Theoretical Insight into the Hydroxyl Production via H_2O_2 Decomposition over Fe_3O_4 (311) Surface

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Table S1. Calculated reaction barriers (Ea in eV) and reaction energies (ΔE in eV) for elementary reactions of H_2O_2 decomposition on the Fe_3O_4 (311) surface in aqueous solution.

Elementary steps	$\mathbf{E_a}$	**ΔE**
Molecular adsorption		
$H_2O_{2(aq)} \rightarrow H_2O_2*$	-	-0.94
$H_2O_2* \rightarrow 2OH*$	0.52	-1.53
$H_2O_2* \rightarrow H* + OOH*$	0.33	0.18
Dissociate adsorption		
$H_2O_{2(ag)} \rightarrow H* + OOH*$	-	-1.49
$H* + OOH* \rightarrow 2OH*$	0.15	-2.16
$H* + OOH* \rightarrow OO* + 2H*$	0.49	-0.06

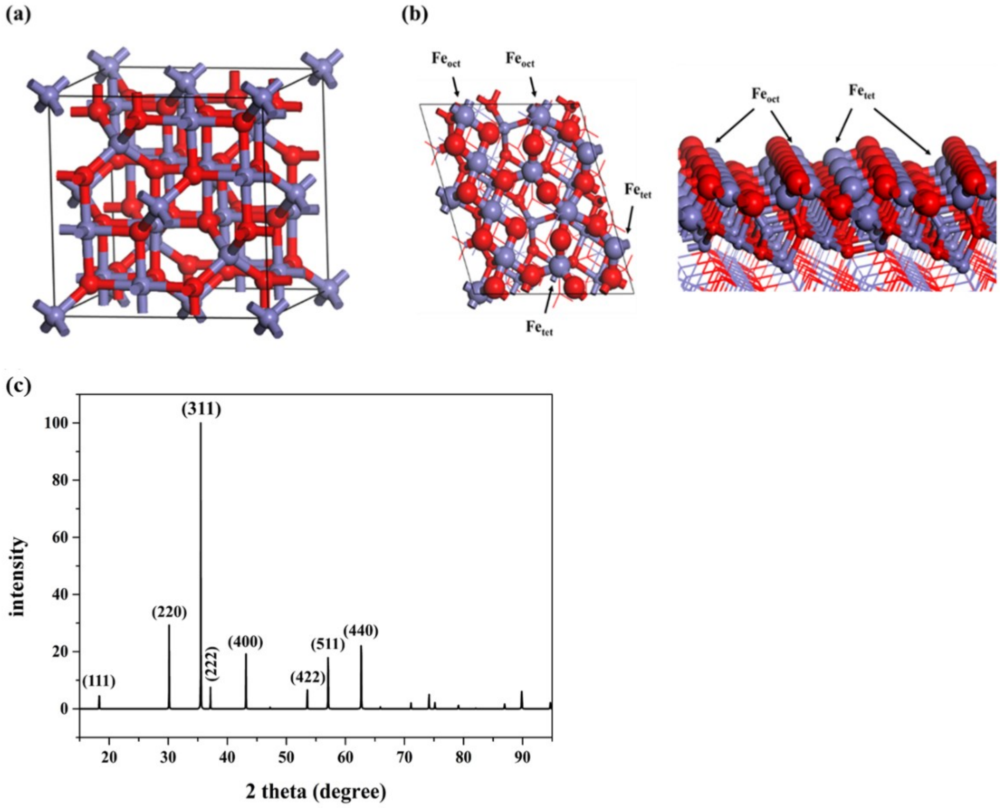

Figure S1. (a) Bulk structure of Fe_3O_4; (b) Top view (left) and side view (right) of Fe_3O_4 (311) surface; (c) Simulated X-ray diffraction pattern (XRD) of Fe_3O_4 bulk structure. Purple and red spheres represent Fe and O atoms, respectively.

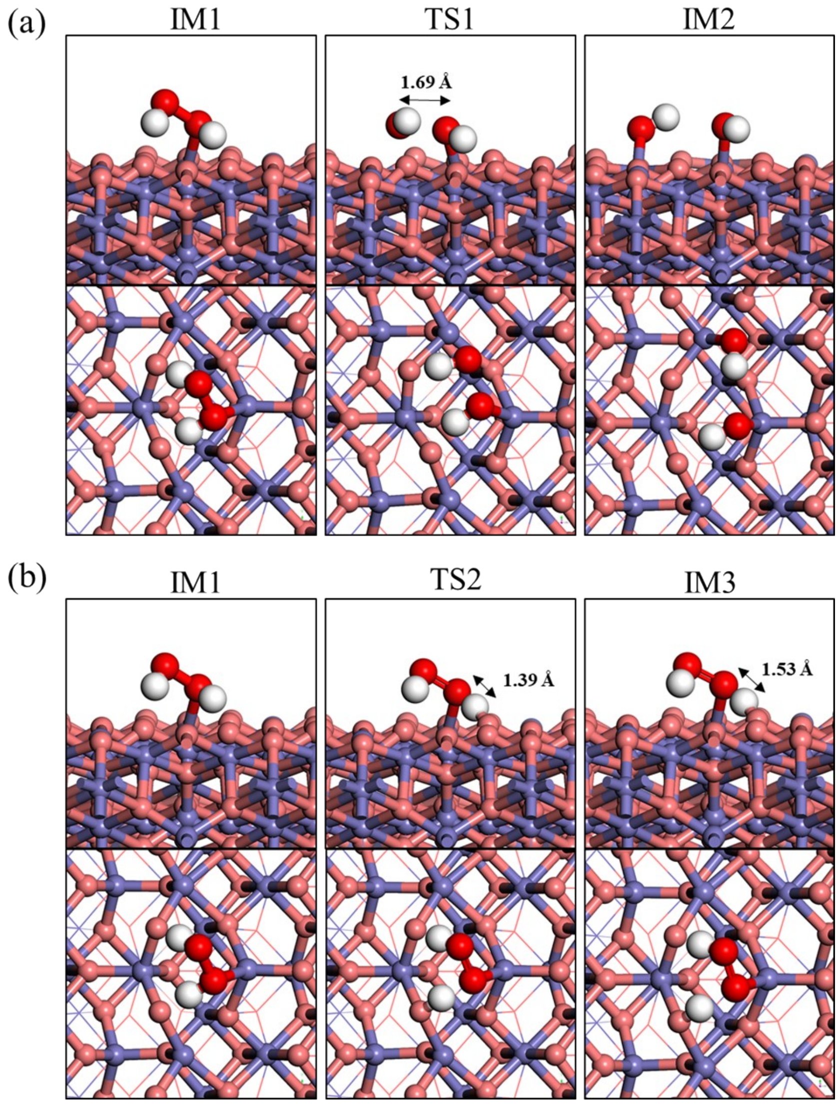

Figure S2. Optimized geometries of the intermediates and transition states during the decomposition of H_2O_2 molecular adsorption along (a) O-O bond and (b) O-H bond dissociation pathways. Purple, red, and white spheres represent Fe, O, and H atoms, respectively. The deep red color represents the oxygen of H_2O_2 while the light red color is the oxygen of Fe_3O_4 (311) surface.

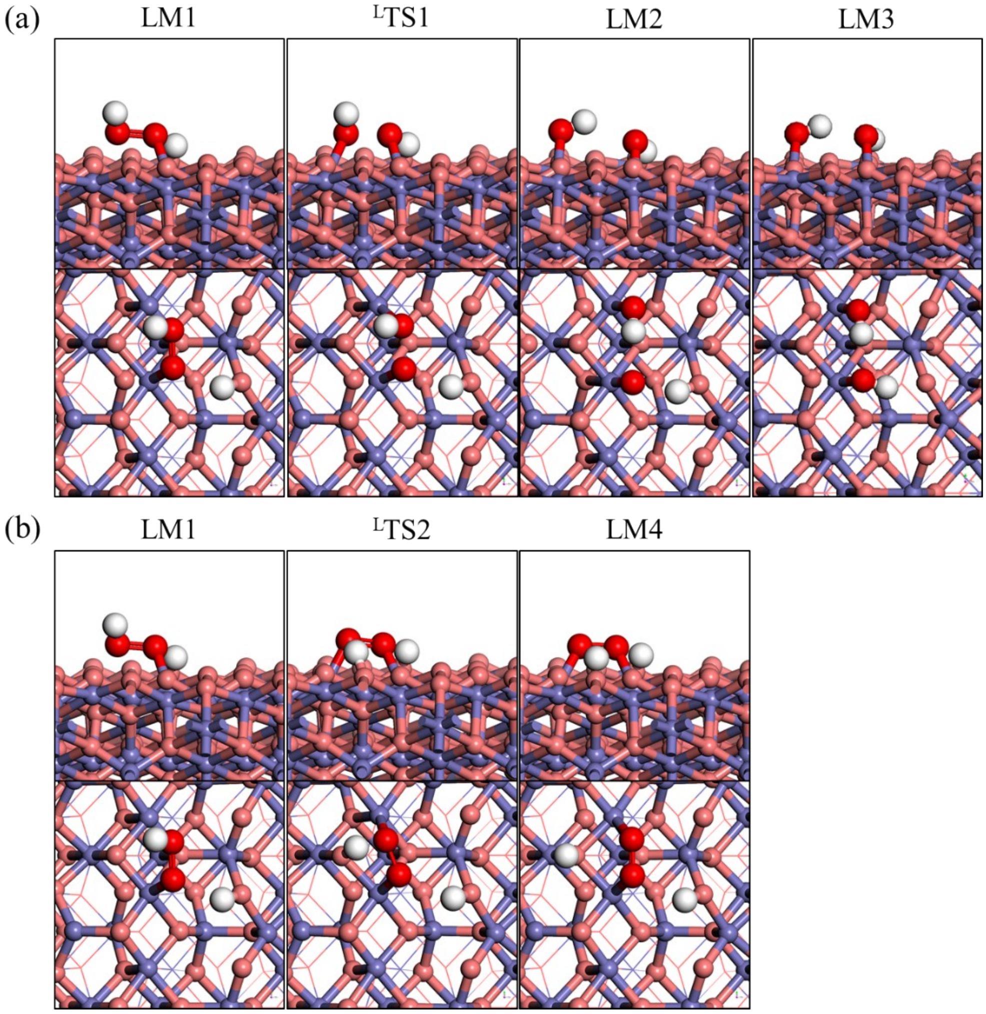

Figure S3. Optimized geometries of the intermediates and transition states during the decomposition of H_2O_2 dissociative adsorption along (a) O-O bond and (b) O-H bond dissociation pathways. Purple, red, and white spheres represent Fe, O, and H atoms, respectively. The deep red color represents the oxygen of H_2O_2 while the light red color is the oxygen of Fe_3O_4 (311) surface.

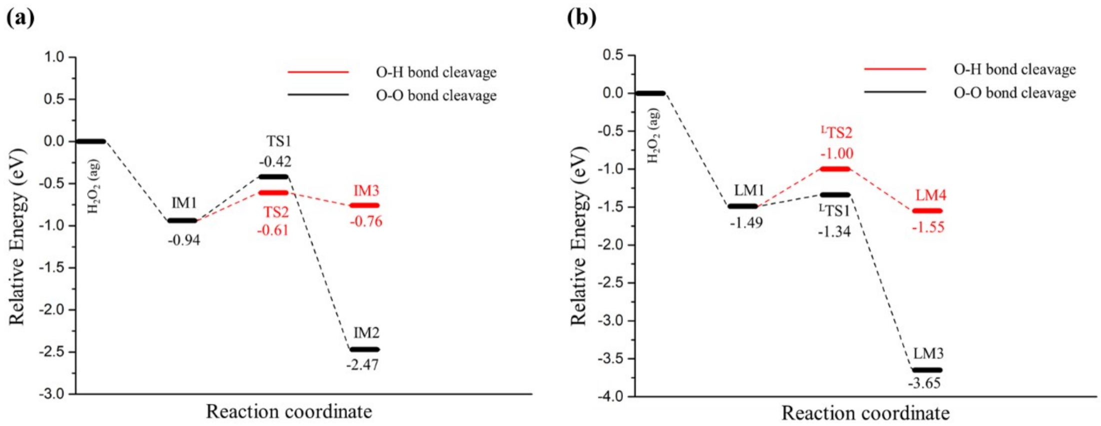

Figure S4. The potential energy profiles of the decomposition of H_2O_2 on the $Fe_3O_4(311)$ surface in aqueous solution via (a) H_2O_2 molecular adsorption and (b) H_2O_2 dissociative adsorption.

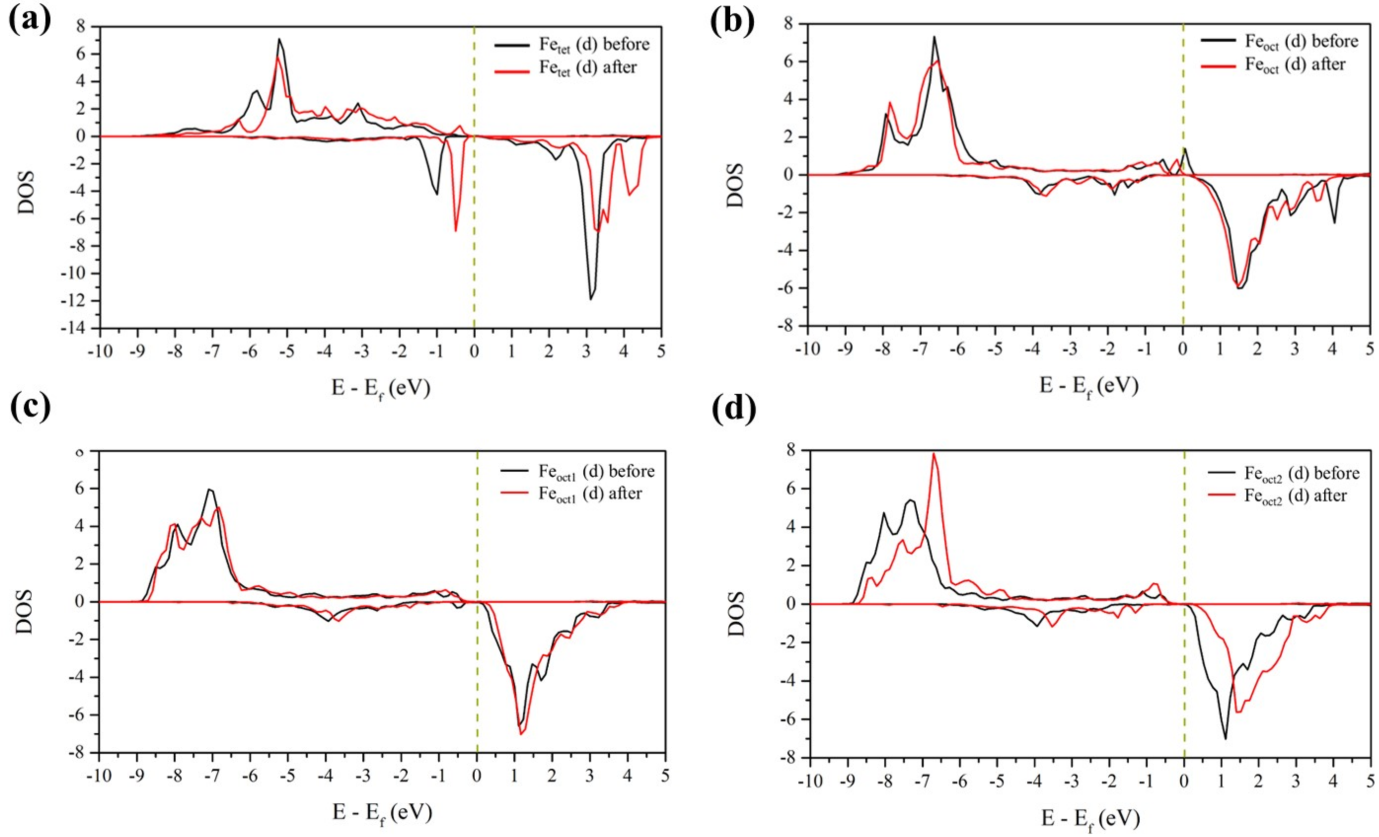

Figure S5. The PDOS plots of (a) d orbitals of Fe_{tet} atom and (b) Fe_{oct} atom before and after H_2O_2 molecular adsorption; and the PDOS plots of (c) d orbitals of Fe_{oct1} atom and (b) Fe_{oct2} atom before and after H_2O_2 dissociative adsorption. The dotted line is the fermi level.

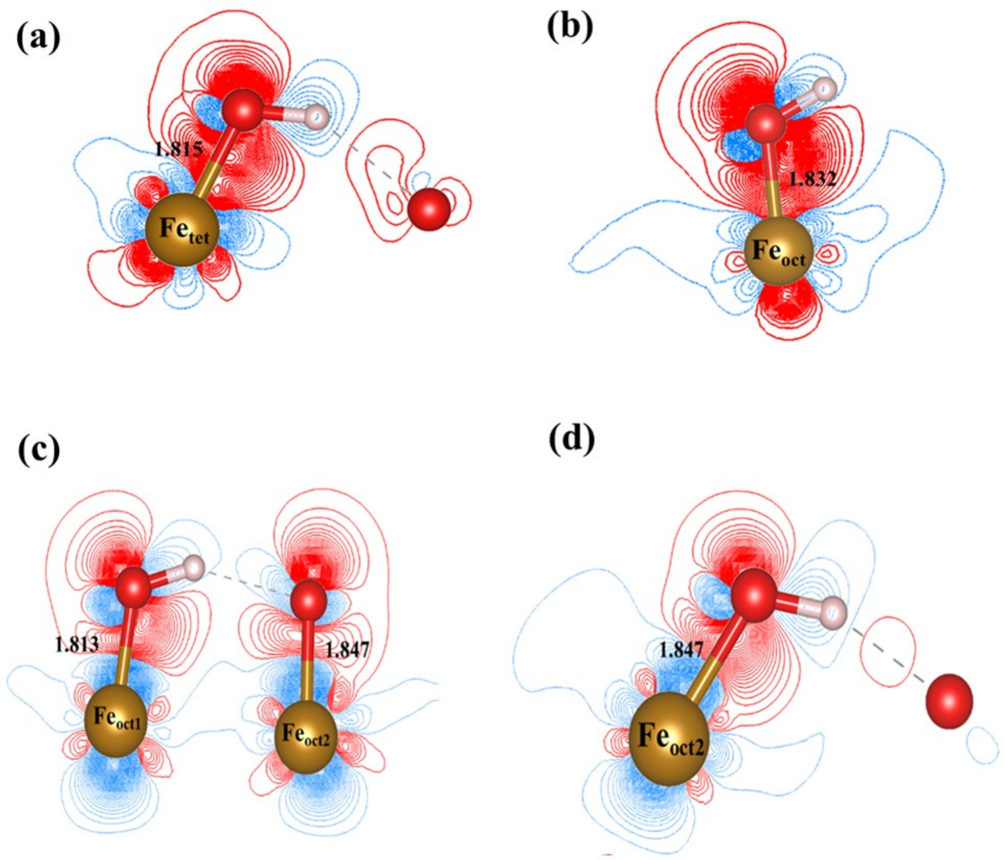

Figure S6. The electron density difference (EDD) plots for the OH groups on (a) Fe_{tet} and (b) Fe_{oct} atoms after the decomposition of H_2O_2 molecular adsorption; the EDD plots for the OH groups on (c) Fe_{oct1} and (d) Fe_{oct2} atoms after the decomposition of H_2O_2 dissociative adsorption. The isosurface level is 0.002 |e|/$Bohr^3$. (Red and blue lines represent electron gain and lose, respectively.) Brown, red, and white spheres represent Fe, O, and H atoms, respectively.

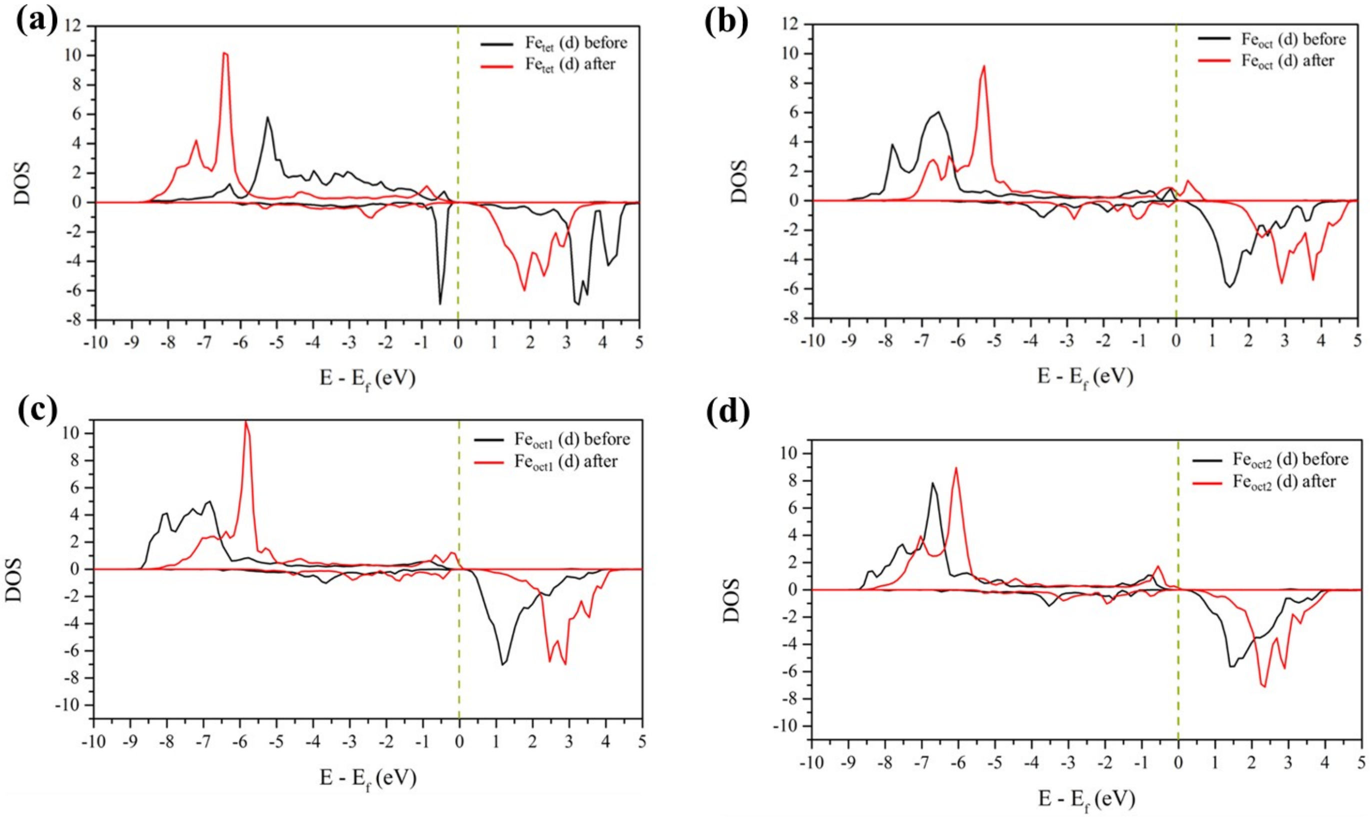

Figure S7. The PDOS plots of (a) d orbitals of Fe_{tet} atom and (b) Fe_{oct} atom before and after H_2O_2 molecular adsorption's decomposition; and the PDOS plots of (c) d orbitals of Fe_{oct1} atom and (b) Fe_{oct2} atom before and after H_2O_2 dissociative adsorption's decomposition. The dotted line is the fermi level.