The Critical Role of Fe 3d-N 2p Orbital Hybridization in Ammonia Decomposition on graphene-supported Fe_6N_x Clusters: A DFT study

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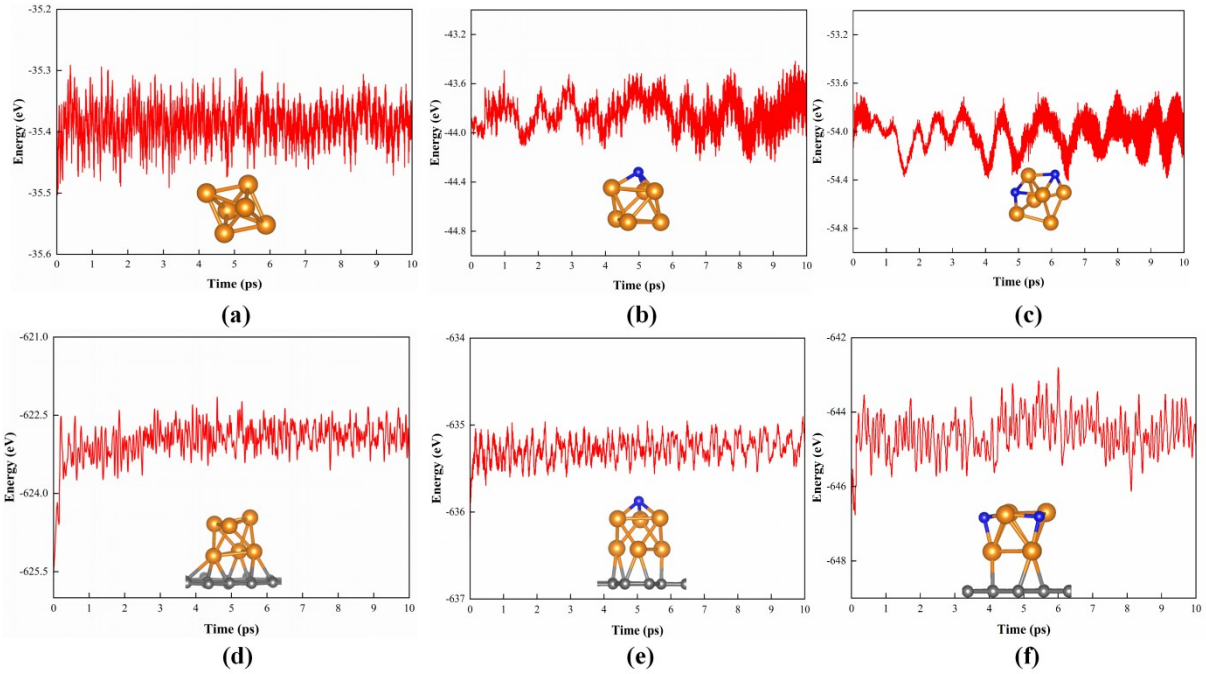

Fig. S1. AIMD simulations of (a) Fe_6N_0, (b) Fe_6N_1, (c) Fe_6N_2, (d) Fe_6N_0@graphene, (e) Fe_6N_1@graphene and (f) Fe_6N_2@graphene at 823 K. The C, N, and Fe atoms are colored in gray, blue, and orange, respectively.

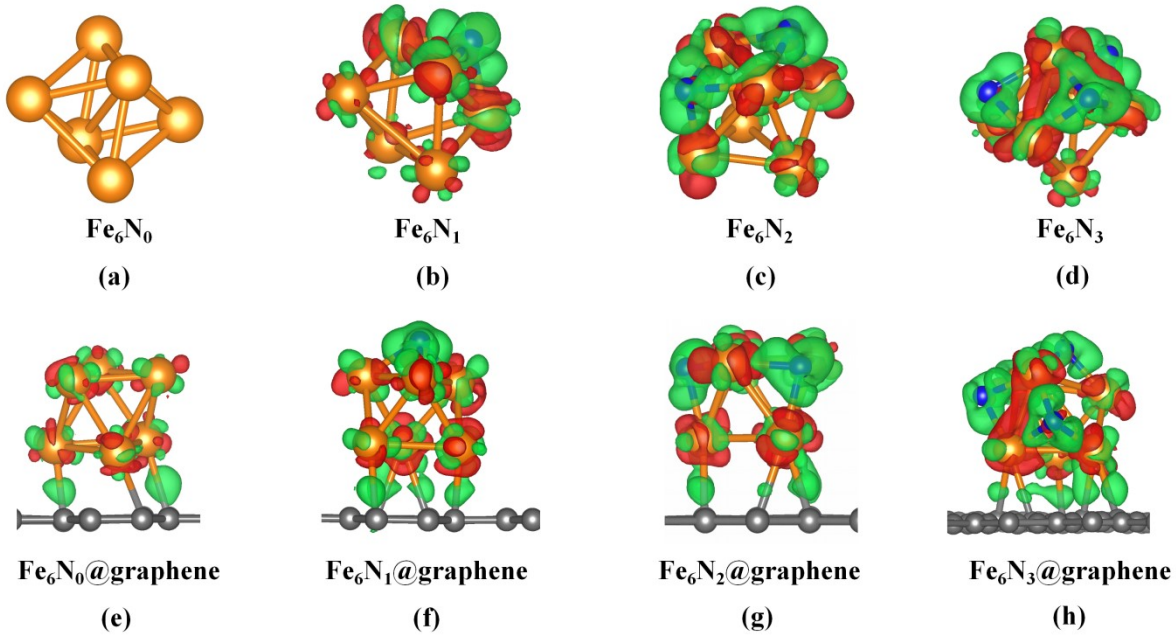

Fig. S2. Differential charge density plots of (a) Fe_6N_0, (b) Fe_6N_1, (c) Fe_6N_2, (d) Fe_6N_3, (e) Fe_6N_0@graphene, (f) Fe_6N_1@grapehen, (g) Fe_6N_2@graphene and (h) Fe_6N_3@graphene. The isosurface level is set at ±0.01 a.u. Green regions correspond to electron accumulation and red regions represent electron depletion. Color codes follow Fig. S1.

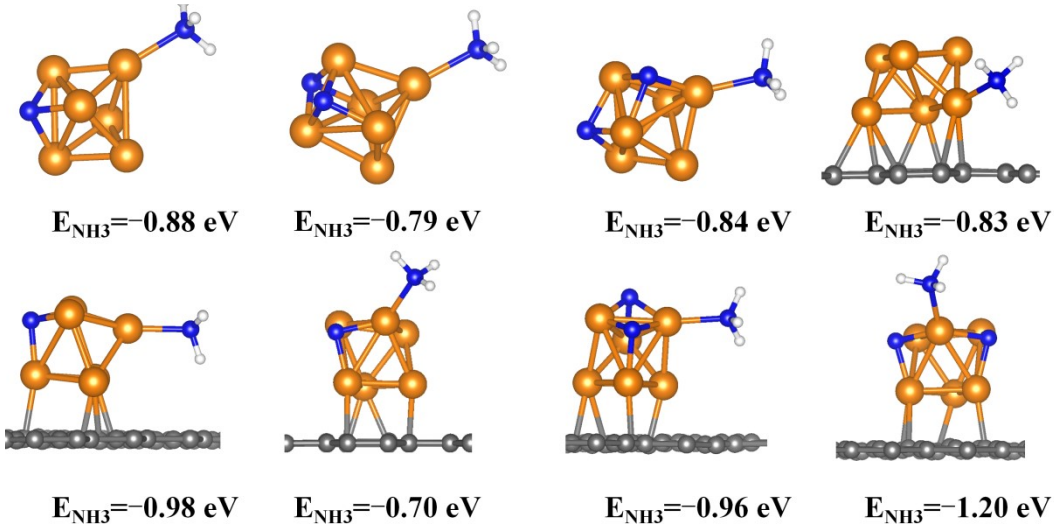

Fig. S3. Configurations and adsorption energies of NH_3 at additional adsorption sites. Color codes follow Fig. S1, with H atoms depicted in white.

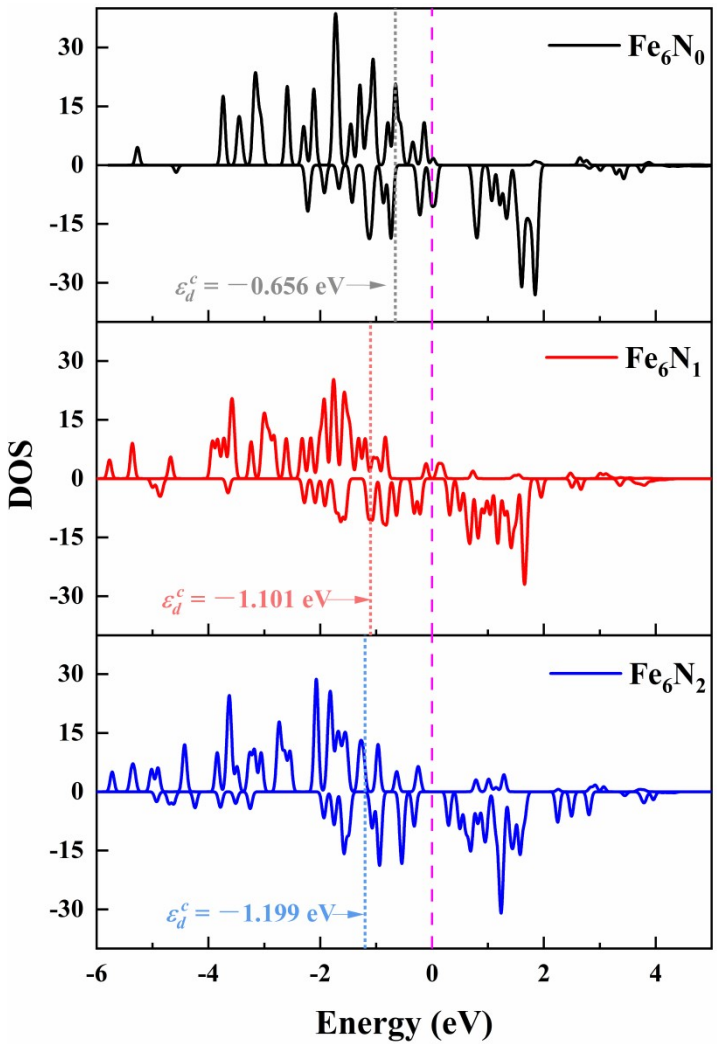

Fig. S4. d-projected density of states (PDOS) of Fe in (a) Fe_6N_0, (b) Fe_6N_1 and (c) Fe_6N_2 configurations. ε_d^c denotes the d-band center. The purple dashed line denotes the Fermi level set at 0 eV.

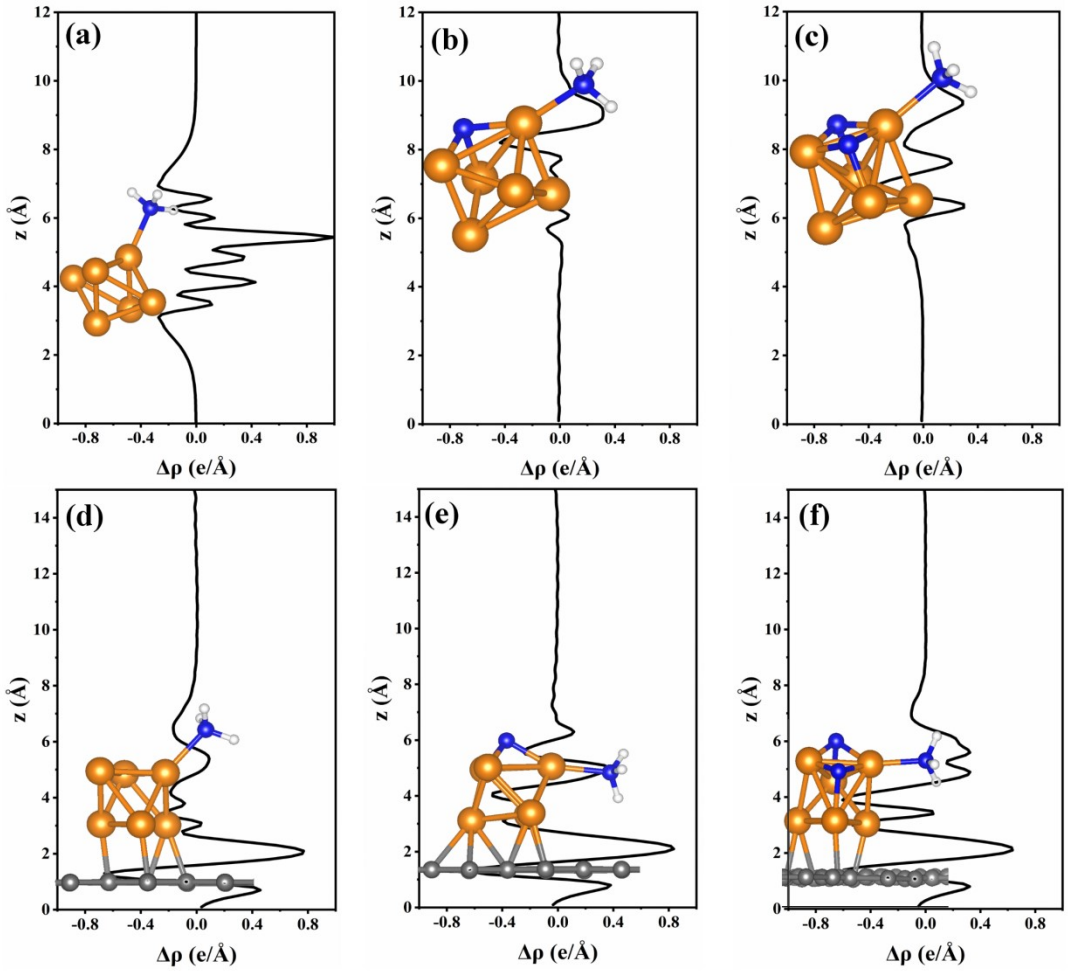

Fig. S5. Plane-averaged charge density difference plot along the z-axis for (a) Fe_6N_0, (b) Fe_6N_1, (c) Fe_6N_2, (d) Fe_6N_0@graphene, (e) Fe_6N_1@graphene and (f) Fe_6N_2@graphene. Color codes follow Fig. S1.

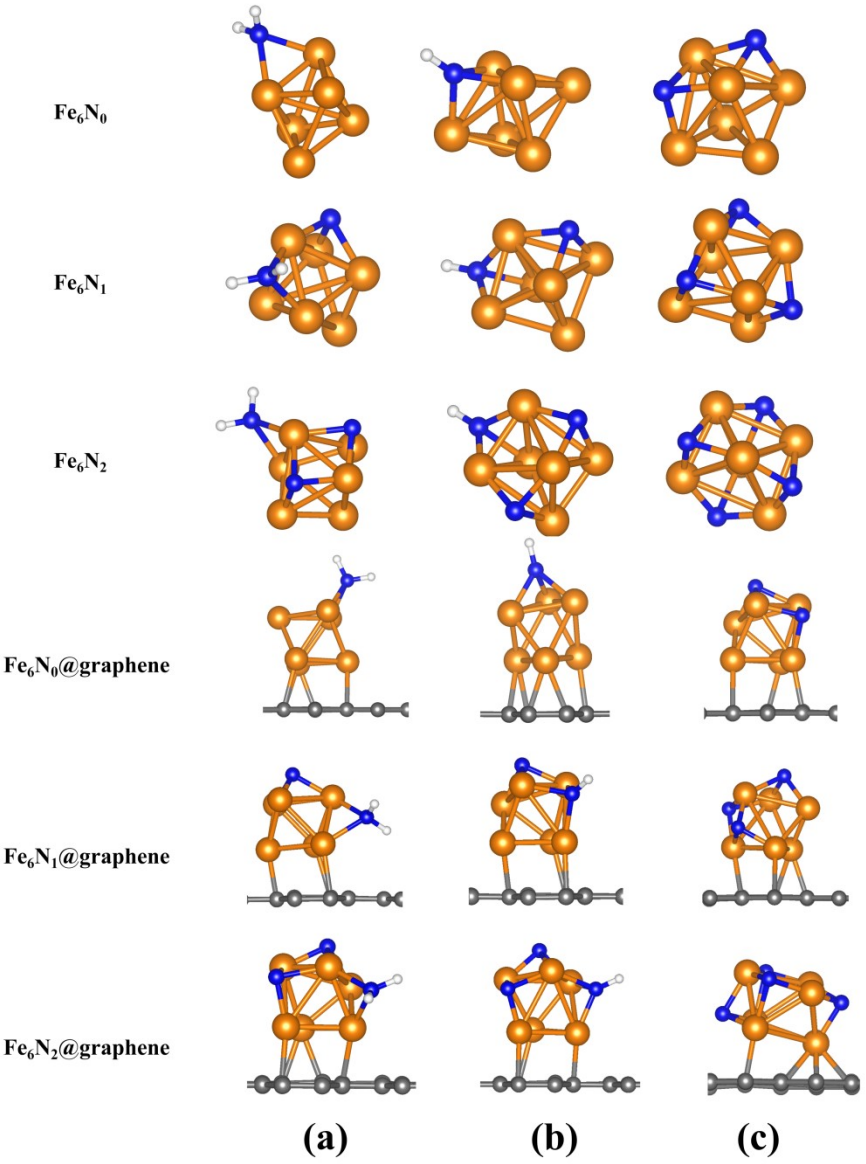

Fig. S6. Optimized adsorption configurations for (a) NH_2, (b) NH, and (c) 2N. Color codes follow Fig. S2.

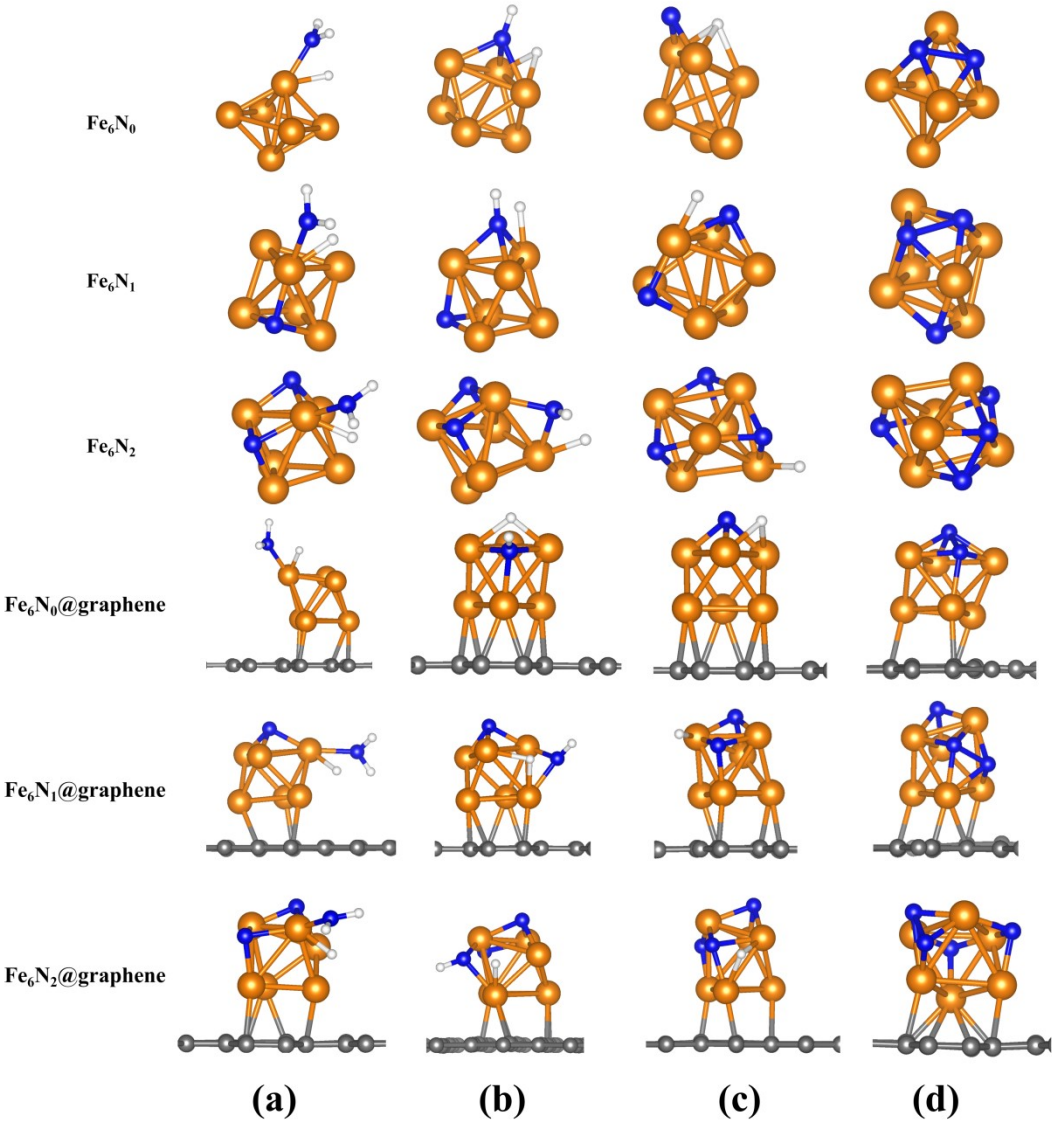

Fig. S7. Transition states (TS) for (a) NH_3* → NH_2* + H*, (b) NH_3* → NH* + H*, (c) NH* → N* + H* and (d) N* + N* → N_2*. Color codes follow Fig. S2.

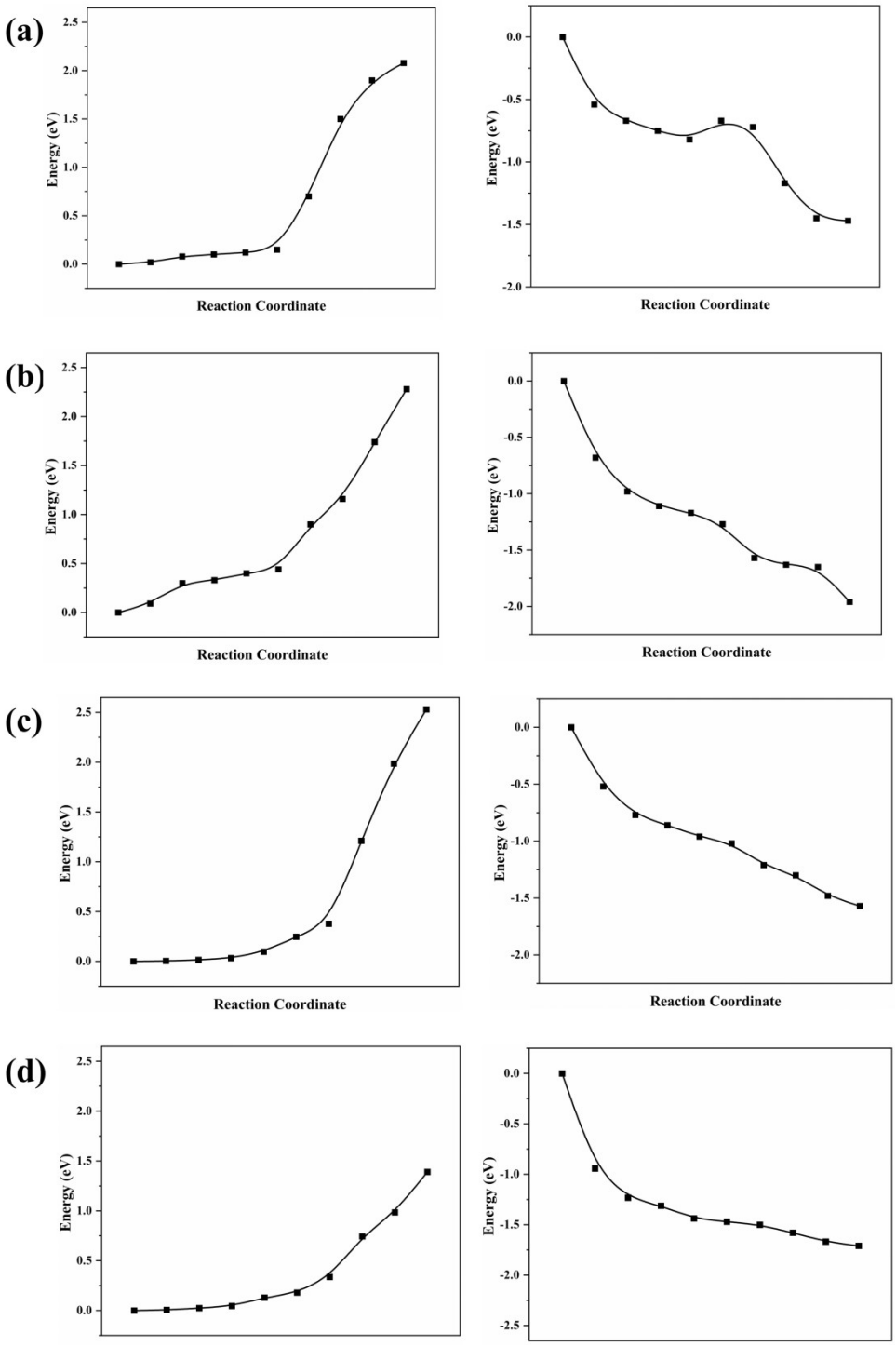

Fig. S8. Reaction pathways using Initial/transition states (IS/TS) as the start/end (left), and transition/final states TS/FS as the start/end (right), respectively. (a) Fe_6N_0, (b) Fe_6N_2, (c) Fe_6N_0@graphene and (d) Fe_6N_2@graphene.

Table S1. Calculated energies and magnetic moments for free-standing and graphene-supported Fe_6N_x (x=0~2) clusters under the default (1 μB/atom) and the high-spin (3 μB/atom) configurations.

Structure /Initial magnetic moments(μB/atom)	**Energy(eV)**	**Convergent magnetic moments(μB)**
Fe_6N_0/1	−36.352	20.000
Fe_6N_0/3	−36.352	20.000
Fe_6N_1/1	−44.787	17.000
Fe_6N_1/3	−44.787	17.000
Fe_6N_2/1	−54.066	18.000
Fe_6N_2/3	−54.066	18.000
Fe_6N_0@graphene/1	−627.785	18.019
Fe_6N_0@graphene/3	−627.785	18.019
Fe_6N_1@graphene/1	−637.334	15.009
Fe_6N_1@graphene/3	−637.334	15.008
Fe_6N_2@graphene/1	−646.221	14.000
Fe_6N_2@graphene/3	−646.221	14.000

Table S2. Activation energy barriers (E_b, eV) and reaction energies (E_r, eV) for NH_3 decomposition on free-standing and graphene-supported Fe_6 clusters with varying numbers of pre-adsorbed N atoms, * denotes an adsorbed species.

Reactions	**Fe_6N_0/Fe_6N_0@graphene**		**Fe_6N_1/Fe_6N_1@graphene**		**Fe_6N_2/Fe_6N_2@graphene**	
	E_b	E_r	E_b	E_r	E_b	E_r
$NH_3^* + * \rightarrow NH_2^* + H^*$	0.80/0.84	-0.77/-1.15	0.65/0.79	-0.75/-0.35	0.88/1.16	-0.65/-0.40
$NH_2^* + * \rightarrow NH^* + H^*$	1.40/0.88	-0.22/-1.05	1.22/1.28	-0.45/-0.12	1.54/1.43	-0.11/0.40
$NH^* + * \rightarrow N^* + H^*$	1.12/0.90	-0.10/-0.50	1.83/1.24	0.16/0.18	1.37/1.23	-0.40/-0.01
$N^* + N^* \rightarrow N_2^* + *$	2.08/2.53	0.61/0.96	2.17/1.97	0.99/-0.01	2.28/1.39	0.32/-0.32