Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Constructing dual active sites for efficient alkaline hydrogen evolution: single-metal-atoms supported on BC_2N monolayers

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Table S1: Calculated bond lengths (in Å) and bond angles (θ in °) for BC_2N and $M@BC_2N$, M=Fe、Co、Ni.

Catalysts		C−C	C−N	C−B	B−N	M−C	M−N	θ_{N-M-C}
BC_2N	This work	1.425	1.405	1.529	1.443	---	---	---
	Ref. 1	1.420	1.390	1.530	1.450			
	Ref. 2	1.430	1.410	1.530	1.450			
	Ref. 3	1.400	1.350	1.490	1.430			
$Fe@BC_2N$		1.415	1.369	1.528	1.432	1.814	1.815	98.95
$Co@BC_2N$		1.413	1.366	1.529	1.435	1.810	1.814	99.54
$Ni@BC_2N$		1.411	1.378	1.531	1.437	1.804	1.806	102.40

References

1 Y. Shao, Q. Wang, L. Hu, H. Pan and X. Shi, *Carbon*, 2019, **149**, 530–537.

2 J. Xie, Z. Y. Zhang, D. Z. Yang, D. S. Xue and M. S. Si, *J. Phys. Chem. Lett.*, 2014, **5**, 4073–4077.

3 H. Nozaki and S. Itoh, *J. Phys. Chem. Solids*, 1996, **57**, 41–49.

Table S2: Calculated adsorption energy of the single H* (ΔE_{ads}(H*)) and co-adsorbed H with H* ($\Delta E_{co\text{-}ads}$(H*)), adsorption energy of the single OH* (ΔE_{ads}(H*)) and co-adsorbed OH* with H* ($\Delta E_{co\text{-}ads}$(OH*)) on M@BC_2N, M=Fe、Co、Ni (in eV).

Catalysts	ΔE_{ads}(H*)	$\Delta E_{co\text{-}ads}$(H*)	ΔE_{ads}(OH*)	$\Delta E_{co\text{-}ads}$(OH*)
Fe@BC_2N	−0.13	−0.32	−0.73	−0.28
Co@BC_2N	−0.40	−0.12	−0.85	−0.31
Ni @BC_2N	−0.51	−0.07	−0.94	−0.34

Note: (1) The corresponding adsorption configurations are shown in Fig. S3 and Fig. S5.

(2) The adsorption energy of the co-adsorbed H ($\Delta E_{co\text{-}ads}$(H*)) on substrates was calculated by the equation:

$$\Delta E_{co-ads}(H^*) = E_{M@BC_2N+2H} - E_{M@BC_2N+H} - E_H$$

where $E_{M@BC_2N+2H}$ is the total energy of the M@BC_2N substrate with adsorbed two H atoms; $E_{M@BC_2N+H}$ is the total energy of the M@BC_2N substrate with adsorbed one H atom; $E_H = 1/2E_{H_2}$, where E_{H_2} is the energy of a H_2 molecule.

(3) After OH* and H* co-adsorption, the adsorption energy of OH* ($\Delta E_{co\text{-}ads}$(OH*)) was calculated by the equation:

$$\Delta E_{co-ads}(OH^*) = E_{M@BC_2N+OH+H} - E_{M@BC_2N+H} - E_{OH}$$

where $E_{M@BC_2N+OH+H}$ is the total energy of the M@BC_2N substrate with the co-adsorbed OH* and H*; $E_{M@BC_2N+H}$ is the total energy of the

M@BC_2N substrate with an adsorbed H atom; $E_{OH} = E_{H_2O} - 1/2E_{H_2}$, where E_{H_2O} is the energy of a H_2O molecule.

Table S3: Calculated adsorption energy (E_{ads}) of H_2O* and H_2* (in eV) at different sites on M@BC_2N, M=Fe、Co、Ni.

Sites	H_2O*			H_2*		
	Fe@BC_2N	Co@BC_2N	Ni@BC_2N	Fe@BC_2N	Co@BC_2N	Ni@BC_2N
M	−0.96	−1.03	−1.04	−0.54	−0.52	−0.47
ortho-C	−0.77	−0.85	−0.91	---	---	---
meta-C	---	---	---	−0.43	---	−0.41
para-C	---	---	−0.96	−0.14	---	−0.47
ortho-N	−0.94	---	−0.90	−0.34	−0.32	−0.32
meta-B	−0.93	---	−0.95	---	---	---

Note: The corresponding adsorption configurations are shown in Fig. S3.

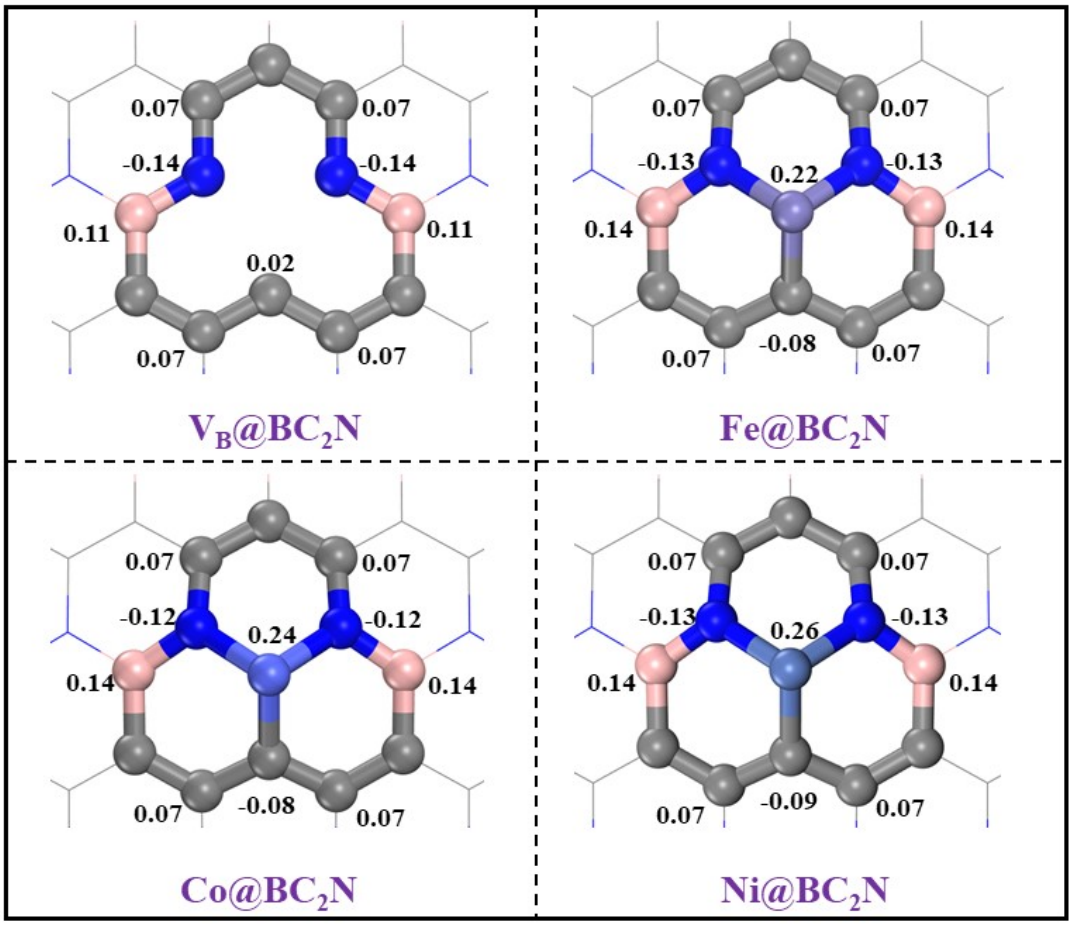

Fig. S1: Hirshfeld charge q (in e) for $V_B@BC_2N$ and $M@BC_2N$, M = Fe, Co, and Ni.

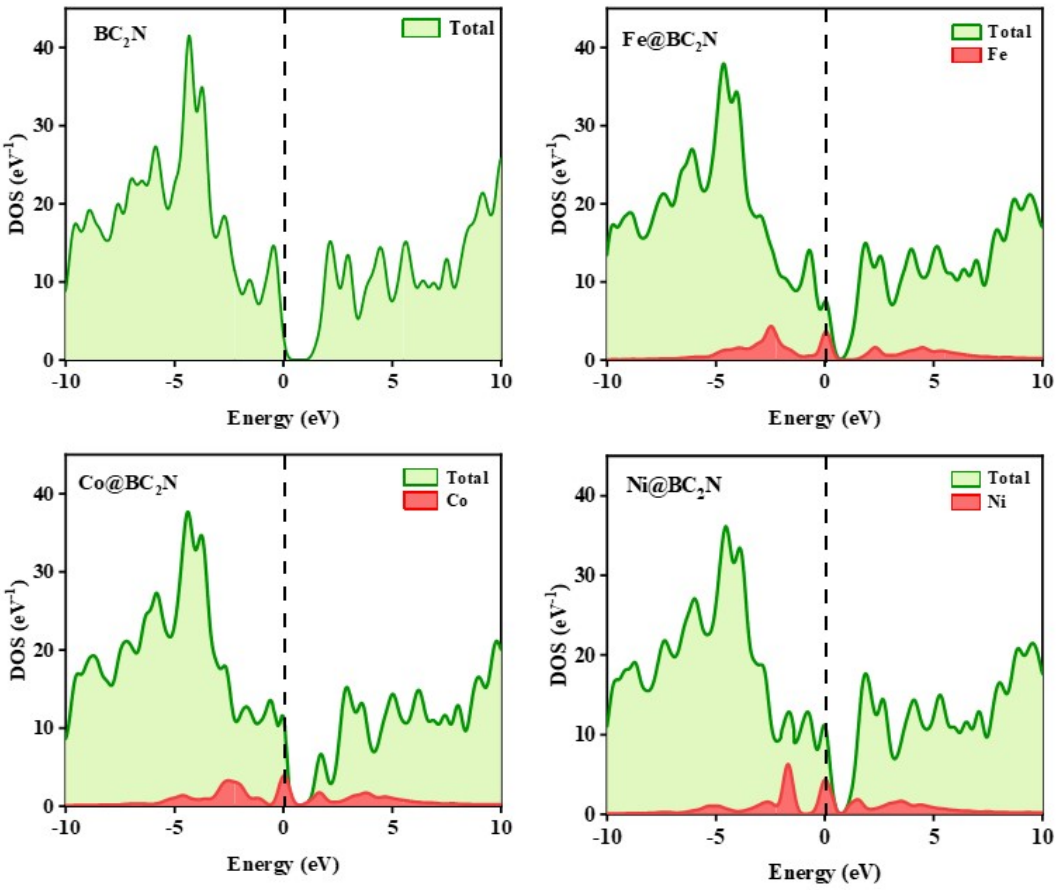

Fig. S2: Density of states (DOSs) of M@BC_2N, M = Fe, Co, and Ni. The green area is the total density of states, and the red area is the partial density of states of the metal atoms M The Fermi level marked by black dashed lines is set as the energy zero.

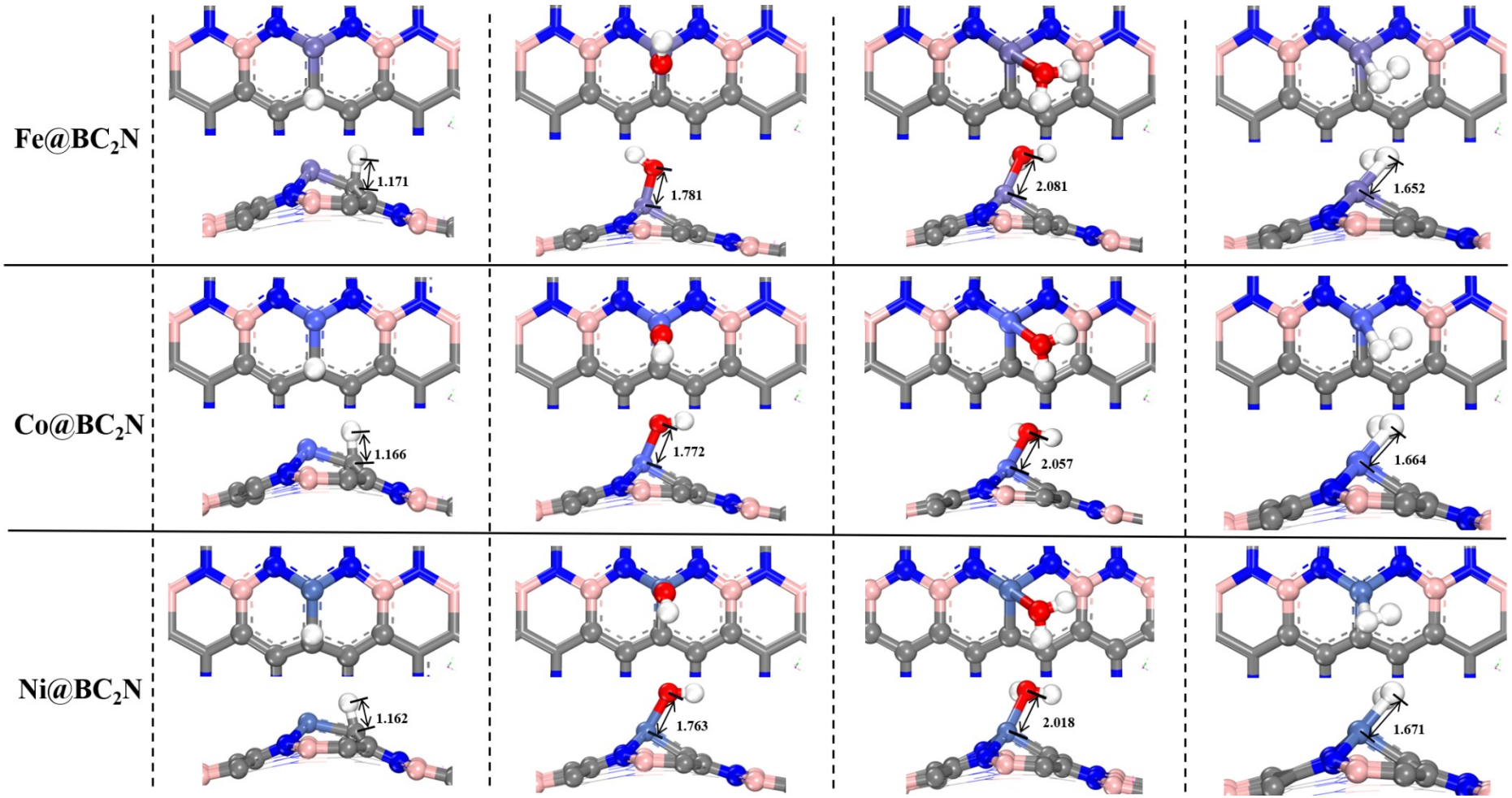

Fig. S3: The most stable adsorption configurations with the relevant bond length (in Å) for H*, OH*, H_2O*, and H_2* on the M@BC_2N catalysts.

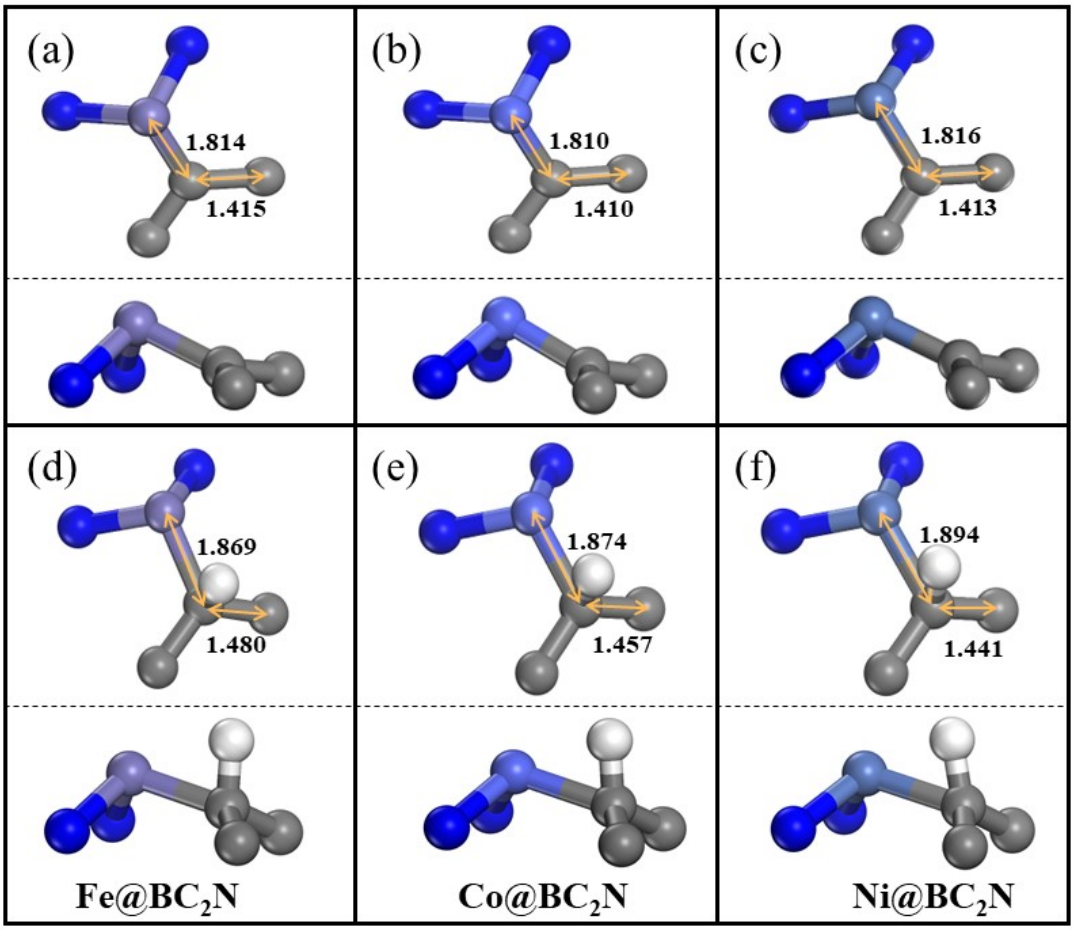

Fig. S4: Bond length (in Å) of the *ortho*-C-*meta*-C and M-*ortho*-C bonds (a)-(c) without and (d)-(f) with H adsorption at *ortho*-C for M@BC_2N, M = Fe, Co, and Ni.

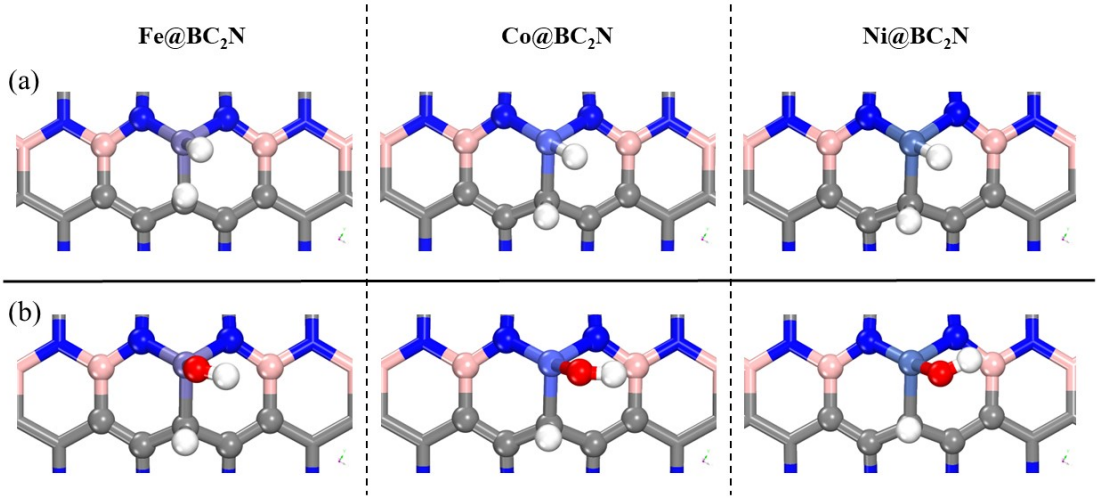

Fig. S5: The co-adsorption configurations of (a) double H* and (b) H* and OH* on M@BC_2N, M=Fe, Co, and Ni.

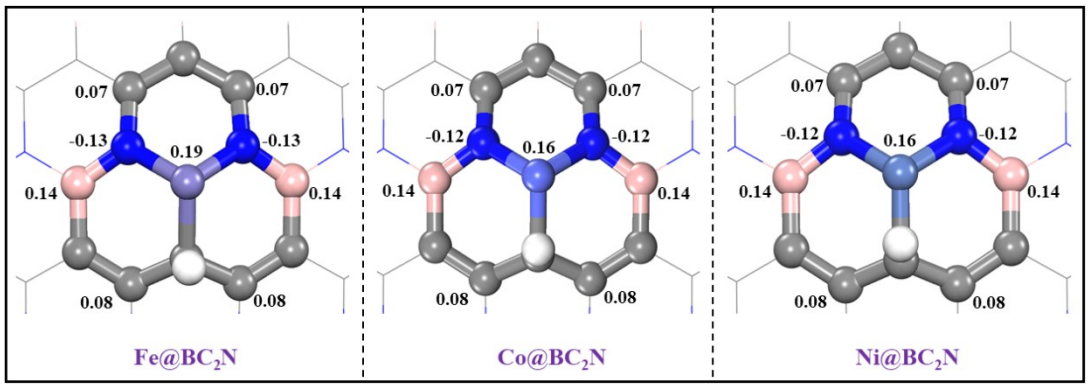

Fig. S6: Hirshfeld charge *q* (in *e*) after H adsorption at $M@BC_2N$, M = Fe、Co、Ni.

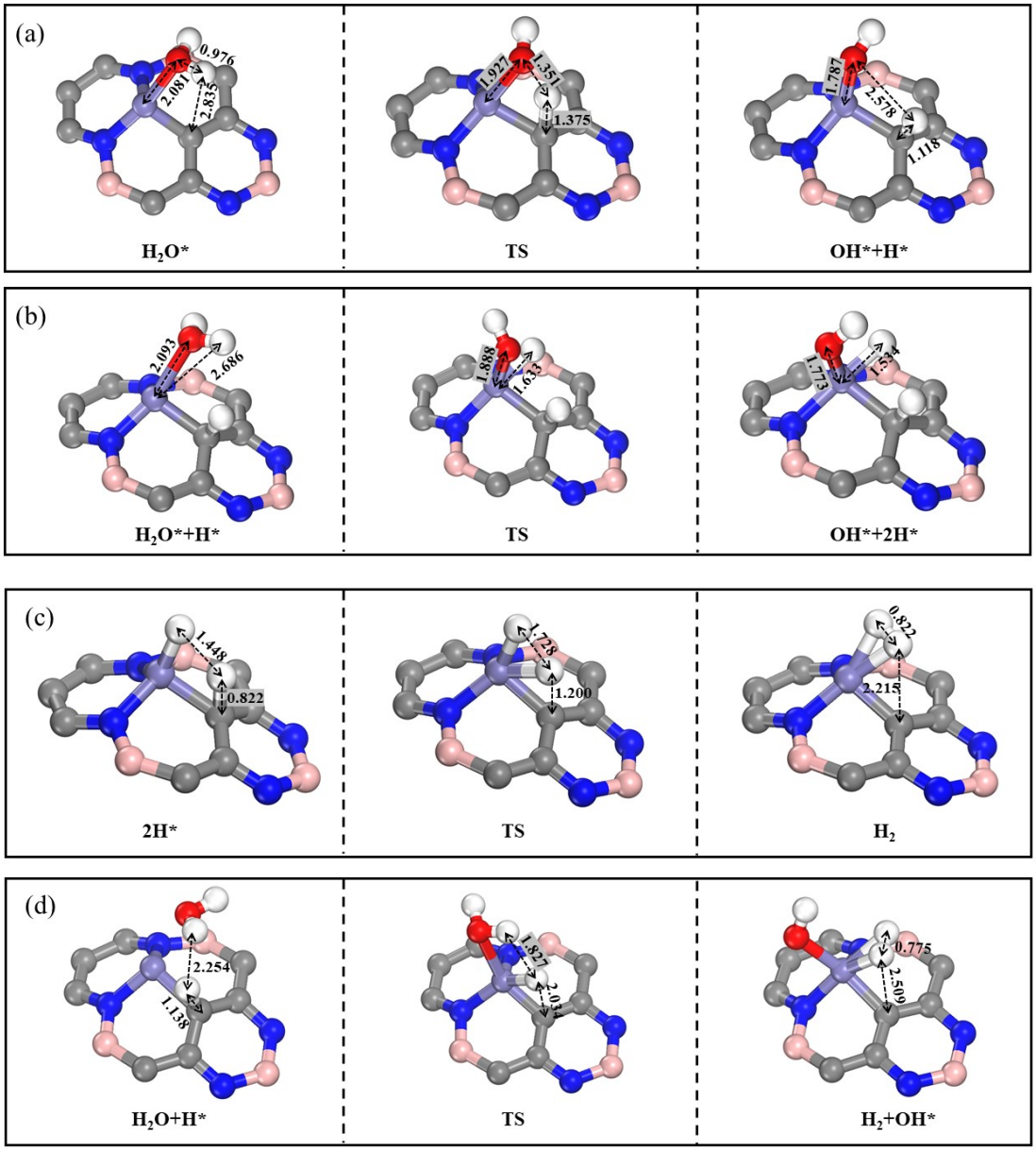

Fig. S7: Geometries and selected structural parameters (in Å) involved in the (a) Volmer-I, (b) Volmer-II, (c) Tafel, and (d) Heyrovsky mechanisms on Fe@BC_2N.

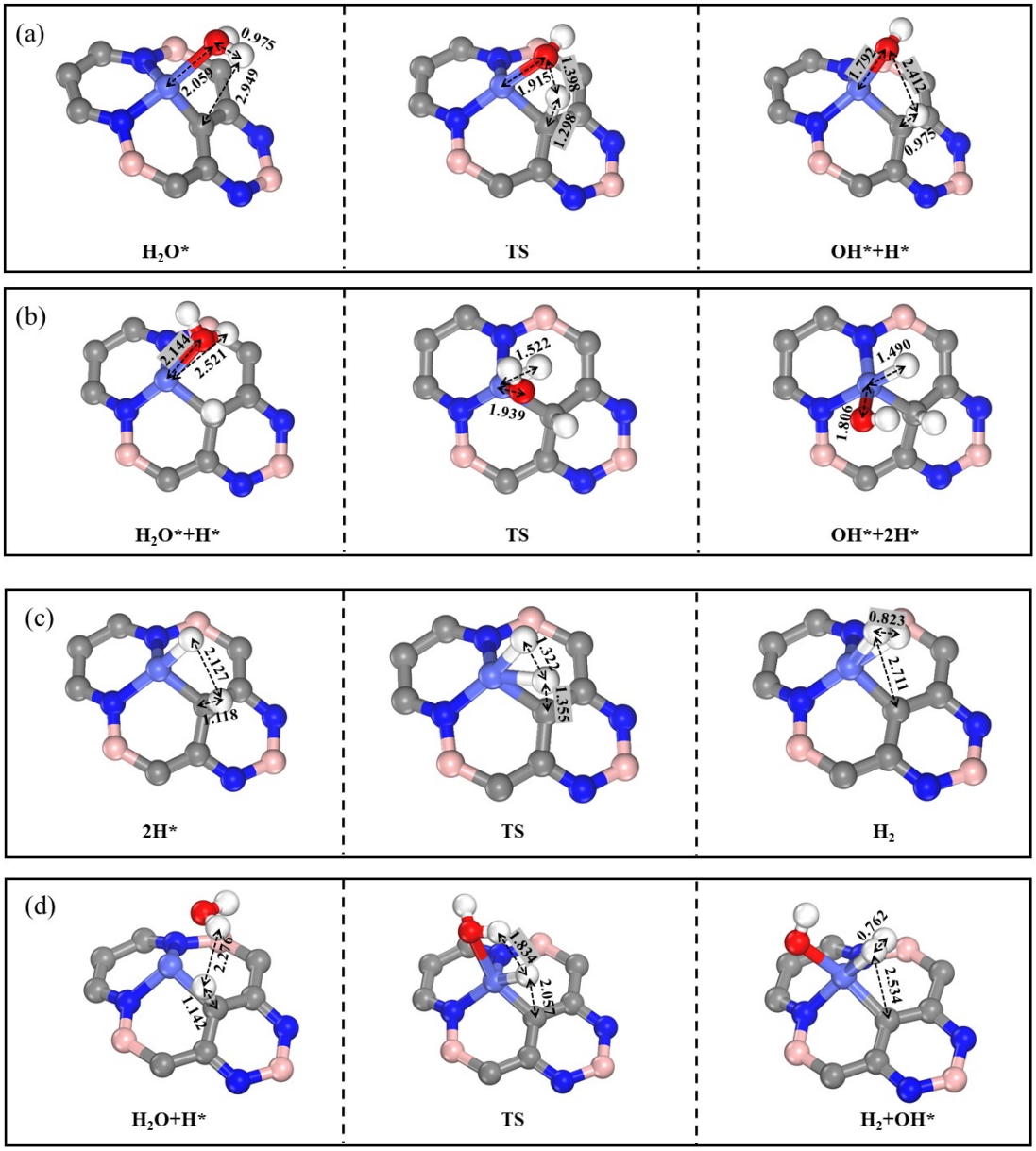

Fig. S8: Geometries and selected structural parameters (in Å) involved in the (a) Volmer-I, (b) Volmer-II, (c) Tafel, and (d) Heyrovsky mechanisms on Co@BC_2N.

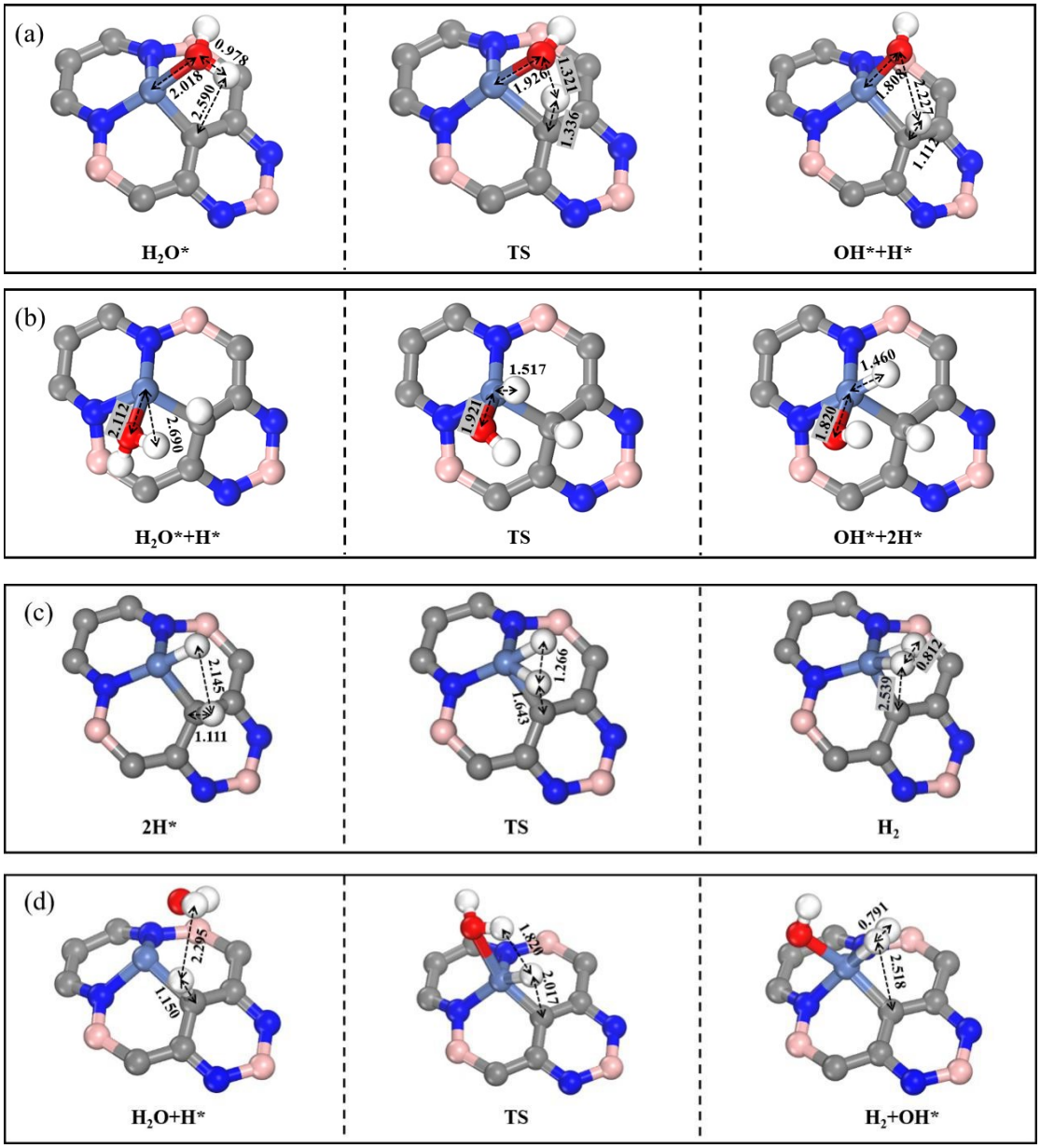

Fig. S9: Geometries and selected structural parameters (in Å) involved in the (a) Volmer-I, (b) Volmer-II, (c) Tafel, and (d) Heyrovsky mechanisms on Ni@BC_2N.