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Supplementary Information File

Electronic structure of non-metal (N, S) doped cobalt phosphide catalysts and catalytic mechanism for hydrogen evolution of ammonia borane: A theoretical study

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Content

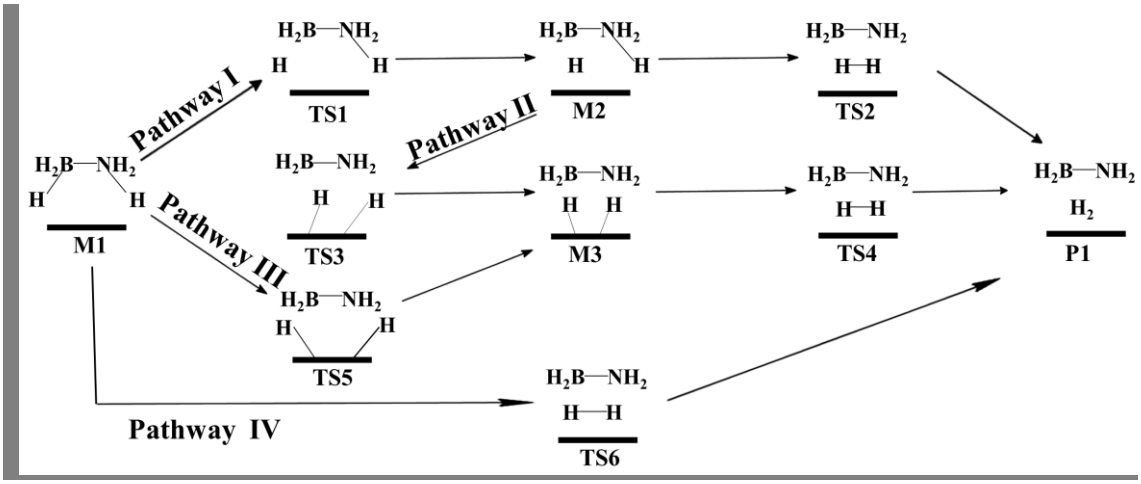

Fig. S1 Mechanism of hydrogen evolution 2D reaction scheme of NH_3BH_3.

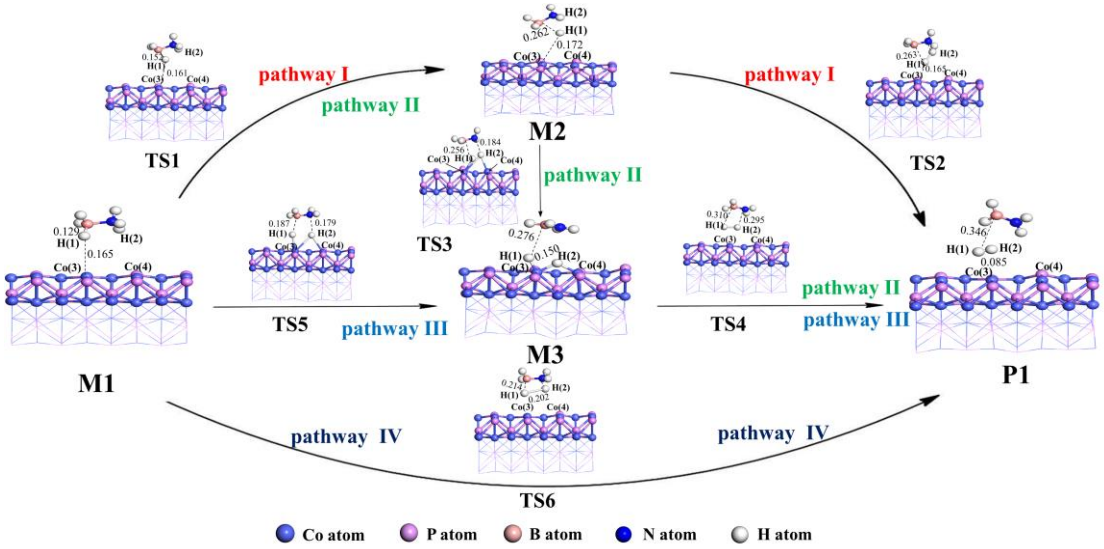

Fig. S2 General flow chart of NH_3BH_3 reaction on CoP (101) plane.

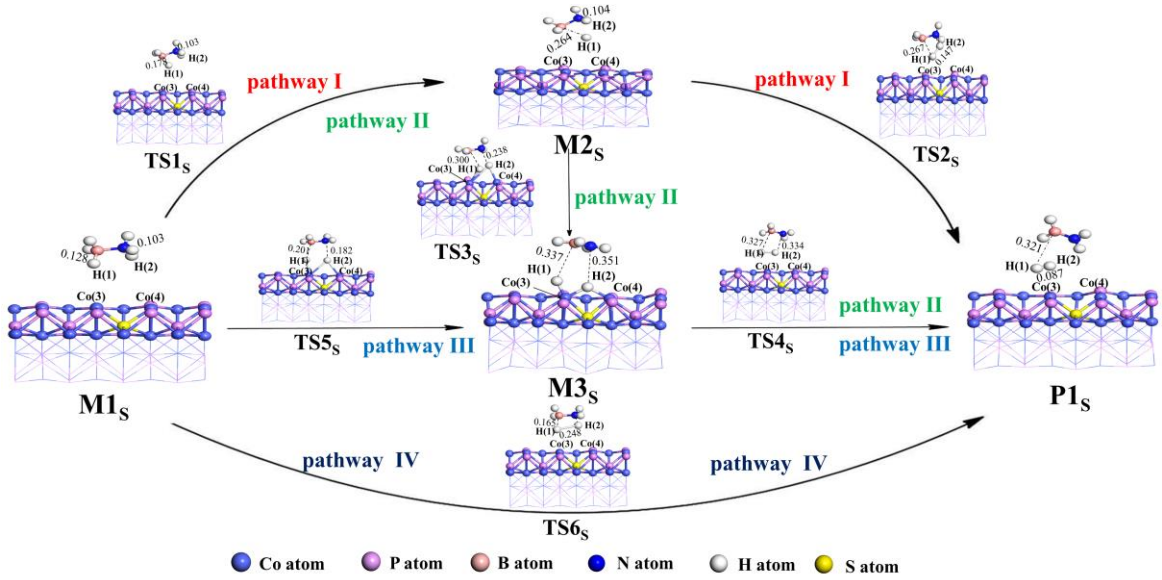

Fig. S3 General flow chart of NH_3BH_3 reaction on S@CoP (101) plane.

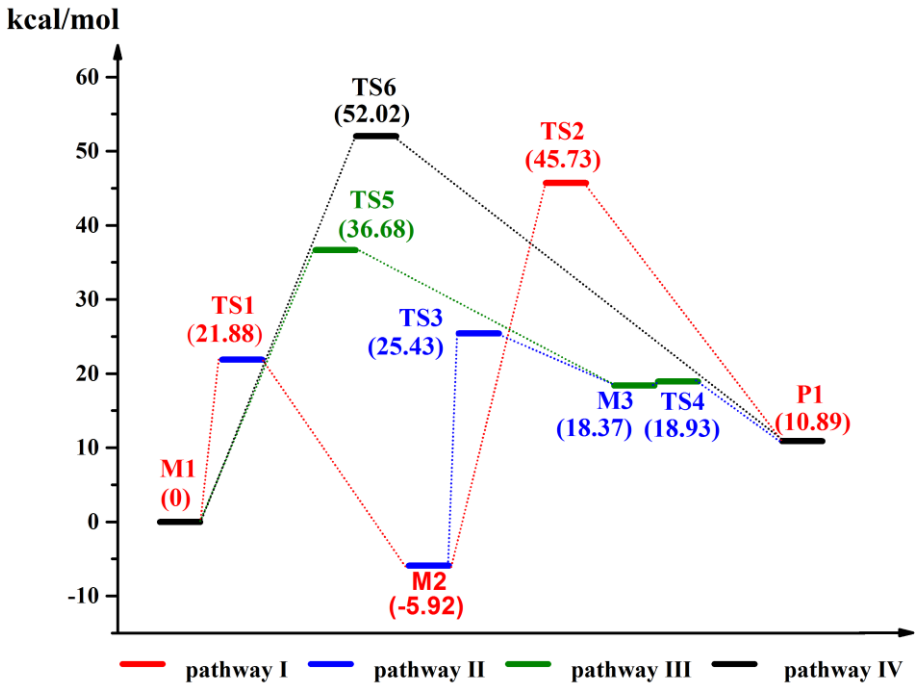

Fig. S4 Energy level diagrams of each pathway of NH_3BH_3 dehydrogenation catalyzed by CoP (101).

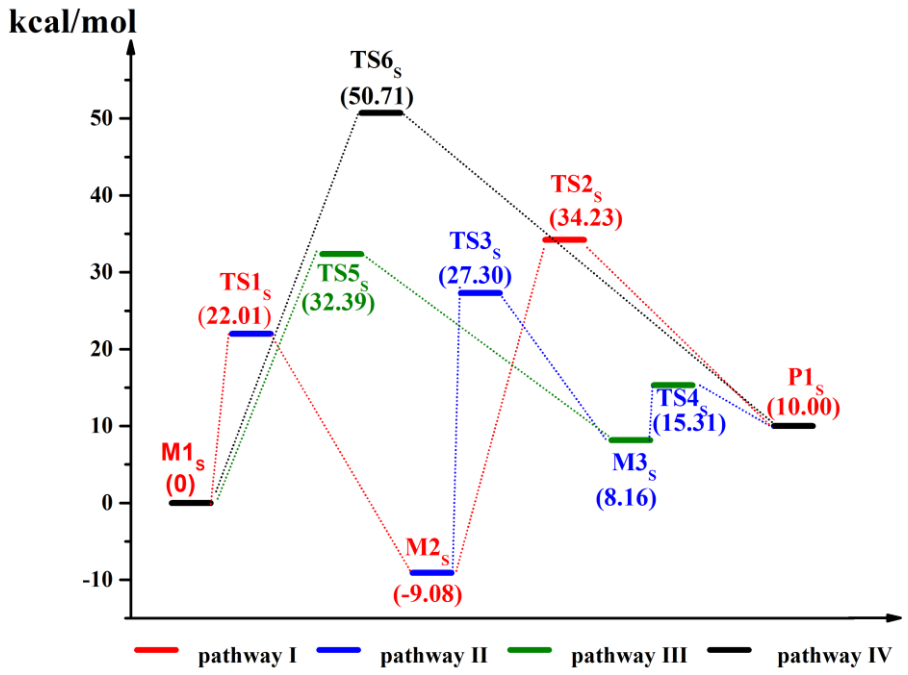

Fig. S5 Energy level diagrams of each pathway of NH_3BH_3 dehydrogenation catalyzed by S@CoP (101).

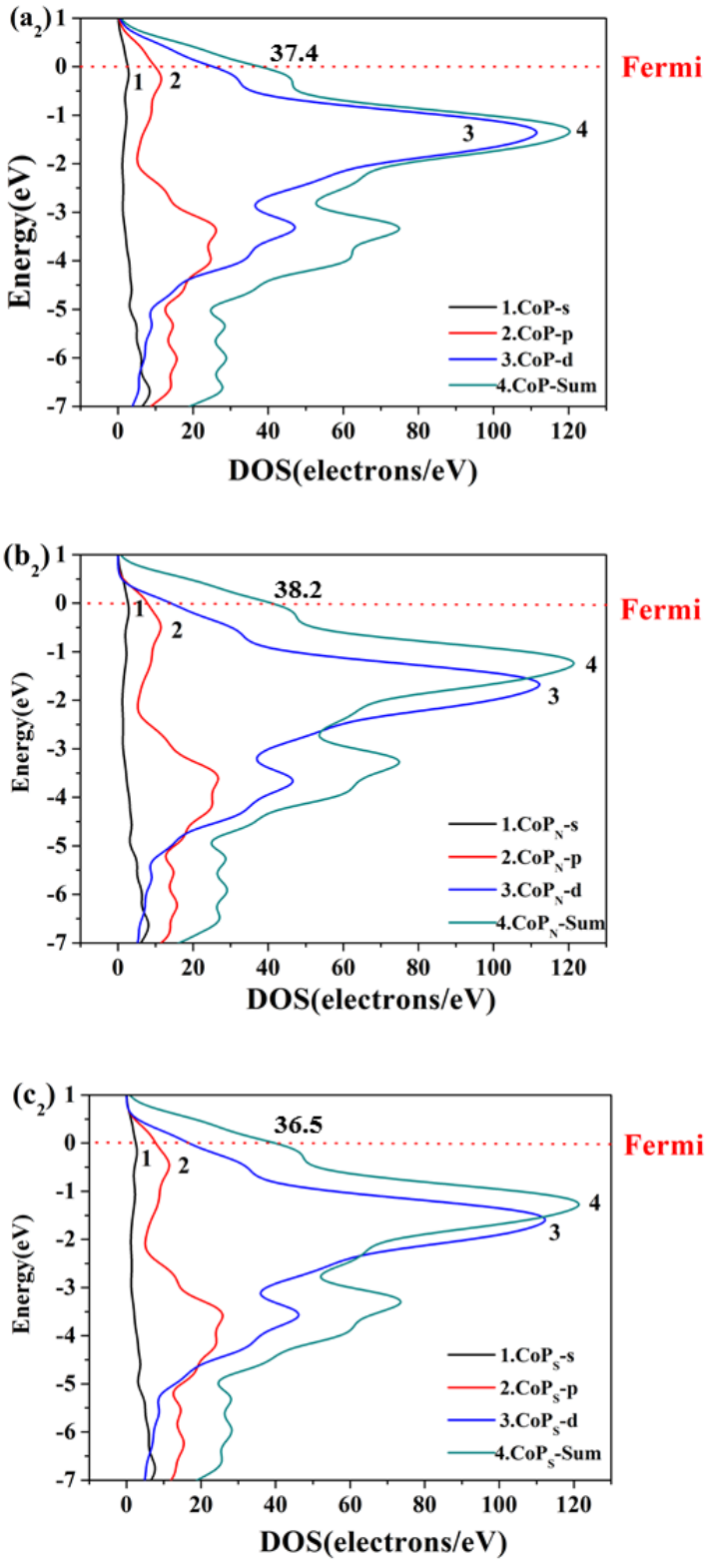

Fig. S6 The density of states (DOS). ((a), (b), (c) refer to CoP, N@CoP, S@CoP, respectively)

Table S1 Bond length (nm) table of reaction process of NH_3BH_3 on CoP (101) crystal plane.

Pathways	Compound	B-H(1)	Co(3)-H(1)	N-H(2)	Co(3)-H(2)	Co(4)-H(2)	H(1)-H(2)
Path I	M1	0.129	0.165	0.103	0.345	0.303	0.253
	TS1	0.152	0.161	0.103	0.345	0.305	0.231
	M2	0.262	0.172	0.103	0.305	0.309	0.193
	TS3	0.263	0.165	0.139	0.300	0.301	0.165
	M3	0.346	0.165	0.257	0.164	0.360	0.853
Path II	TS4	0.129	0.165	0.103	0.345	0.303	0.253
	P1	0.152	0.161	0.103	0.345	0.305	0.231
	M1	0.262	0.172	0.103	0.305	0.309	0.193
	TS5	0.256	0.171	0.184	0.285	0.240	0.171
	M3	0.276	0.150	0.316	0.168	0.173	0.208
	TS4	0.310	0.149	0.295	0.152	0.233	0.145
	P1	0.346	0.165	0.257	0.164	0.360	0.085
Path III	M1	0.129	0.165	0.103	0.345	0.303	0.253
	P1	0.187	0.159	0.179	0.240	0.209	0.239
	M1	0.276	0.150	0.316	0.168	0.173	0.208
	TS1	0.310	0.149	0.295	0.152	0.233	0.145
	M2	0.346	0.165	0.257	0.164	0.360	0.085
Path IV	TS3	0.129	0.165	0.103	0.345	0.303	0.253
	M3	0.346	0.165	0.257	0.164	0.360	0.085
	TS4	0.129	0.165	0.103	0.345	0.303	0.253

Table S2 Bond length (nm) table of reaction process of NH_3BH_3 on S@CoP (101) crystal plane.

Pathway	Compounds	B-H(1)	Co(3)-H(1)	N-H(2)	Co(3)-H(2)	Co(4)-H(2)	H(1)-H(2)
Path I	$M1_S$	0.128	0.164	0.103	0.344	0.306	0.256
	$TS1_S$	0.178	0.159	0.103	0.336	0.289	0.211
	$M2_S$	0.264	0.173	0.104	0.302	0.281	0.197
	$TS2_S$	0.267	0.162	0.183	0.260	0.246	0.147
	$P1_S$	0.321	0.162	0.321	0.163	0.299	0.087
Path II	$M1_S$	0.128	0.164	0.103	0.344	0.306	0.256
	$TS1_S$	0.178	0.159	0.103	0.336	0.289	0.211
	$M2_S$	0.264	0.173	0.104	0.302	0.281	0.197
	$TS3_S$	0.300	0.187	0.238	0.295	0.160	0.167
	$M3_S$	0.337	0.152	0.351	0.171	0.173	0.24
	$TS4_S$	0.327	0.155	0.334	0.167	0.224	0.180
	$P1_S$	0.321	0.162	0.321	0.163	0.299	0.087
Path III	$M1_S$	0.128	0.164	0.104	0.315	0.306	0.277
	$TS5_S$	0.201	0.158	0.182	0.249	0.215	0.257
	$M3_S$	0.337	0.152	0.351	0.171	0.173	0.24
	$TS4_S$	0.327	0.155	0.334	0.167	0.224	0.180
	$P1_S$	0.321	0.162	0.321	0.163	0.299	0.087
Path IV	$M1_S$	0.128	0.164	0.104	0.315	0.306	0.277
	$P1_S$	0.321	0.162	0.321	0.163	0.299	0.087
	$M1_S$	0.128	0.164	0.103	0.344	0.306	0.256

Table S3 Each position energy (E), relative energy (E_{rel}) and activation energy (E_a) of CoP catalyzed NH_3BH_3 reaction process.

Pathway	Intermediate/transition state	E_r	E_a
		kcal/mol	kcal/mol
Path I	M1	0.0	
	TS1	21.9	21.9
	M2	-5.9	
	TS2	45.7	51.7
	P1	10.9	
Path II	M1	0.0	
	TS1	21.9	21.9
	M2	-5.9	
	TS3	25.4	31.4
	M3	18.4	
	TS4	18.9	0.6
	P1	10.9	
Path III	M1	0.0	
	TS5	36.7	36.7
	M3	18.4	
	TS4	18.9	0.6
	P1	10.9	
Path IV	M1	0.0	
	TS6	52.0	52.0
	P1	10.9	

Table S4 Each position energy (*E*), relative energy (E_{rel}) and activation energy (E_a) of S@CoP catalyzed NH_3BH_3 reaction process.

Pathway	Intermediate/transition state	E_r	E_a
		kcal/mol	kcal/mol
Path I	$M1_S$	0.0	
	$TS1_S$	22.0	22.0
	$M2_S$	-9.1	
	$TS2_S$	34.2	43.3
	$P1_S$	10.0	
Path II	$M1_S$	0.0	
	$TS1_S$	22.0	22.0
	$M2_S$	-9.1	
	$TS3_S$	27.3	36.4
	$M3_S$	8.2	
	$TS4_S$	15.3	7.2
	$P1_S$	10.0	
Path III	$M1_S$	0.0	
	$TS5_S$	32.4	32.4
	$M3_S$	8.2	
	$TS4_S$	15.3	7.2
	$P1_S$	10.0	
Path IV	$M1_S$	0.0	
	$TS6_S$	50.7	50.7
	$P1_S$	10.0	