G and 4G') states in the 3rd step and 3G-O-8P_H2 state in the 4th step. We expect that the decomposition reaction pathway from the H2O-3G state to the HO-3G_H-1P state will require a high activation energy due to the long H transportation distance. However, with additional waters or dissociated water species to help H transfer, there may exist other low barrier pathways for this reaction (requiring higher water coverage than 0.125 ML). Otherwise, decomposition proceeds from

the H2O-3G state to the 3G-O-5G_H-1P_XGa state through another HO/H decomposition state whose adsorption energy is not lower than that of the HO-3G_H-1P state though.

c. Blue mechanism

The blue lines represent the adsorption energies of for the mechanism; H2O-4G ➔ HO-4G_H-1P ➔ 4G-O-6G_H-1P_H-XG ➔ 4G-O-6G_H2 (XG=2G, 3G, 3G', 4G and 4G'). The dark blue lines represent the adsorption energies of 4G-O-9P_H-1P_H-XG (XG=2G, 3G, 3G', 4G and 4G') states in the 3rd step and 4G-O-9P_H2 state in the 4th step. The light blue lines represent the adsorption energies of 4G-O-8P_H-1P_H-XG (XG=2G, 3G, 3G', 4G and 4G') states in the 3rd step and 4G-O-8P_H2 state in the 4th step. The decomposition pathway from H2O-4G to HO-4G_H-1P would have a high activation barrier just as in the H2O-3G decomposition. Since the hydrogen transportation distance is even longer than in either the H2O-2G or H2O-3G cases, it is unlikely for H2O-4Ga to be directly transformed to 4G-O-6G_H-1P_H-XG unless a second water or decomposed water species is involved.