Supporting Information

Selective Hydrogenation of Acetylene to Ethylene on Anatase TiO_2 through First Principles Studies

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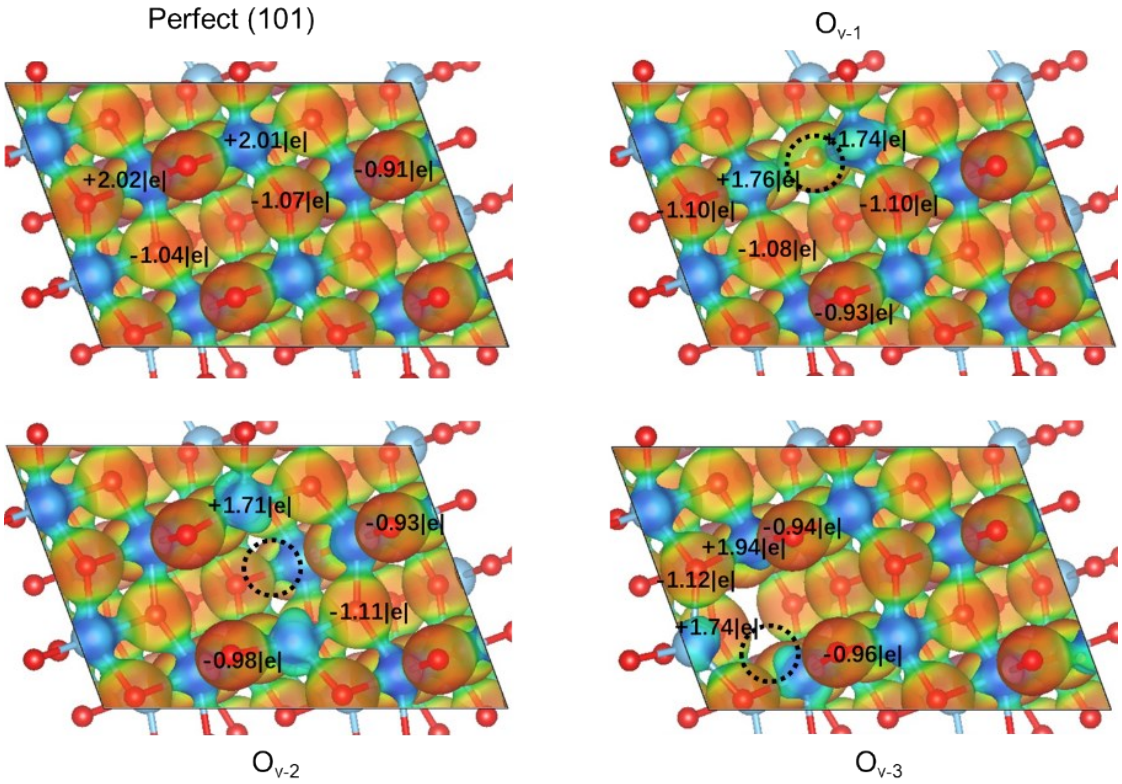

Figure S1. Charge density of pristine and defective TiO_2(101) surfaces colored electrostatic potential value with Bader charges indicated.

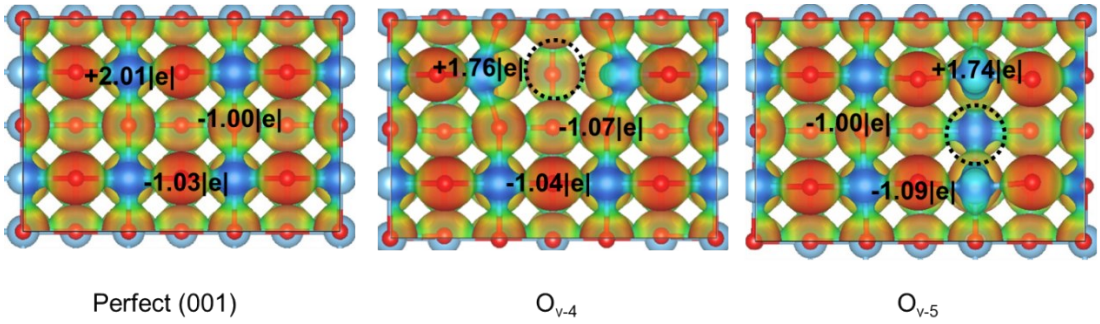

Figure S2. Charge density of pristine and defective TiO_2(001) surfaces colored by electrostatic potential with Bader charges indicated.

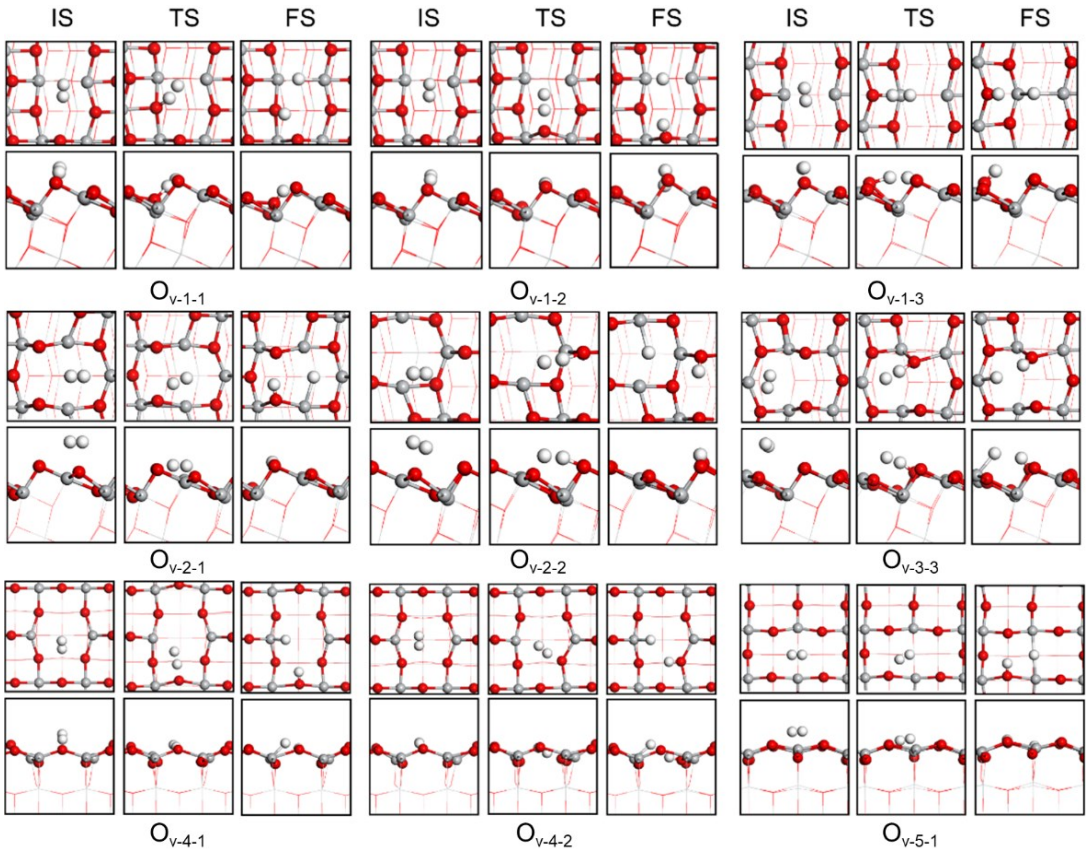

Figure S3. Structures of IS, TS, and FS for the heterolytic H_2 dissociation following FLP mechanism. Color scheme: O, red; Ti, grey; H, white.

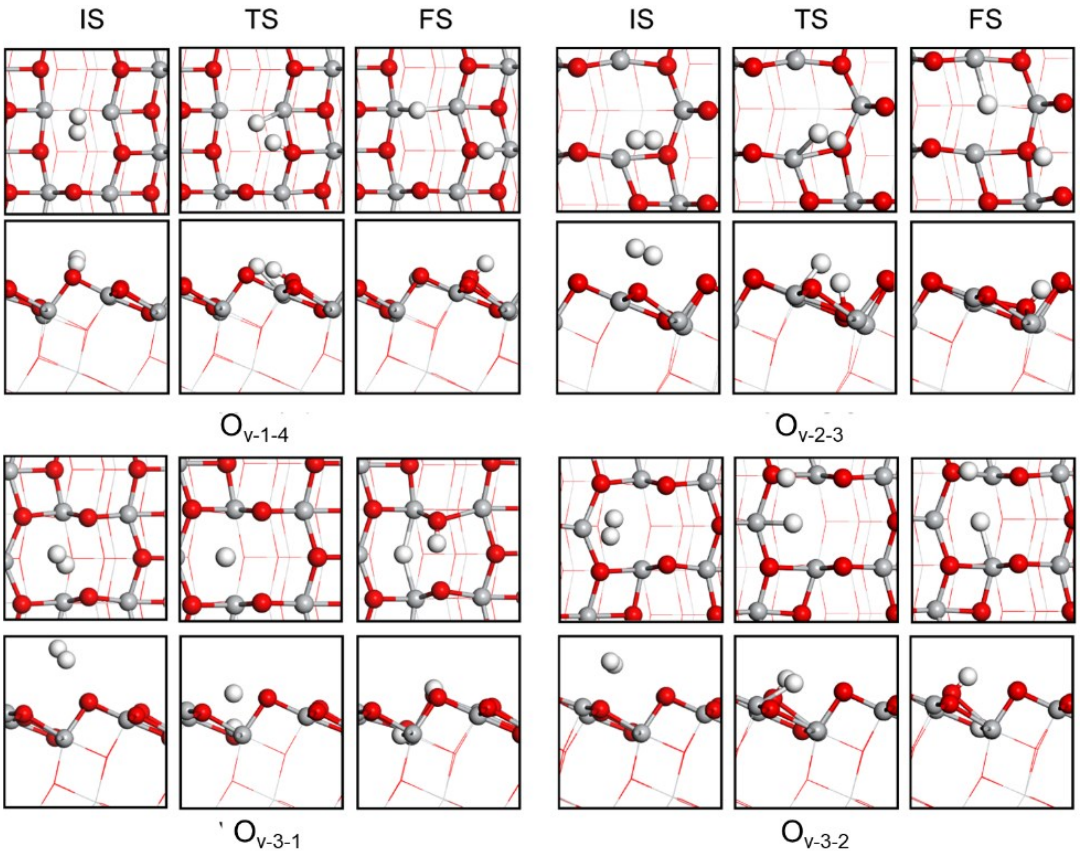

Figure S4. Structures of IS, TS, and FS for H_2 dissociation following non-FLP mechanism. Color scheme: O, red; Ti, grey; H, white.

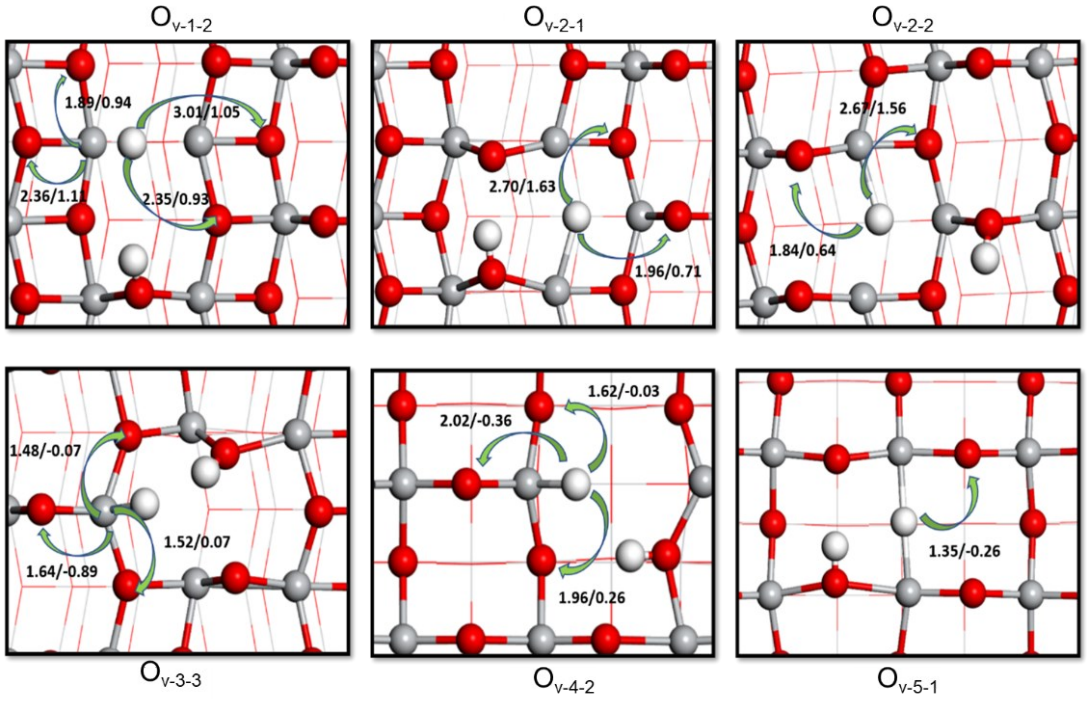

Figure S5. Conversion of hydride to hydroxyl, in which the energy barrier (eV)/reaction energy (eV) were labeled. Color scheme: O, red; Ti, grey; H, white.

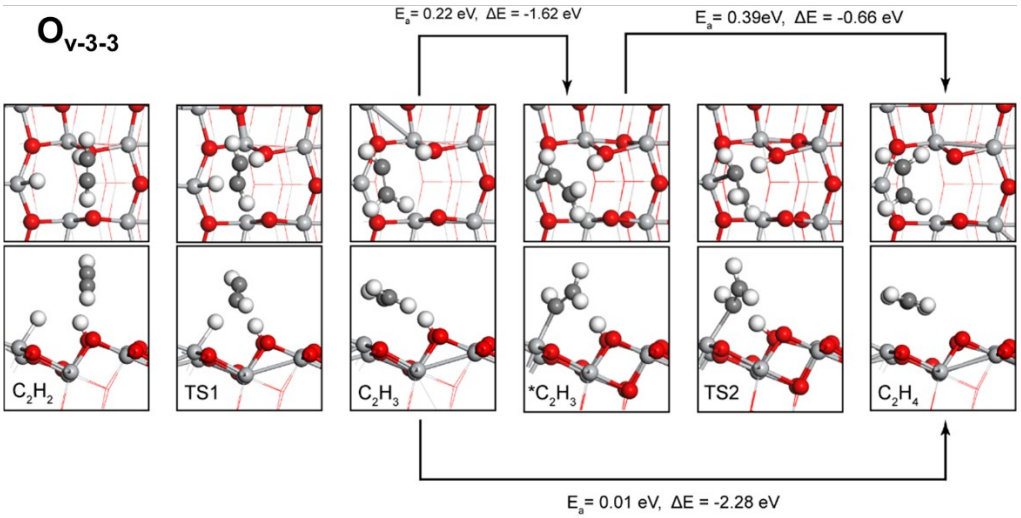

Figure S6. Diagrams of acetylene hydrogenation above the FLP of $O_{v\text{-}3\text{-}3}$ via C_2H_3 radical-assistant mechanism. Color scheme: O, red; Ti, grey; H, white; C, dark grey.

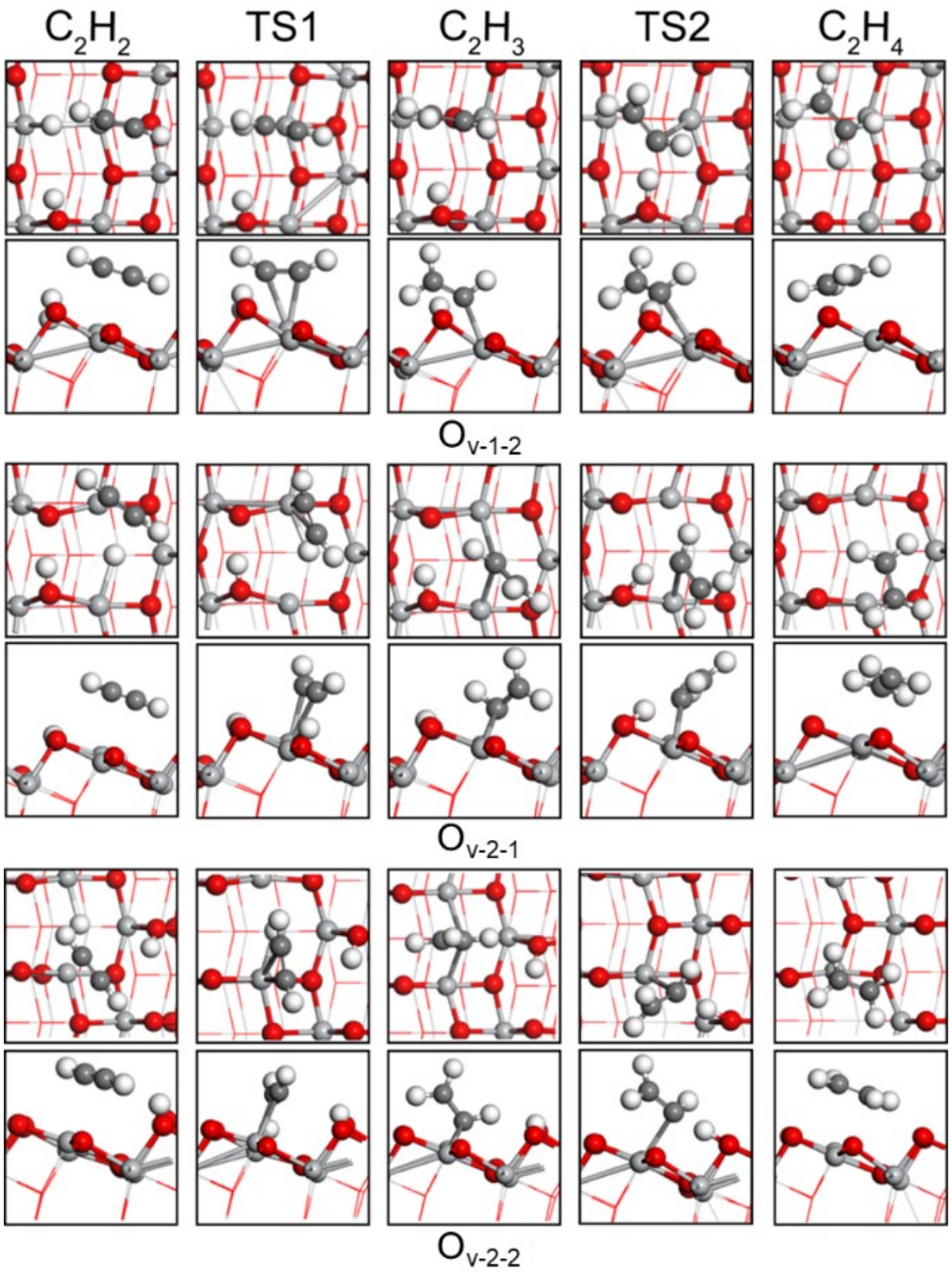

Figure S7. Acetylene hydrogenation processes above other FLPs of $O_{v\text{-}1\text{-}2}$, $O_{v\text{-}2\text{-}1}$, and $O_{v\text{-}2\text{-}2}$ on anatase $TiO_2(101)$ surface. Color scheme: O, red; Ti, grey; H, white; C, dark grey.

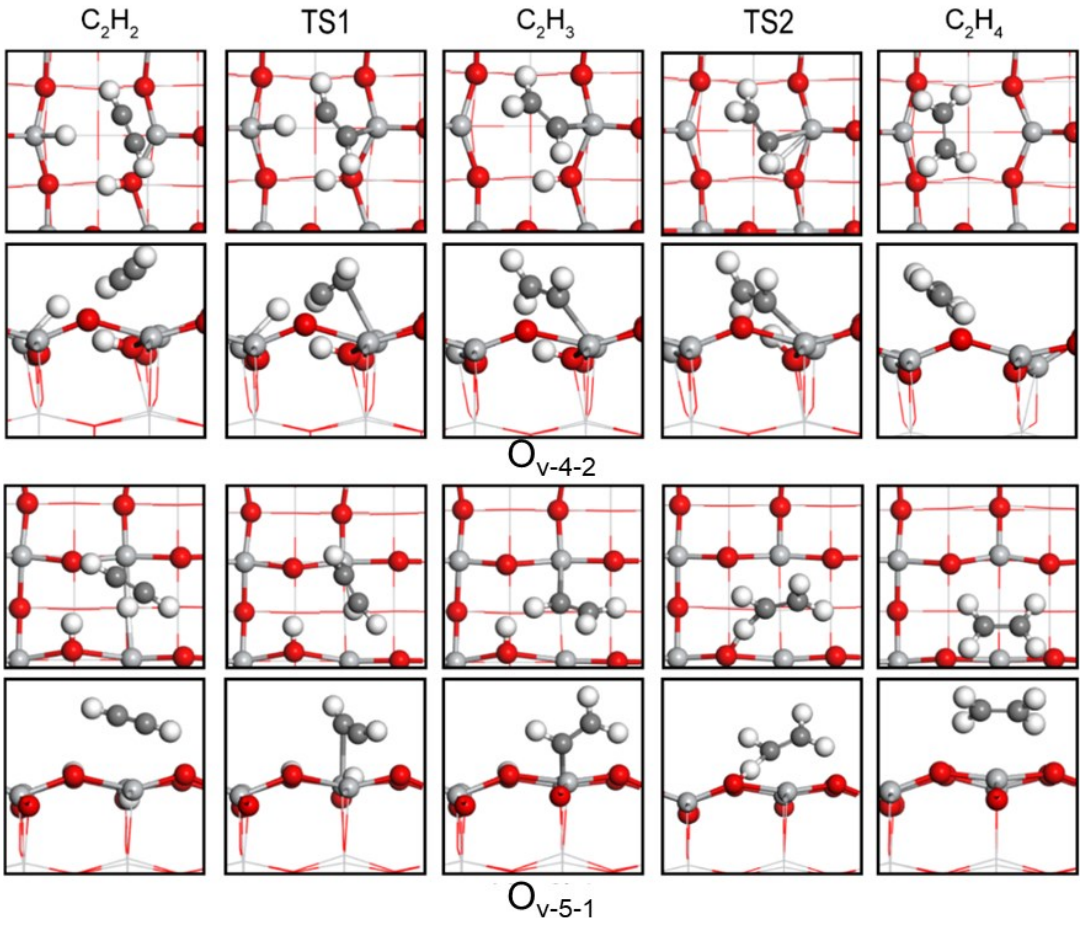

Figure S8. Acetylene hydrogenation processes above the FLPs of $O_{v\text{-}4\text{-}2}$, and $O_{v\text{-}5\text{-}1}$ in anatase TiO_2(001) surface. Color scheme: O, red; Ti, grey; H, white; C, dark grey.

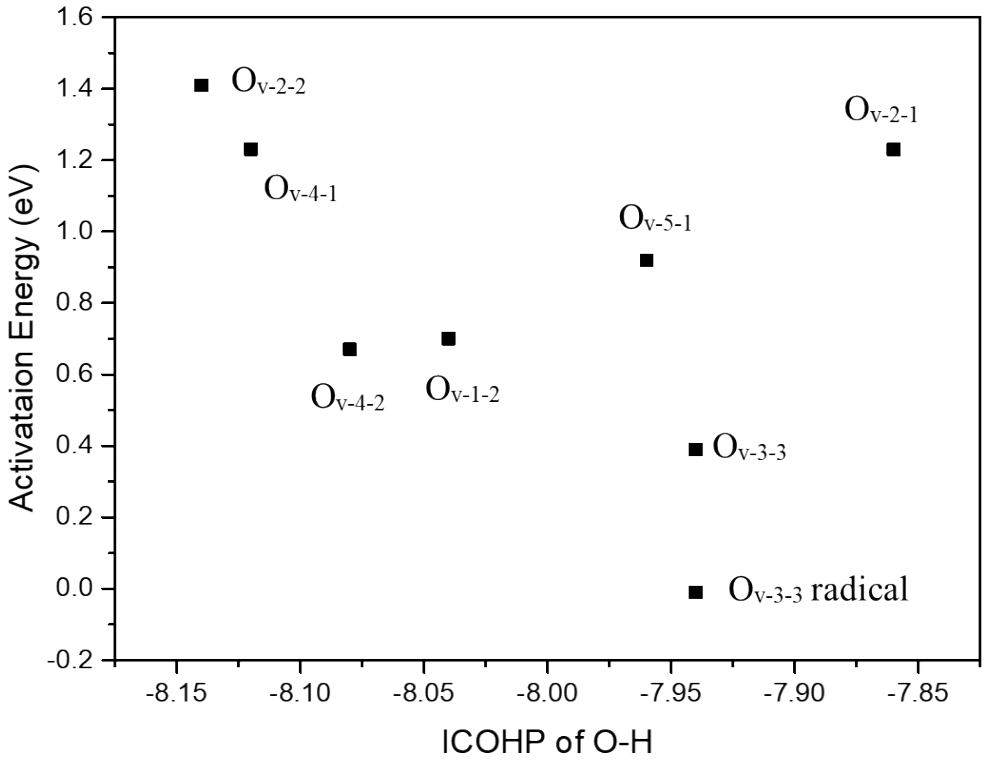

Figure S9. Relationships of the second hydrogenation energy barrier with the ICOHP value of O−H bond

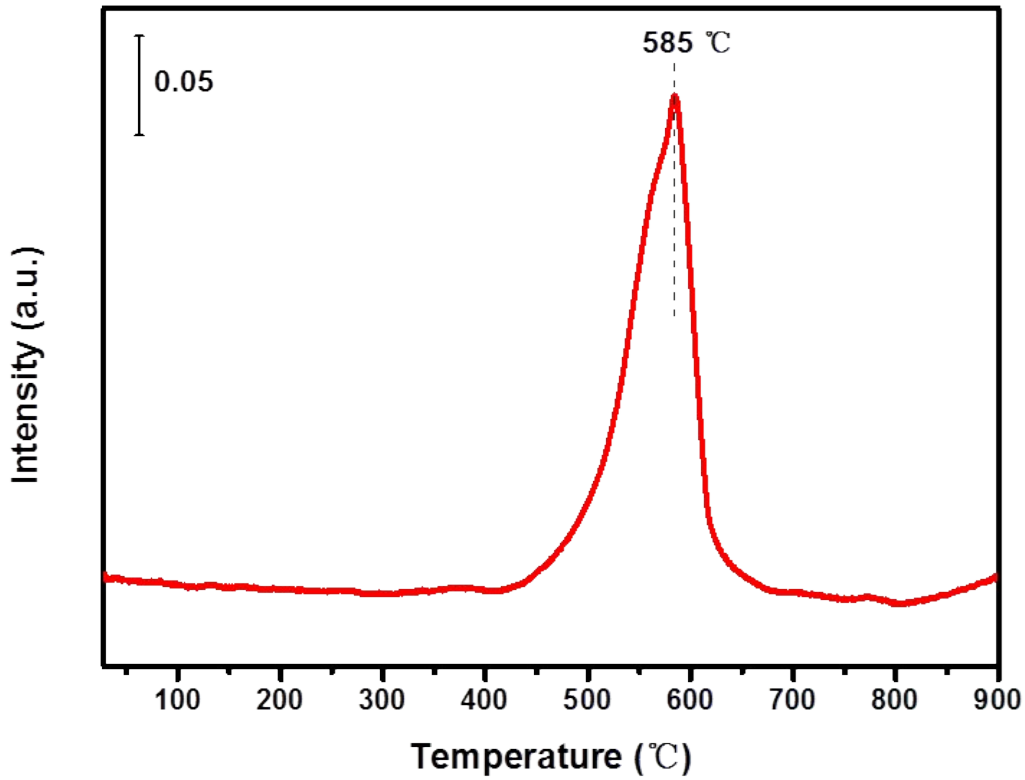

Figure S10. H_2-TPR profile for the anatase TiO_2 sample. The consumption amount of H_2 is 786.5 μmol g^{-1}.

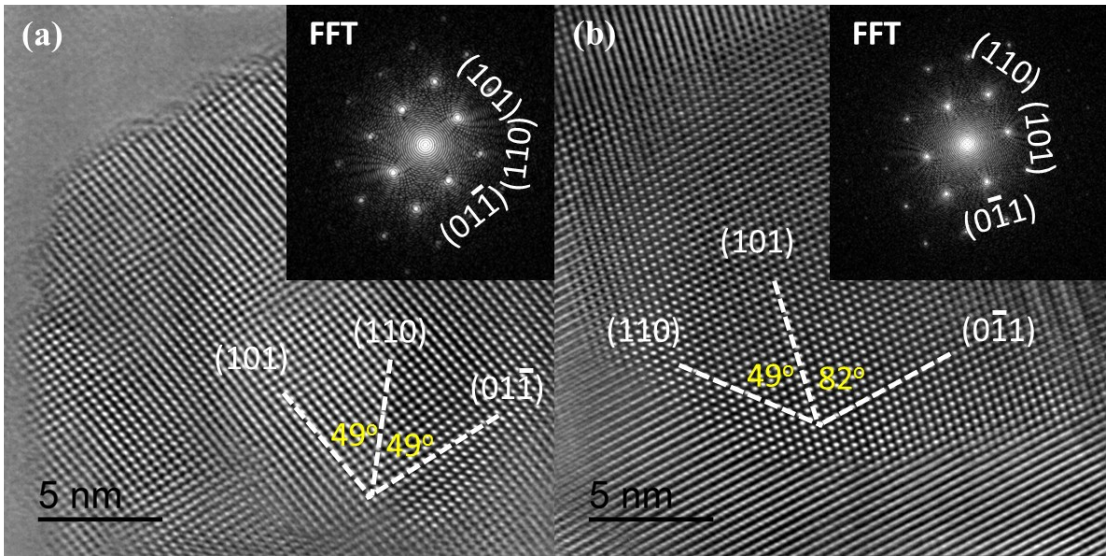

Figure S11. HRTEM images of the (a) anatase TiO_2 and (b) TiO_2-H600 samples.

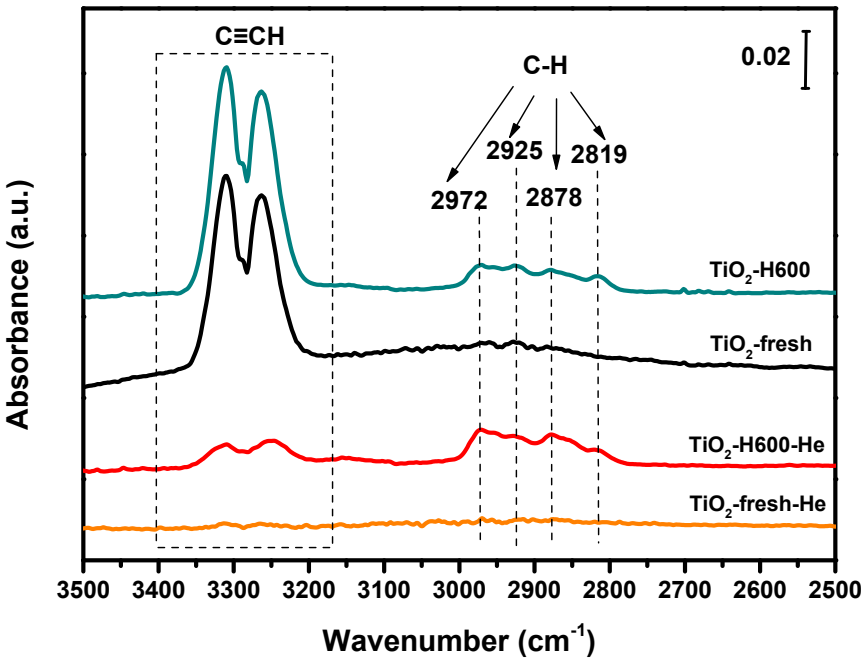

Figure S12. In situ DRIFT spectra of C_2H_2 adsorption on TiO_2-fresh and TiO_2-H600 at the steady state and then purging with He.

Table S1. Calculated distance (d_{H-H}/Å) between H−H and charge (Q) of $H^{\delta-}$ and $H^{\delta+}$ at the TS of H_2 dissociation as well as the corresponding energy barrier (E_a) above FLPs on (101) and (001) surfaces.

□	FLP	d_{H-H}/Å	Q/e (TS)		E_a/eV
□	sites		H(O)	H(Ti)	
101	$O_{v\text{-}1\text{-}1}$	1.01	0.39	-0.37	0.81
	$O_{v\text{-}1\text{-}2}$	0.99	0.48	-0.51	0.35
	$O_{v\text{-}1\text{-}3}$	1.07	0.35	-0.32	0.73
	$O_{v\text{-}2\text{-}1}$	0.91	0.21	-0.22	0.51
	$O_{v\text{-}2\text{-}2}$	1.03	0.39	-0.50	0.65
	$O_{v\text{-}3\text{-}3}$	1.01	0.40	-0.42	0.27
001	$O_{v\text{-}4\text{-}1}$	1.04	0.40	-0.45	0.74
	$O_{v\text{-}4\text{-}2}$	0.98	0.37	-0.39	0.49
	$O_{v\text{-}5\text{-}1}$	0.87	0.28	-0.33	0.23

Table S2. ICOHP values of Ti-H and O-H bonds for FS of H_2 dissociation above various FLPs.

	ICOHP	
	Ti-H	O-H
$O_{v\text{-}1\text{-}1}$	-3.00	-7.68
$O_{v\text{-}1\text{-}2}$	-3.08	-8.04
$O_{v\text{-}1\text{-}3}$	-3.04	-8.18
$O_{v\text{-}2\text{-}1}$	-3.54	-7.86
$O_{v\text{-}2\text{-}2}$	-3.48	-8.14
$O_{v\text{-}3\text{-}3}$	-2.26	-7.94
$O_{v\text{-}4\text{-}1}$	-2.46	-8.12
$O_{v\text{-}4\text{-}2}$	-2.46	-8.08
$O_{v\text{-}5\text{-}1}$	-2.82	-7.96