Electronic Supporting Information

Sodium Catalytic Phenylpentazole Cracking: A Theoretical Study

Content

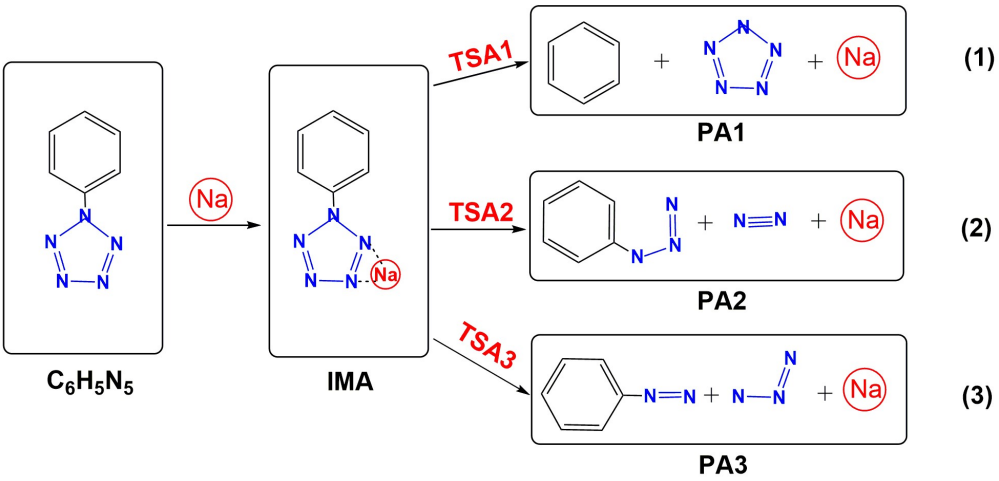

Fig. S1 The three reaction paths during single-atom Na catalytic $C_6H_5N_5$ cracking process.

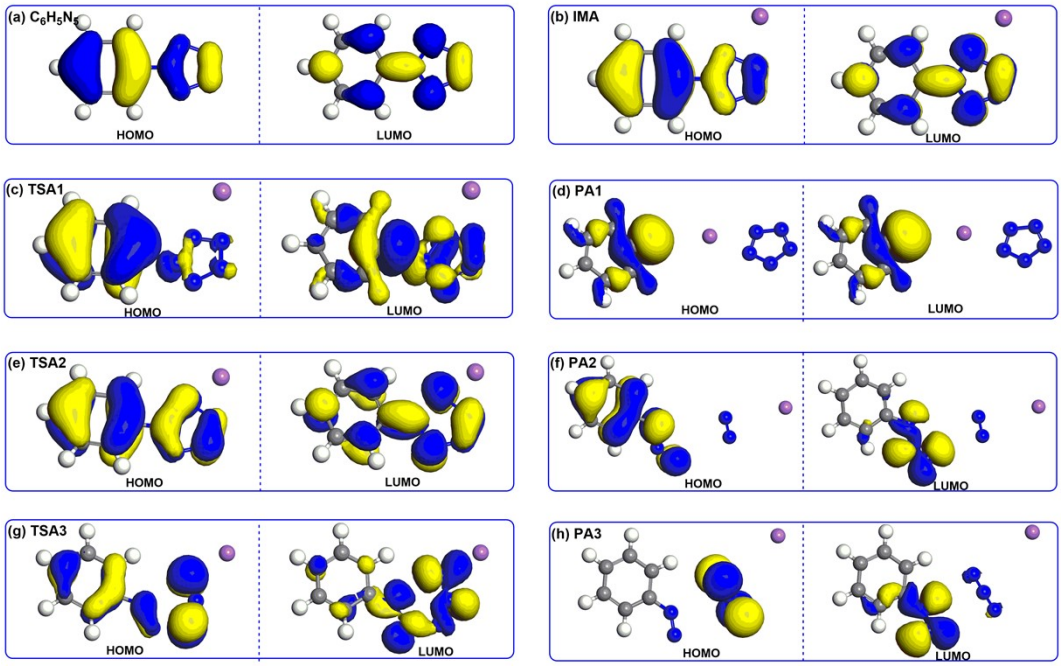

Fig. S2 The front-line orbital morphology of all compounds for catalytic $C_6H_5N_5$ cracking by single-atom Na.

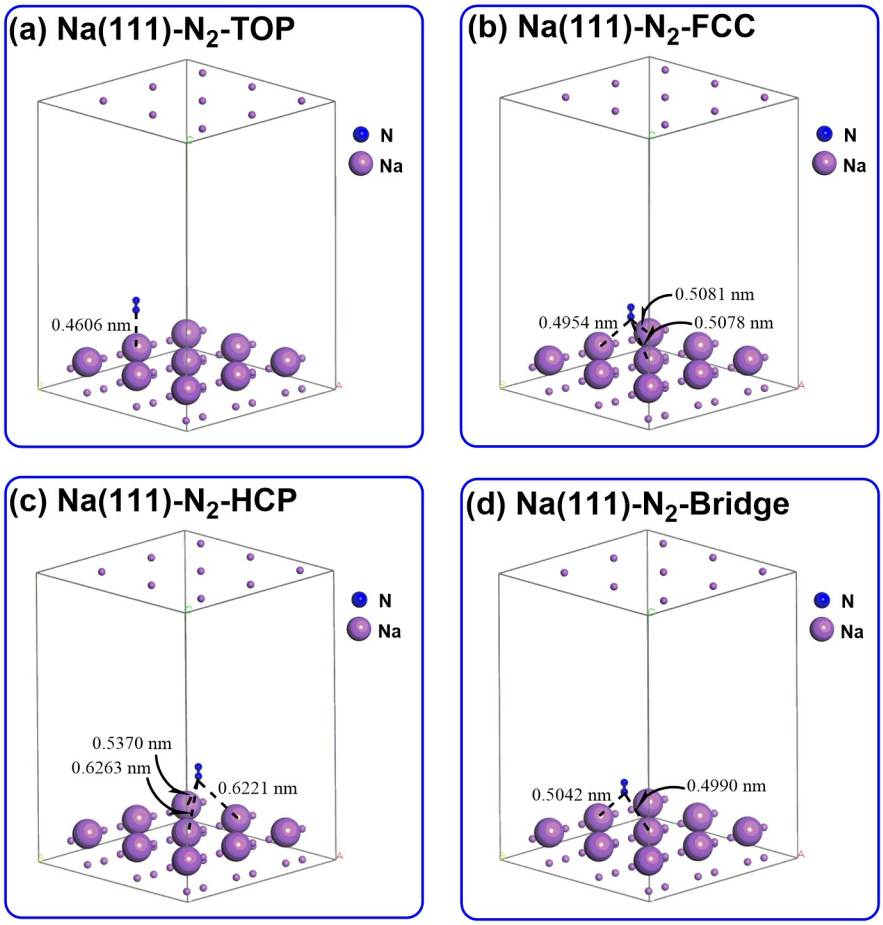

Fig. S3 Geometric parameters of N_2 adsorption on Na(111) surface [Bond length in nm].

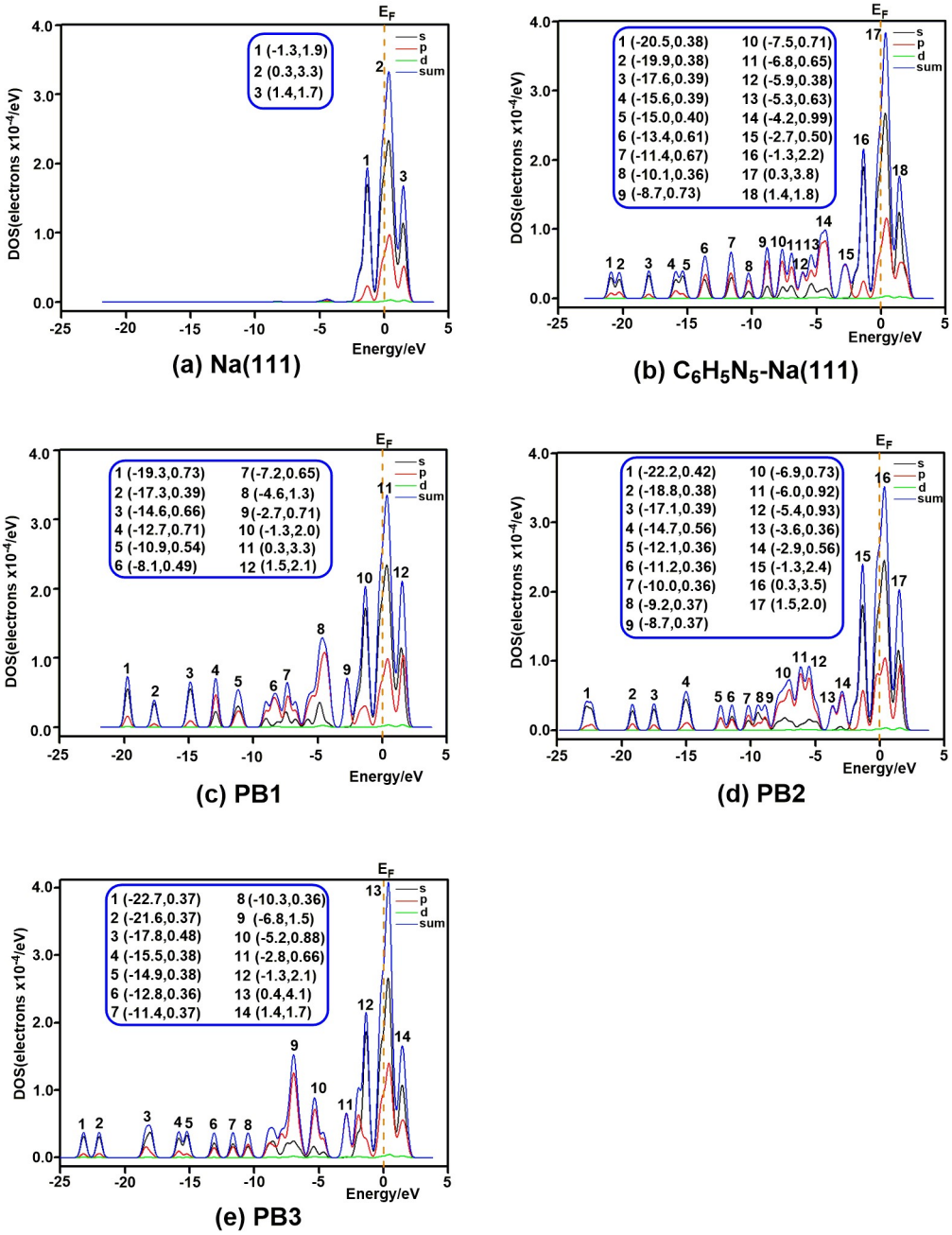

Fig. S4 The PDOS of the Na(111), $C_6H_5N_5$-Na(111), PB1, PB2, and PB3.

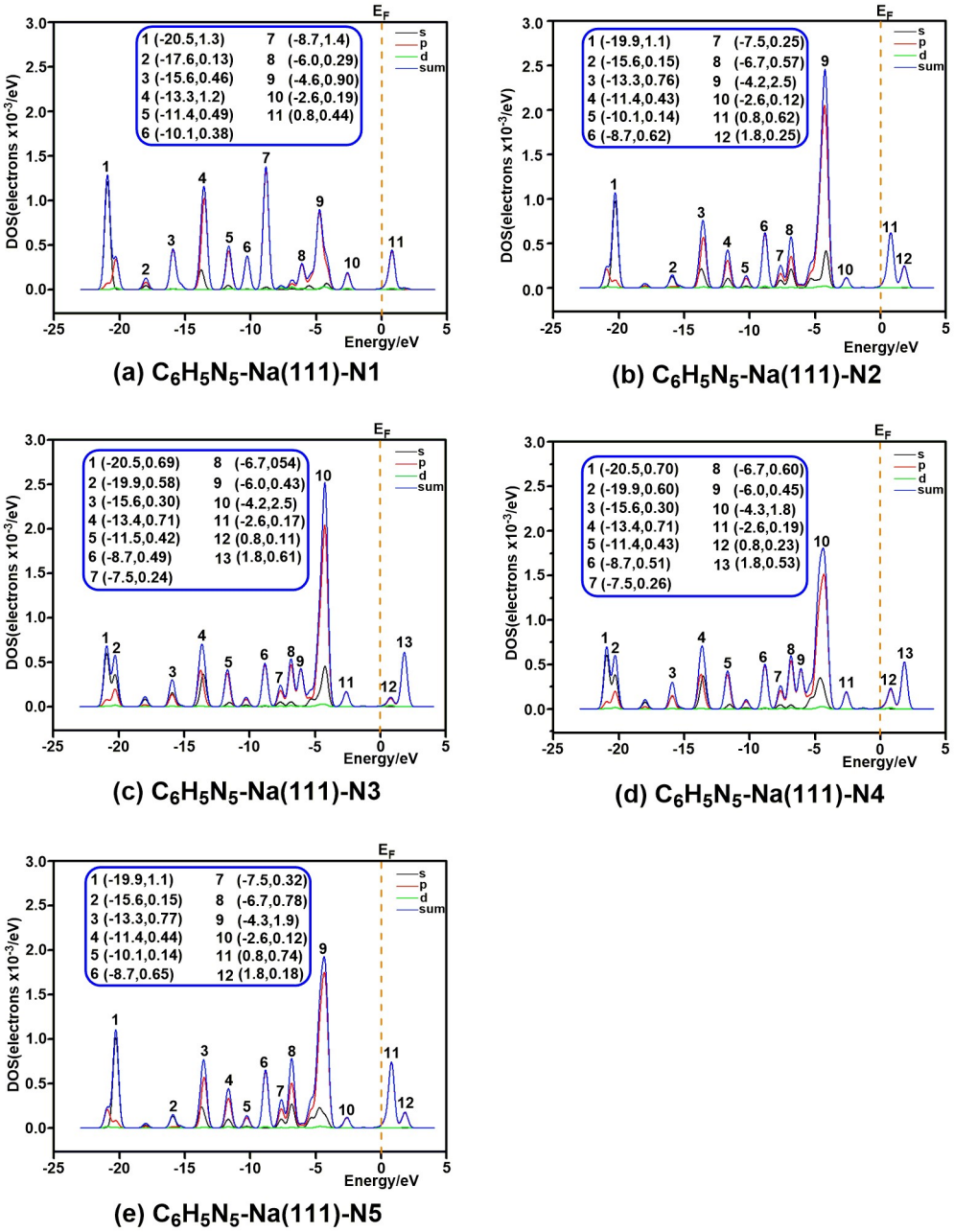

Fig. S5 The PDOS of five N atoms in the $C_6H_5N_5$-Na(111).

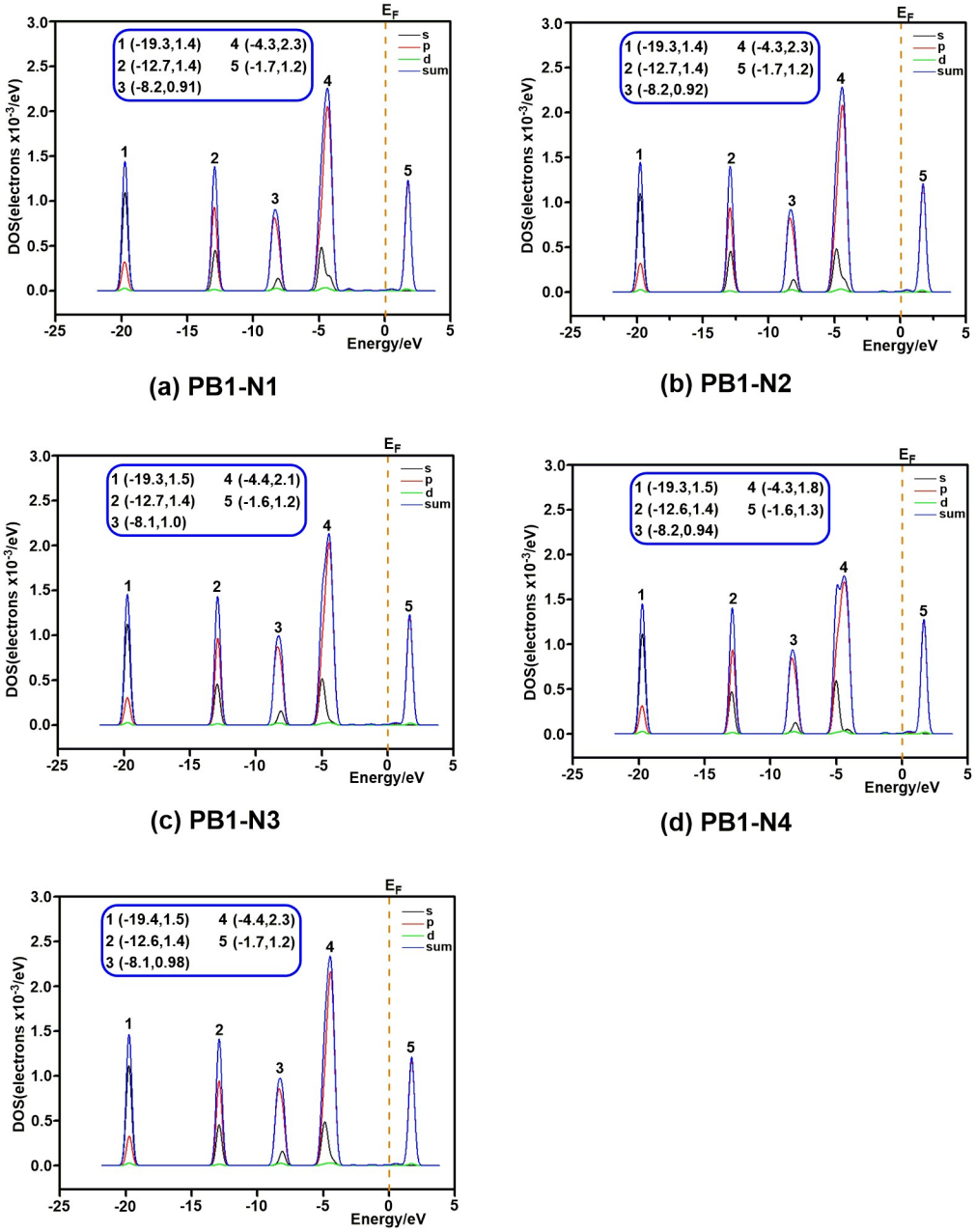

Fig. S6 The PDOS of five N atoms in the PB1.

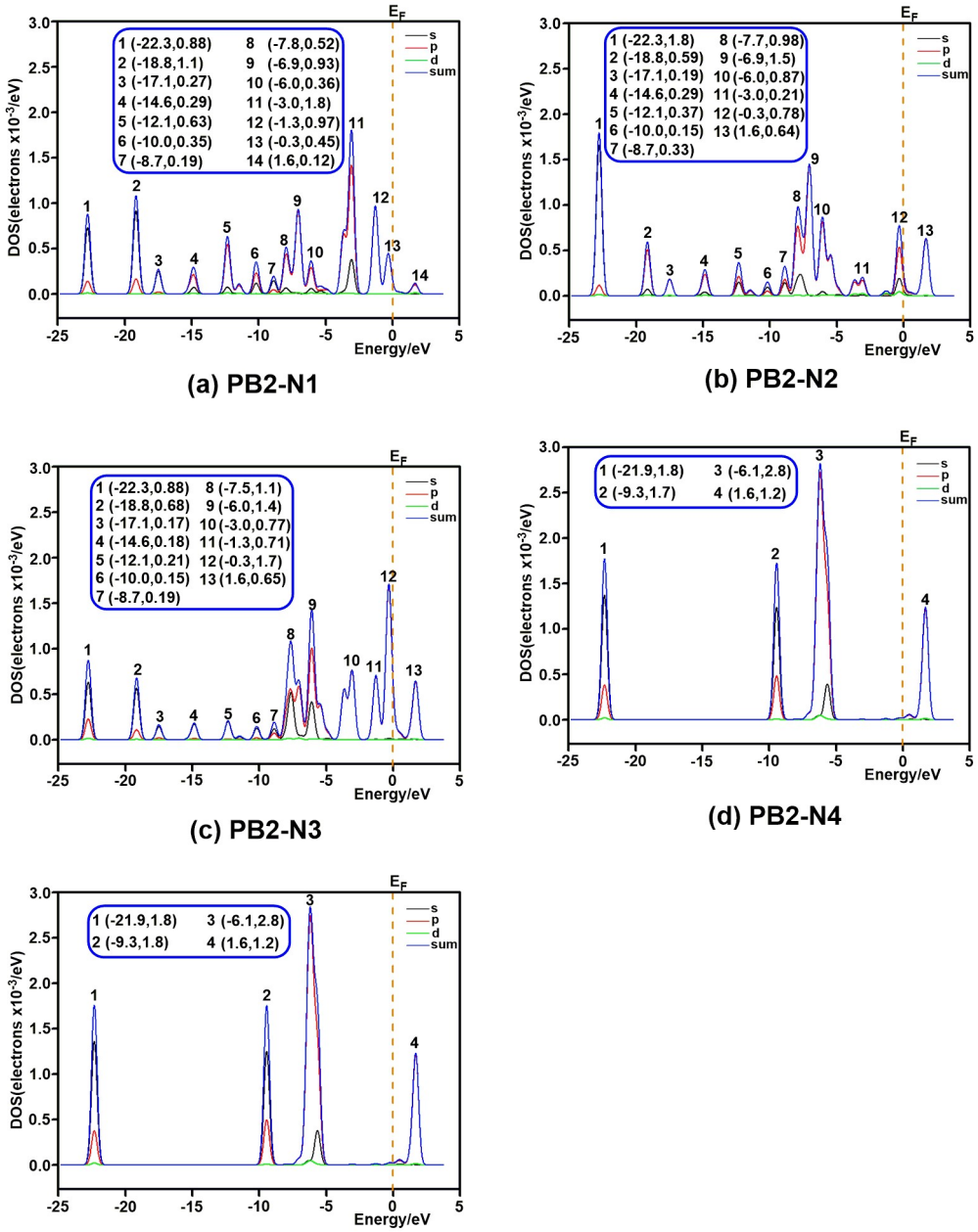

Fig. S7 The PDOS of five N atoms in the PB2.

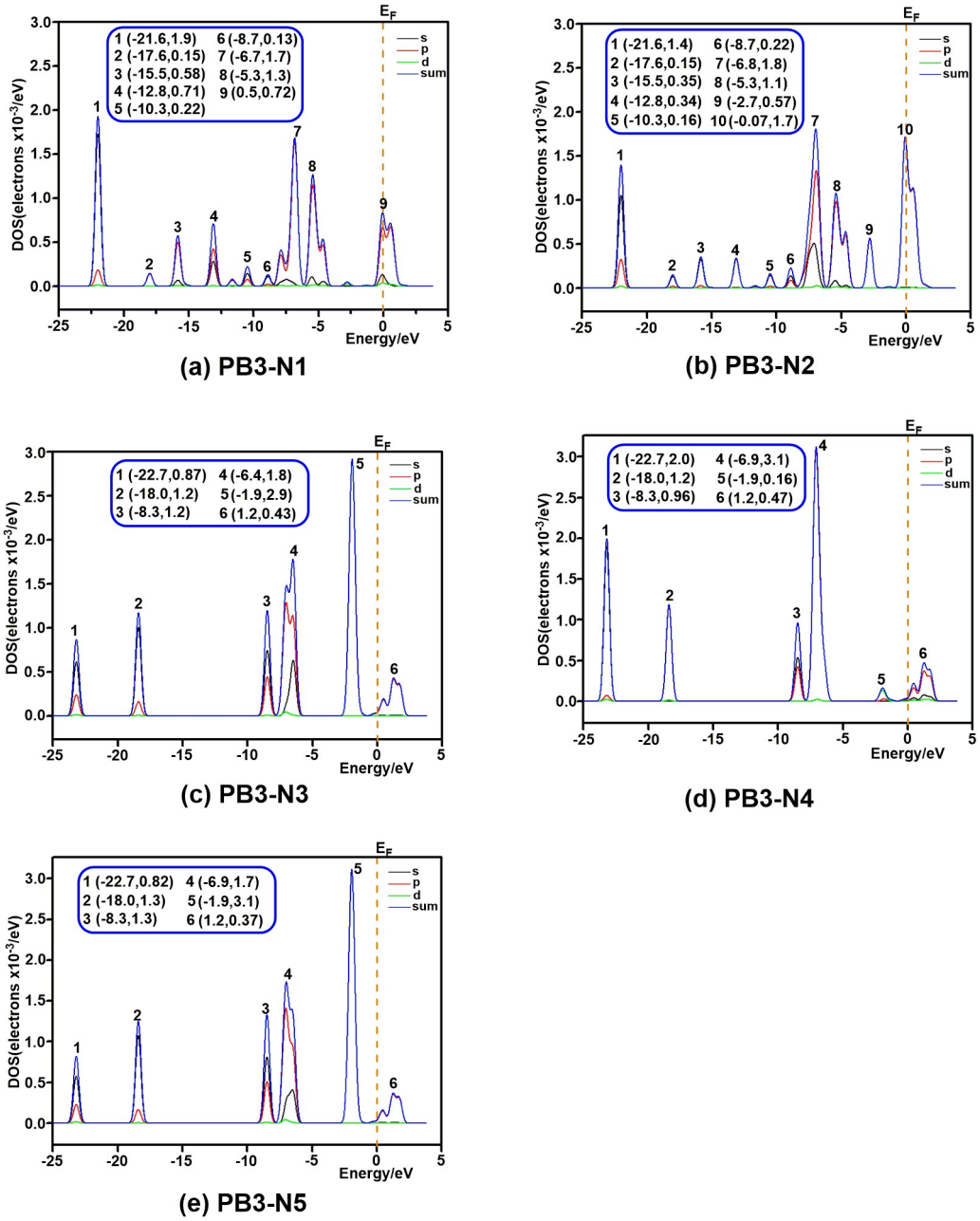

Fig. S8 The PDOS of five N atoms in the PB3.

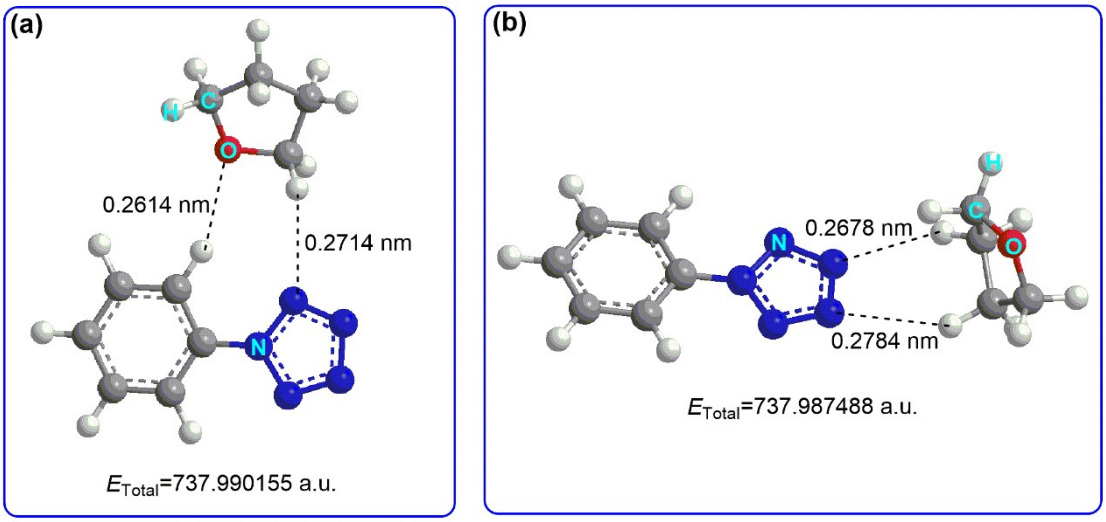

Fig. S9 The configuration diagram of a hydrogen bond between $C_6H_5N_5$ and a THF molecule. In (a), one hydrogen bond is O in THF and H in the benzene ring to form O-H bond, the other is methylene H in THF and N to form N-H bond, and both hydrogen bonds in (b) are N-H bonds.

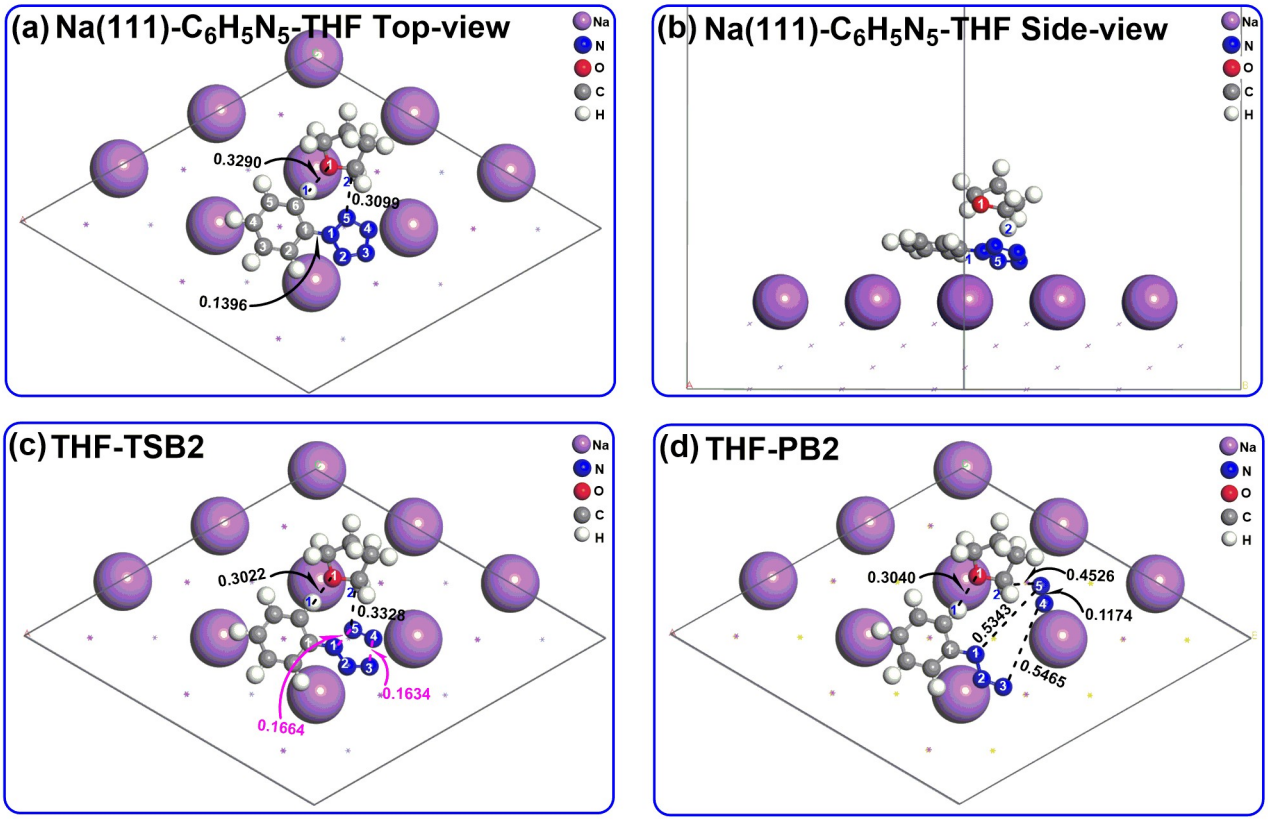

Fig. S10 Geometric parameters of the Na(111) surface catalytic $C_6H_5N_5$ cracking to release N_2 under an explicit solvent model(in GGA-PW91 level) [Bond length in nm].

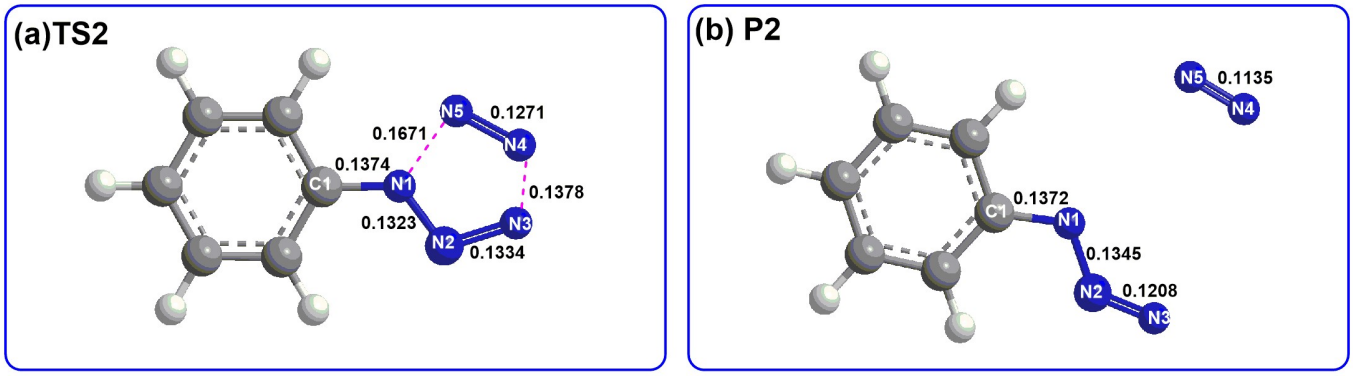

Fig. S11 Geometric parameters of all compounds on the $C_6H_5N_5$ pyrolysis to release N_2 without catalyst [Bond length in nm].

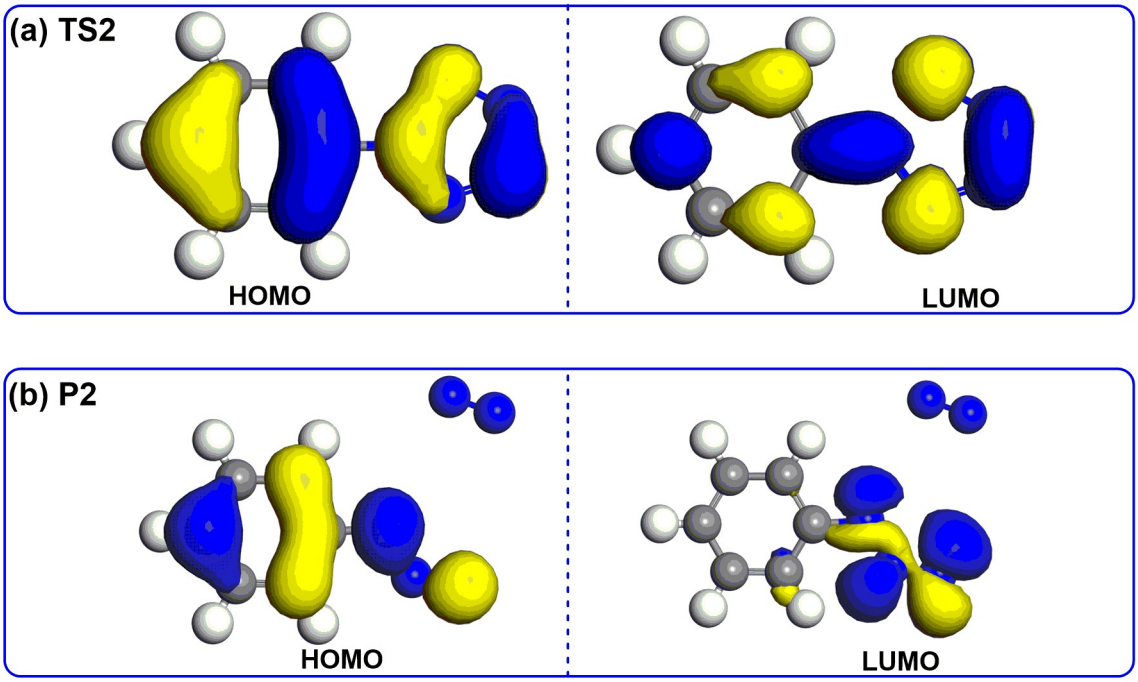

Fig. S12 The front-line orbital morphology of all compounds on the $C_6H_5N_5$ pyrolysis to release N_2 without catalyst.

Table S1 The charge (in e) of some atoms and groups in compounds during single-atom Na catalytic $C_6H_5N_5$ cracking process.

Species	C1	N1	N2	N3	N4	N5	Na
$C_6H_5N_5$	0.197	-0.025	-0.088	-0.060	-0.060	-0.088	-
IMA	0.108	-0.012	-0.134	-0.085	-0.201	-0.236	0.588
TSA1	-0.034	-0.081	-0.069	-0.069	-0.143	-0.143	0.416
PA1	-0.089	-0.121	-0.123	-0.121	-0.213	-0.214	0.787
TSA2	0.141	-0.088	-0.061	-0.084	-0.104	-0.212	0.363
PA2	0.027	-0.159	0.039	-0.142	-0.082	-0.098	0.252
TSA3	0.148	-0.072	-0.111	-0.130	0.077	-0.326	0.413
PA3	0.055	-0.034	-0.139	-0.192	0.177	-0.235	0.244

Table S2 Relative energies [E_{rel}/(kcal/mol)] and frequencies v(cm^{-1}) of the reaction paths during catalytic $C_6H_5N_5$ cracking reaction by single-atom Na.

Species	Gas		COSMO	
	E_{rel}(kcal/mol)*	v(cm^{-1})	E_{rel}(kcal/mol)**	v(cm^{-1})
IMA	-18.6	-	-10.8	-
TSA1	3.6	-146.9	11.8	-169.4
PA1	-0.3	-	0.5	-
TSA2	-16.3	-411.4	-6.5	-413.6
PA2	-54.1	-	-49.5	-
TSA3	-18.4	-466.2	-6.6	-392.6
PA3	-35.1	-	-34.6	-

*The relative reference data is E_0(Gas)=-666.241883 a.u., and E_0(Gas) is the total energy of $C_6H_5N_5$ and one Na atom in the gas phase condition.

**The relative reference data is E_0(Solvation)=-666.494934 a.u., where E_0(Solvation) is the total energy of $C_6H_5N_5$ and one Na atom under COSMO conditions.

Table S3 Total energy [*E*(a.u)] and adsorption energy of $C_6H_5N_5$ at various adsorption sites on Na(111) surface under gas phase and COSMO conditions.

Adsorption site	Gas	COSMO
	– *E*/(a.u.)	– *E*/(a.u.)
$C_6H_5N_5$+Na(111)	13477.722133	13477.731416
Top	13477.684909	13477.692712
FCC	13477.693251	13477.698760
HCP	13477.687032	13477.689129
LB	13477.689157	13477.688483
SB	13477.679287	13477.691028

Table S4 Total energy [*E*(a.u)] and adsorption energy [E_{ads}/(eV)] of N_2 at various adsorption sites on Na(111) surface under gas phase conditions.

Adsorption site	Gas	
	– *E*/(a.u.)	E_{ads}/(eV)
N_2+Na(111)	7415.309509	-
Top	7415.324420	-0.41
FCC	7415.325530	-0.44
HCP	7415.323979	-0.39
Bridge	7415.324981	-0.42

Table S5 Relative energies [E_{rel}/(kcal/mol)] of the released N_2 reaction paths.

Species	COSMO		Explicit Solvation	
	GGA-PW91*	GGA-PBE**	GGA-PW91*	GGA-PBE**
TSB2	5.2	7.4	9.8	10.2
PB2	-55.5	-55.4	-58.7	-57.4

Notes:

* In GGA-PW91 level, the relative reference data E_0 are -7801.943028 and -8043.814061 a.u. under the continuum solvent model (COSMO) and explicit solvent model, respectively.

** In GGA-PBE level, the relative reference data E_0 are -7806.770315 and -8039.056739 a.u. under the continuum solvent model (COSMO) and explicit solvent model, respectively.

Table S6 Relative energies [E_{rel}/(kcal/mol)] and frequencies v(cm^{-1}) of the reaction paths during $C_6H_5N_5$ cracking reaction.

Species	Gas		COSMO	
	E_{rel}(kcal/mol)*	v(cm^{-1})	E_{rel}(kcal/mol)**	v(cm^{-1})
TS2	10.2	-387.3	13.2	-381.8
P2	-45.3	-	-44.0	-

Notes:

*The relative reference data is E_0(Gas)=-505.493958 a.u., and E_0(Gas) is the total energy of $C_6H_5N_5$ in the gas phase.

**The relative reference data is E_0(Solvation)=-505.502106 a.u., where E_0(Solvation) is the total energy of $C_6H_5N_5$ under COSMO.