Electronic Supplementary Information

Coverage-Dependent Thermodynamic Analysis of the Formation of Water and Hydrogen Peroxide on Platinum Model Catalyst

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The adsorptions and coadsorptions geometries for different sites have been tested for each intermediate species for H_2O and H_2O_2 formation on Pt(111). The correspond energies for the adsorption energy (E_{ads}) adsorption have been exposed in the article (table 1) and the reactive coadsorption energy (E_{rcoads}) is exposed in Table 1 in this supplementary material.

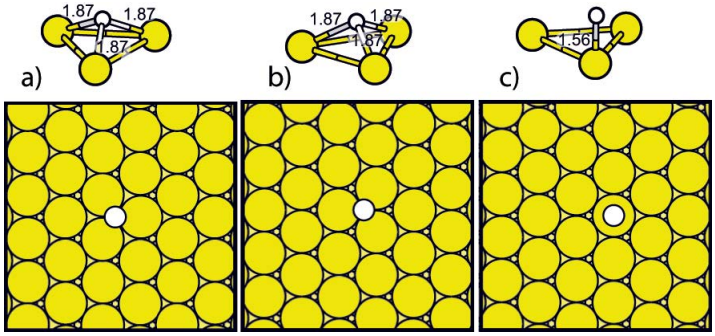

Fig. 1 Top and side views of atomic hydrogen adsorption on Pt(111). a) H(F) b) H(H) c) H(T)

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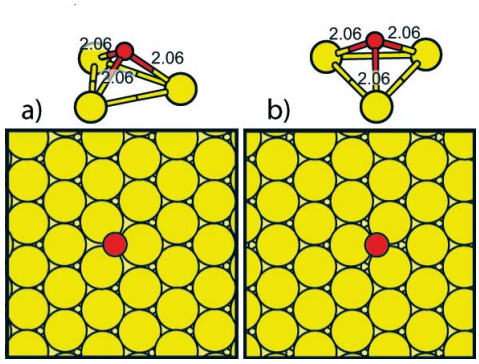

Fig. 2 Top and side views of atomic oxygen adsorption on Pt(111). a) O(F) b) O(H)

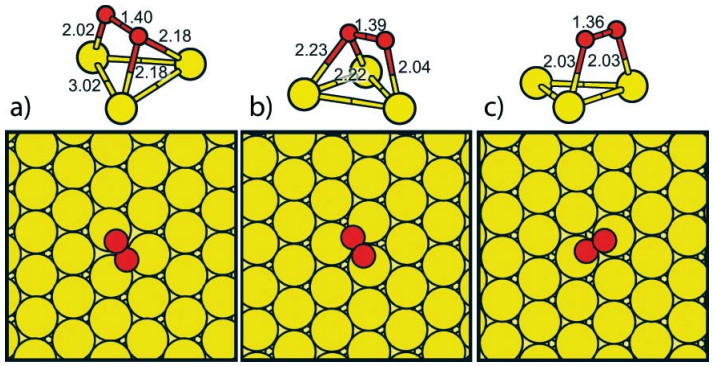

Fig. 3 Top and side views of molecular oxygen adsorption on Pt(111). a) O_2(TB) b) O_2(BT) c) O_2(TT)

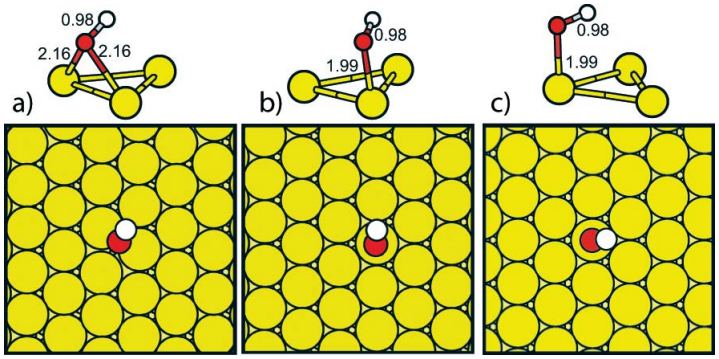

Fig. 4 Top and side views of hydroxide adsorption on Pt(111). a) O(B)-H(H) b) O(T)-H(B) c) O(T)-H(H). The O(T)-H(B) and O(T)-H(H) have the same adsorption energy (E_{ads}).

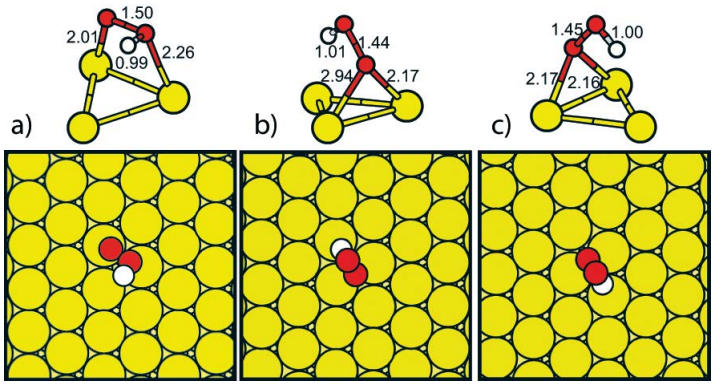

Fig. 5 Top and side views of hydroperoxyl adsorption on Pt(111). a) O_2(TT)-H(B) b) O(B)-OH(TB_F) c) O(B)-OH(TB_H). The O(B)-OH(TB_F) and O(B)-OH(TB_H) have the same adsorption energy (E_{ads}).

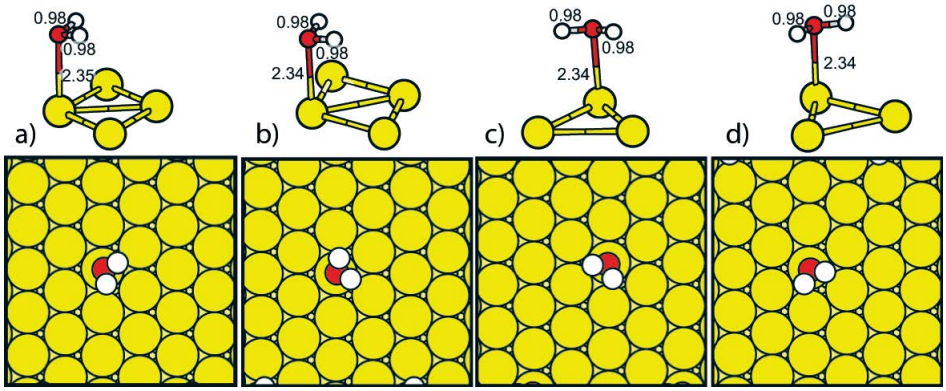

Fig. 6 Top and side views of water adsorption on Pt(111). a) O(T)-2H(B) b) O(T)-H(H)H(F) c) O(T)-2H(B) c) O(T)-2H(B). All the tested geometries of the H_2O adsorption on Pt(111) have the same adsorption energy (E_{ads}).

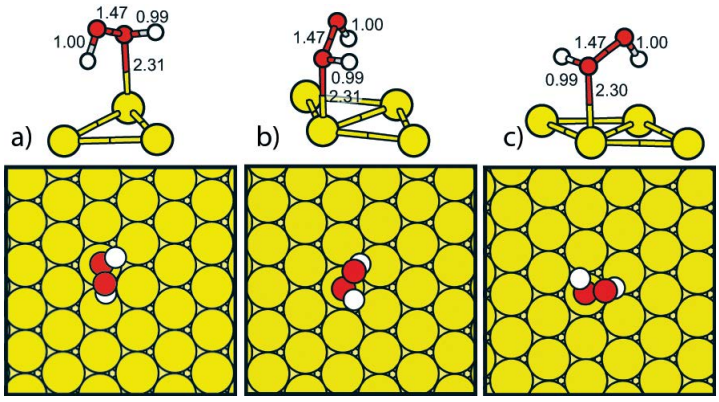

Fig. 7 Top and side views of hydrogen peroxide adsorption on Pt(111). a) O(T)-H(B)OH(F) b) O(T)-H(B)OH(F) c) O(T)-H(B)OH(F). All the tested geometries of the H_2O_2 adsorption on Pt(111) have the same adsorption energy (E_{ads}).

Table 1 Reactive coadsorption energy (E_{rcoads}) and coadsorption energy balance (ΔE_{coads}) for the surface reaction intermediates involved in the formation of water and hydrogen peroxide on Pt(111). S_{conn} and H_{conn} are the connectivity between coadsorbed atoms sharing a surface platinum, and the hydrogen bond networking between coadsorbates, respectively. d is the smallest distance between surface bonded coadsorbed atoms.

co-adsorption structure	E_{rcoads}	S_{conn}	H_{conn}	$d(A_1\text{-}A_2)$	ΔE_{coads}
$H_{2(g)} + 2S \rightarrow 2H_{(coads)}$					
H(F)+H(F)	-98	Yes	No	2.88	0
H(T)+H(T)	-96	No	No	2.95	3
H(F)+H(H)	-91	Yes	No	3.32	2
H(T)+H(F)	-90	Yes	No	2.25	8
H(H)+H(H)	-88	Yes	No	2.88	1
H(T)+H(H)	-86	Yes	No	2.27	8
H(F)+H(H)*	-77	Yes	No	2.08	16
$O_{2(g)} + 2S \rightarrow 2O_{(coads)}$					
O(F)+O(F)	-228	No	No	4.87	7
O(F)+O(F)*	-214	Yes	No	3.01	21
O(F)+O(F)**	-193	No	No	4.29	42
O(F)+O(H)	-193	No	No	4.28	7
O(H)+O(H)*	-157	No	No	4.89	43
O(H)+O(H)	-150	Yes	No	3.36	14
$1/2\ H_{2(g)} + 1/2\ O_{2(g)} + 2S \rightarrow (O+H)_{(coads)}$					
O(F)+H(T)	-165	No	No	3.36	-3
O(F)+H(F)	-158	Yes	No	3.03	9
O(F)+H(B)	-153	Yes	No	3.06	13
O(F)+H(H)	-151	Yes	No	3.49	11
$1/2\ H_{2(g)} + O_{2(g)} + 2S \rightarrow (O_2+H)_{(coads)}$					
O_2(TT)+H(H)	-123	No	No	4.06	2
O_2(TT)+H(H)*	-122	No	No	3.54	3
O_2(TT)+H(F)	-122	No	No	4.74	4
O_2(TT)+H(T)	-119	No	No	2.87	6
O_2(TT)+H(B)	-119	No	No	3.25	7
O_2(TB)-(F)+H(T)	-118	No	No	2.91	4
O_2(TT)+H(B)*	-116	No	No	2.90	9
O_2(TB)-(F)+H(F)	-115	No	No	4.09	7
O_2(TB)-(F)+H(B)	-113	No	No	3.09	10
O_2(TB)-(F)+H(B)*	-112	No	No	3.23	11
O_2(TB)-(H)+H(T)	-105	No	No	2.92	5
O_2(TB)-(H)+H(B)	-98	No	No	3.41	12
$H_{2(g)} + 1/2\ O_{2(g)} + 2S \rightarrow (OH+H)_{(coads)}$					
OH(B)-H(H)+H(F)	-217	No	No	3.54	6
OH(T)-H(B)+H(F)	-216	No	No	3.20	2
OH(B)-H(H)+H(F)*	-215	Yes	No	3.16	3
OH(T)-H(H)+H(T)	-214	No	No	3.03	2
OH(T)-H(B)+H(T)	-214	No	No	3.10	2
OH(T)-H(H)+H(B)	-209	No	No	2.84	7
$H_{2(g)} + O_{2(g)} + 2S \rightarrow (OOH+H)_{(coads)}$					
OOH(TT)-H(B)+H(T)	-171	No	No	2.88	12
OOH(TT)-H(B)+H(T)*	-165	No	No	2.88	12
OOH(TT)-H(B)+H(B)	-162	No	No	2.88	9
OOH(T)-OH(B)+H(B)	-159	No	No	2.84	12
OOH(B)-OH(F)+H(T)	-143	No	No	2.62	10
$1/2\ H_{2(g)} + O_{2(g)} + 2S \rightarrow (OH+O)_{(coads)}$					
OH(T)-H(F)+O(F)	-285	No	No	4.47	-1
OH(T)-H(H)+O(F)	-282	No	No	4.53	2
OH(T)-H(F)+O(F)*	-282	No	No	4.50	3
OH(T)-H(H)+O(H)	-248	No	No	3.37	2
$H_{2(g)} + O_{2(g)} + 2S \rightarrow 2OH_{(coads)}$					
OH(T)-H(F)+OH(B)-H(F)	-378	No	Yes	1.48	-39
OH(T)-H(H)+OH(B)-H(H)	-374	No	Yes	1.53	-36
OH(T)-H(B)+OH(T)-H(B)	-356	No	Yes	1.79	-22
OH(T)-H(H)+OH(B)-H(H)*	-332	No	No	2.75	7
$H_{2(g)} + O_{2(g)} + 2S \rightarrow (H_2O+O)_{(coads)}$					
H_2O(T)-H(B)H(H)+O(F)	-152	No	Yes	2.38	12
H_2O(T)-H(B)H(F)+O(H)	-115	No	Yes	2.22	12

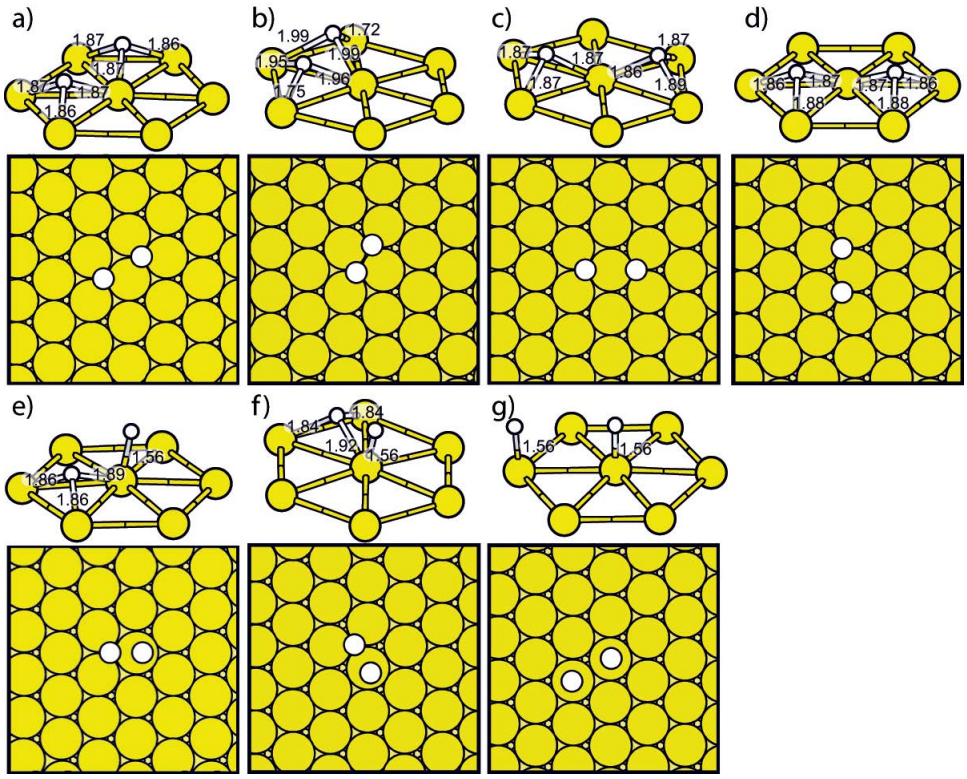

Fig. 8 Top and side views of the co-adsorption between two atomic hydrogen on Pt(111). a) H(F)+H(F) b) H(F)+H(H)* c) H(F)+H(H) d) H(H)+H(H) e) H(T)+H(F) f) H(T)+H(H) g) H(T)+H(T)

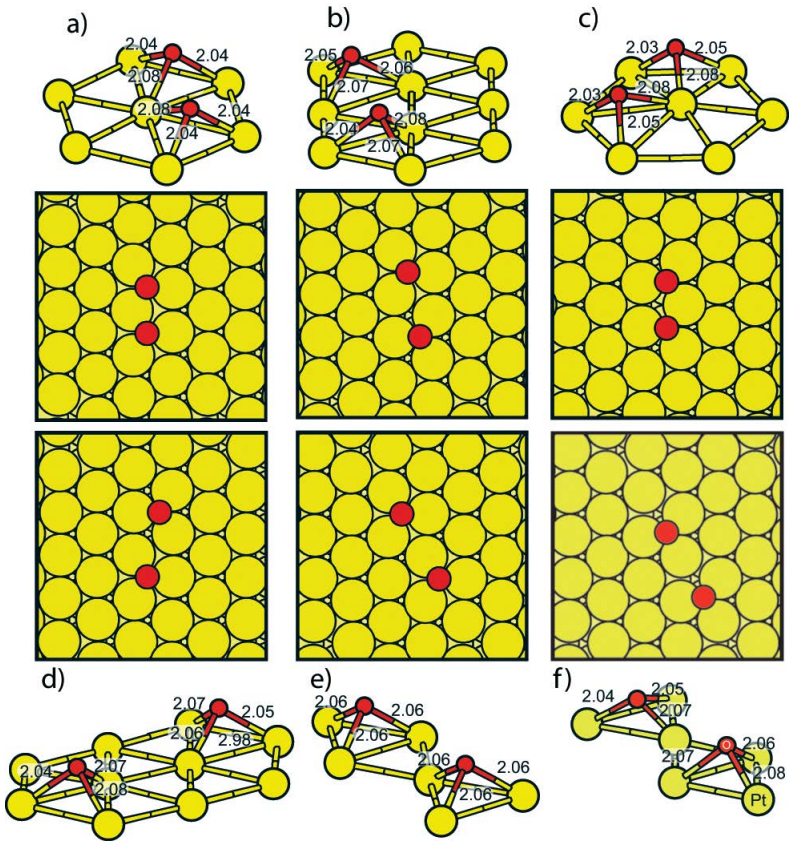

Fig. 9 Top and side views of the co-adsorption between two atomic oxygen on Pt(111). a) O(F)+O(F)* b) O(F)+O(H) c) O(H)+O(H) d) O(F)+O(F)** e) O(F)+O(F) f) O(H)+O(H)*

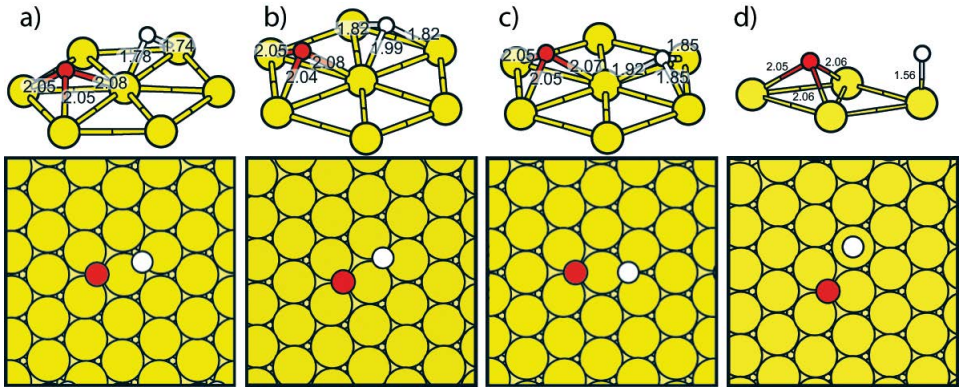

Fig. 10 Top and side views of the co-adsorption between atomic oxygen and atomic hydrogen on Pt(111). a) O(F)+H(B) b) O(F)+H(F) c) O(F)+H(H) d) O(F)+H(T)

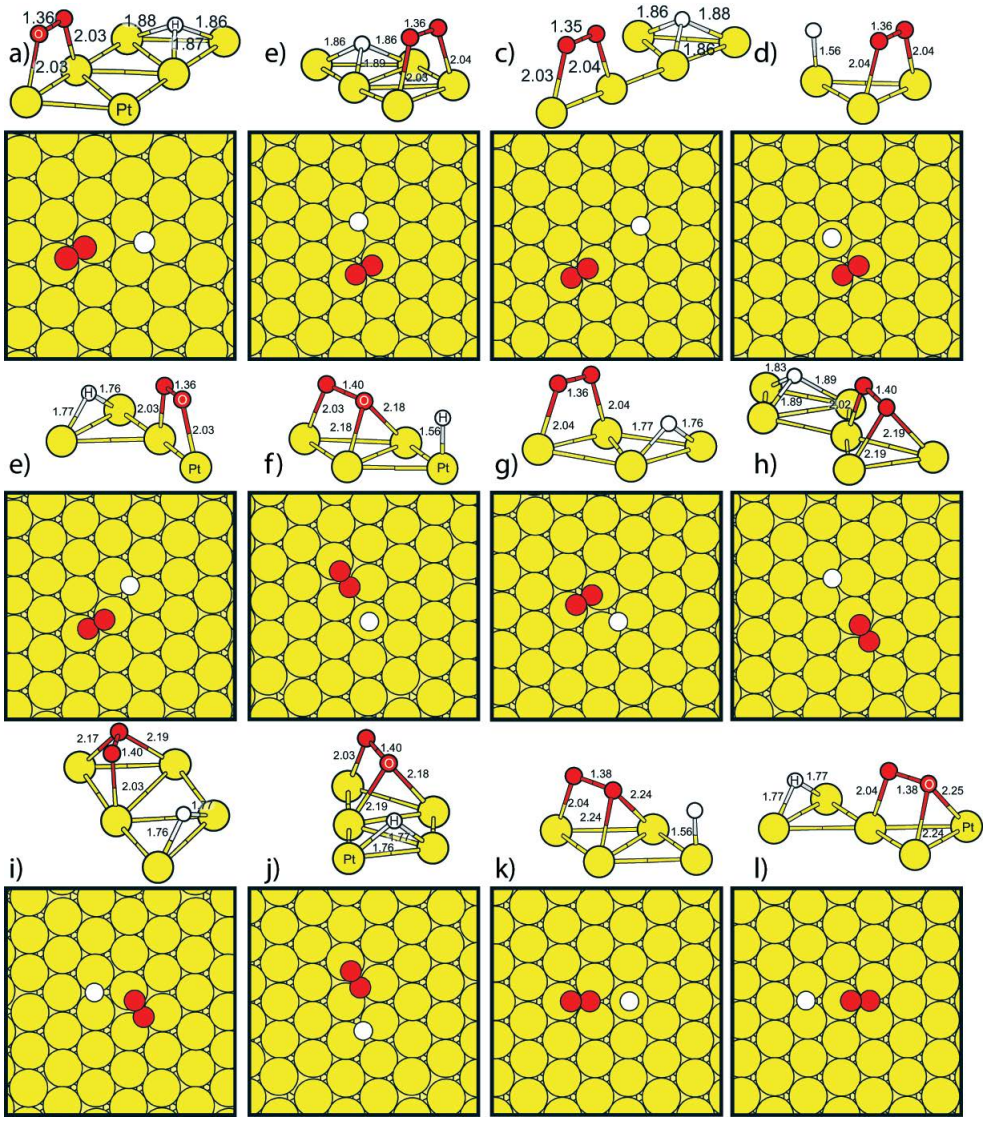

Fig. 11 Top and side views of the co-adsorption between molecluar oxygen and atomic hydrogen on Pt(111). a) O_2(TT) + H(H) b) O_2(TT) + H(H)* c) O_2(TT)+H(F) d) O_2(TT)+H(T) e) O_2(TT) + H(B) f) O_2(TB)-(F)+H(T) g) O_2(TT) + H(B)* h) O_2(TB)-(F)+H(F) i) O_2(TB)-(F)+H(B) j) O_2(TB)-(F)+H(B)* k) O_2(TB)-(H)+H(T)

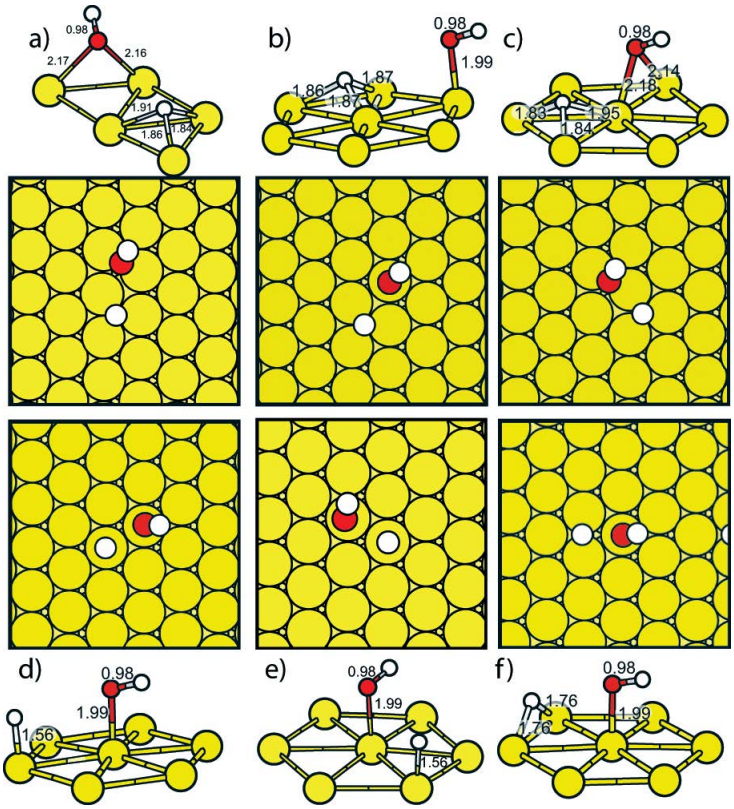

Fig. 12 Top and side views of the co-adsorption between hydroxide and atomic hydrogen on Pt(111). a) OH(B)-H(H)+H(F) b) OH(T)-H(B)+H(F) c) OH(B)-H(H)+H(F)* d) OH(T)-H(H)+H(T) e) OH(T)-H(B)+H(T) f) OH(T)-H(H)+H(B)

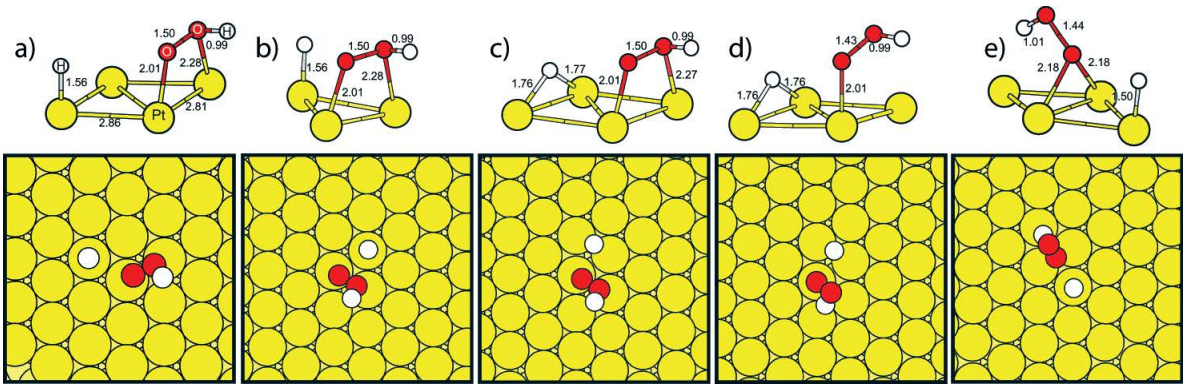

Fig. 13 Top and side views of the co-adsorption between hydroperoxyl and atomic hydrogen on Pt(111). a) OOH(TT)-H(B)+H(T) b) OOH(TT)-H(B)+H(T)* c) OOH(TT)-H(B)+H(B) d) OOH(T)-OH(B)+H(B) e) OOH(B)-OH(F)+H(T)

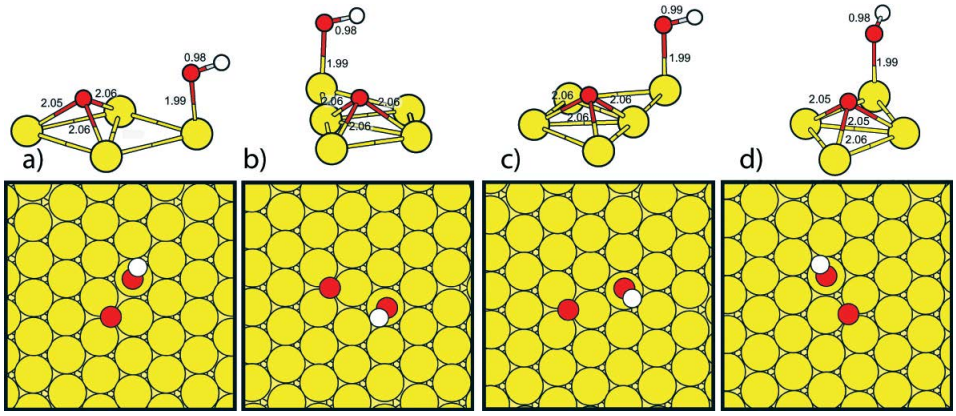

Fig. 14 Top and side views of the co-adsorption between hydroxyl and atomic oxygen on Pt(111). a) OH(T)-H(F)+O(F) b) OH(T)-H(H)+O(F) c) OH(T)-H(F)+O(F)* d) OH(T)-H(H)+O(H)

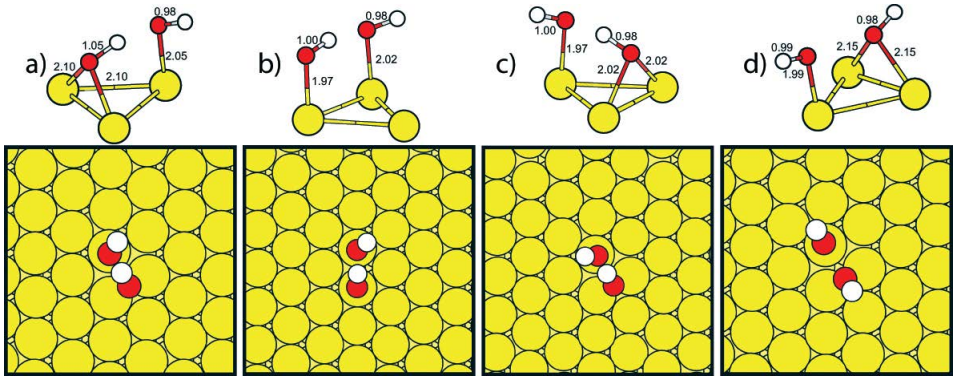

Fig. 15 Top and side views of the co-adsorption between two hydroxyl on Pt(111). a) OH(T)-H(F)+OH(B)-H(F) b) OH(T)-H(H)+OH(B)-H(H) c) OH(T)-H(B)+OH(T)-H(B) d) OH(T)-H(H)+OH(B)-H(H)*

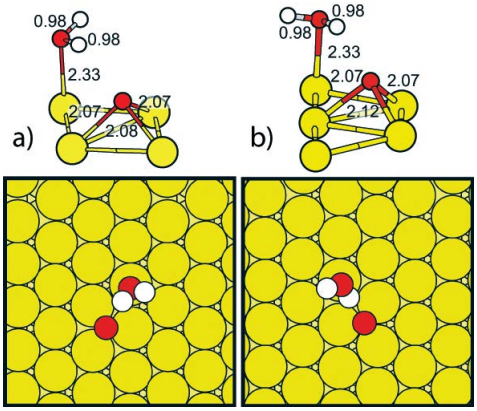

Fig. 16 Top and side views of the co-adsorption between water and atomic oxygen on Pt(111). a) H_2O(T)-H(B)H(H)+O(F) b) H_2O(T)-H(B)H(F)+O(H)