Supplementary Information

The mechanism of Controllable dehydrogenation: CPMD study of the decomposition of $M(BH_4)_x(NH_3)_y$ (M=Li, Mg)

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The total and partial density of states (DOS) of ALB and AMgB are showed in Figure S1.The total DOS of ALB is comprised of 3 groups. The states of the lowest energy at about -20 to -10 eV mainly consists of the N 2*s* states and small part of H(N) 1*s* states. The second region, around -10 to -4 eV, is filled by N 2*p* and B 2*s* states hybridized with H 1s states. The top of the valence band consists of B 2*p* and H(B) 1*s* states. Such distribution of the electronic states suggests the covalence properties of the B-N, N-H and B-H bonds and electrostatic relationship between Li^+ and B.

For AMgB, it is similar with that of ALB where 3 groups are found in the total DOS map. The lowest energy part from -20 eV to -10 eV is contributed from N 2*s* states and small part of H(N) 1*s* states. The second energy region is filled by N 2*p* and B 2*s* states hybridized with H 1s states. The top of the valence band consists of B 2*p* and H(B) 1*s* states. But we can find an obvious overlap consists of the Mg 3*s* states and N 2*s* states around Fermi level. This covalence property proves Mg^{2+} polarizes part of N 2*s*orbitals.

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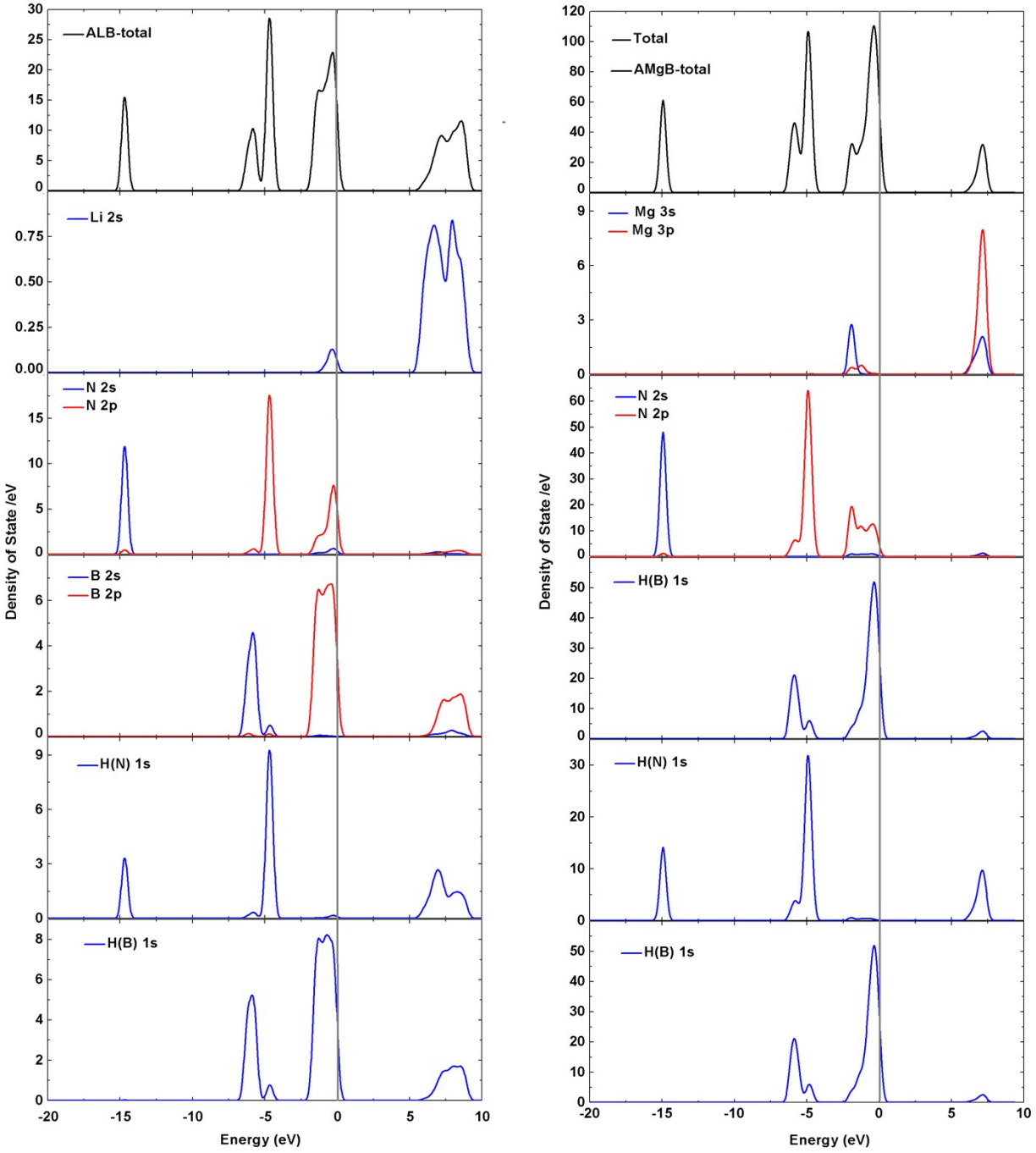


Figure S1. The total and partial density of states (DOS) of ALB (Left) and AMgB (Right).

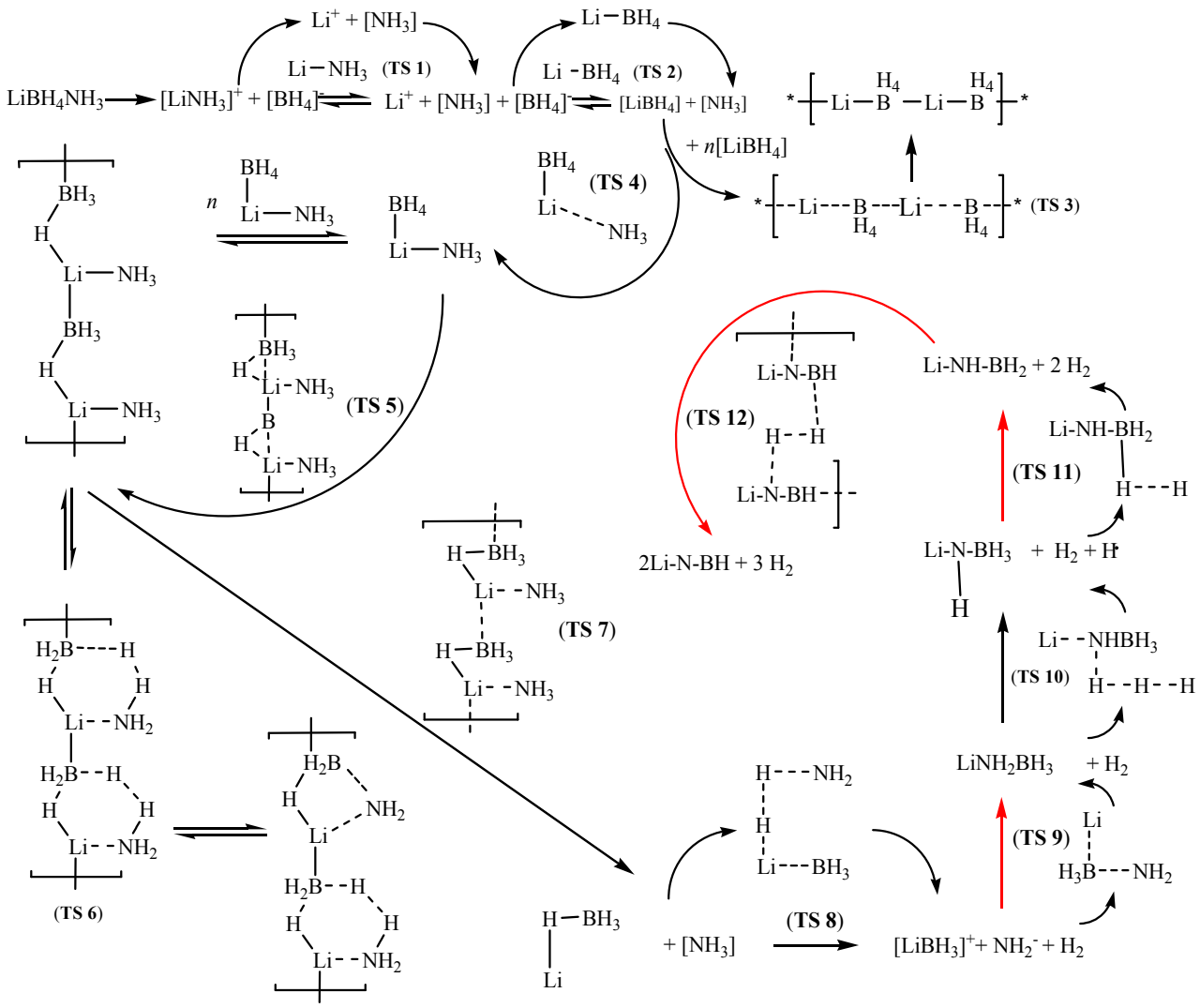


Figure S2. Theoverall decomposition scheme of ALB. (Red arrows highlight the dehydrogenation at high temperature theoretically)

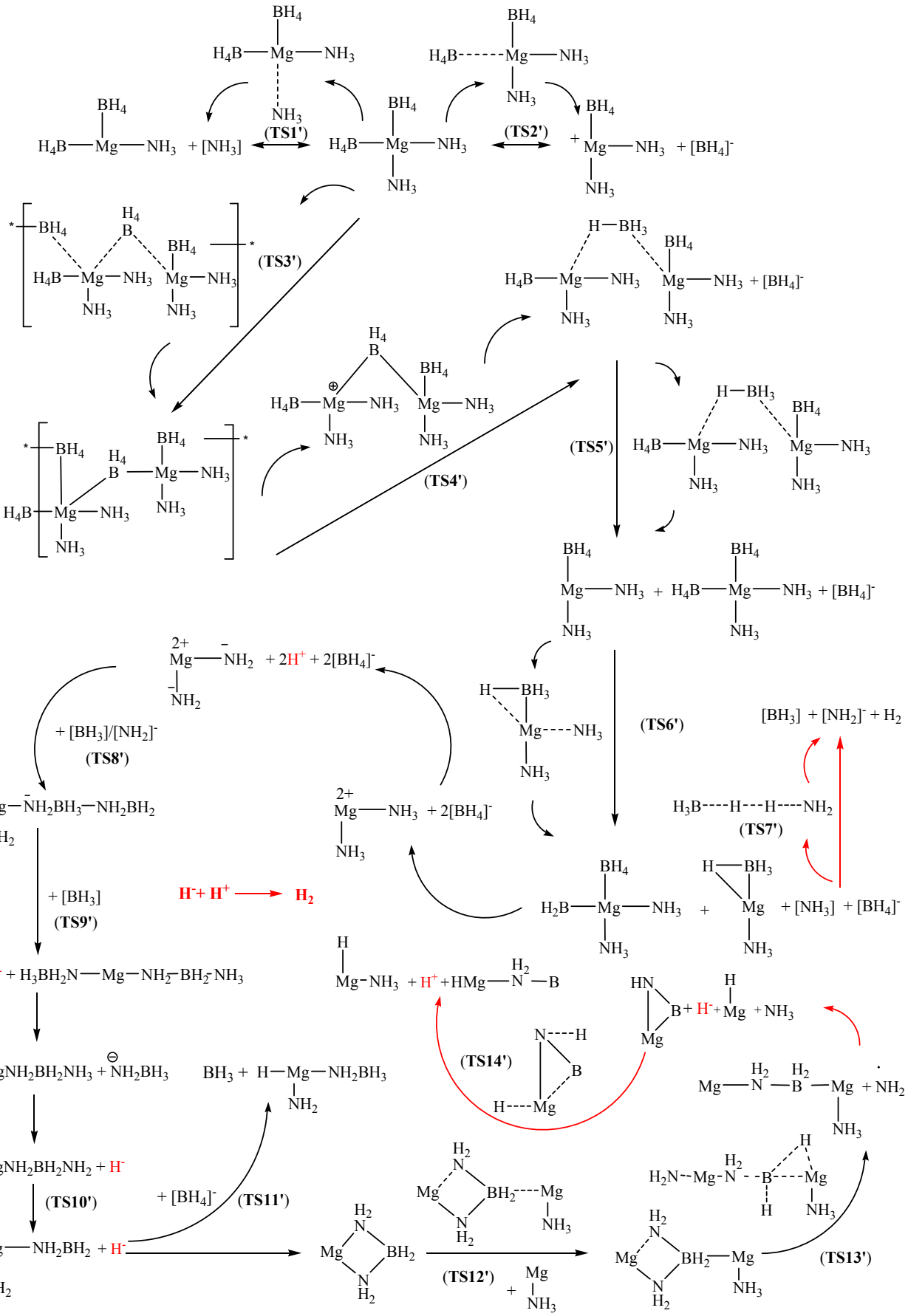


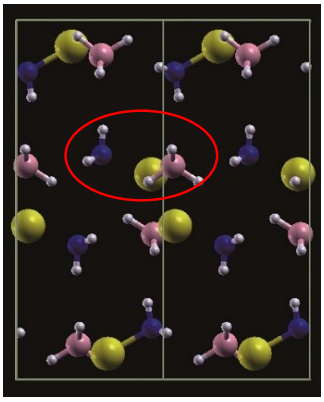
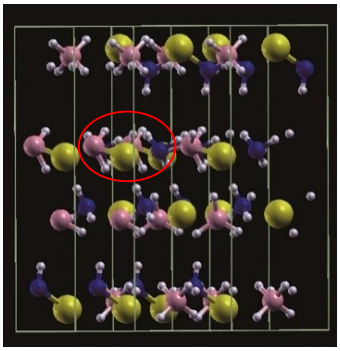
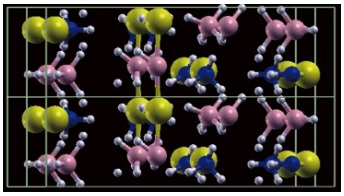
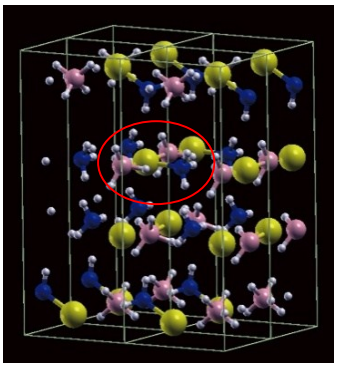
Figure S3. Theoverall decomposition scheme ofAMgB. (Red arrows highlight the steps of dehydrogenation, which is caused by the combination of dissociative hydrogen ions)

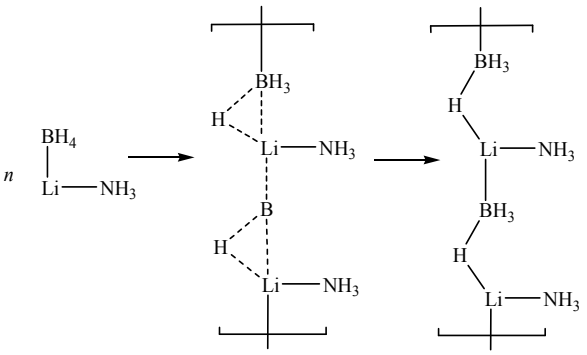
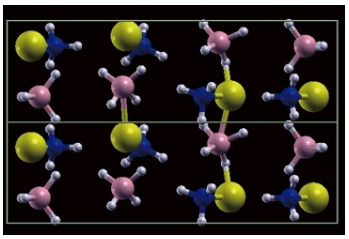
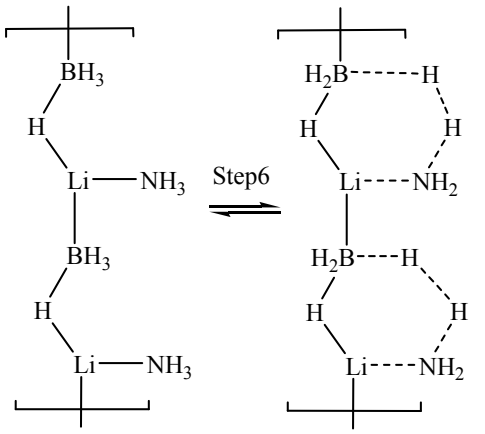
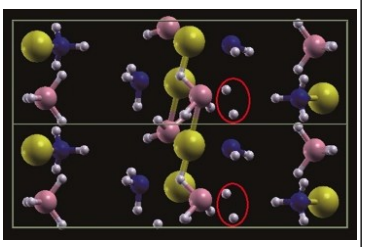
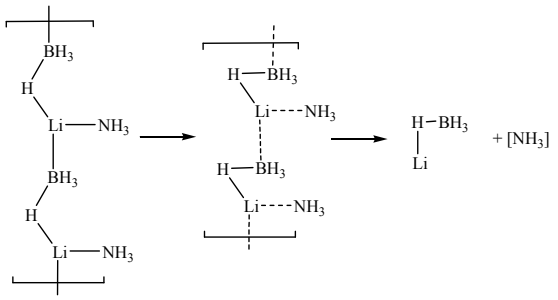
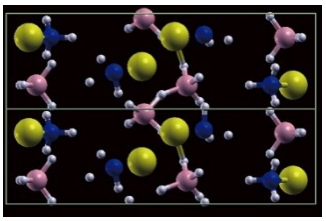
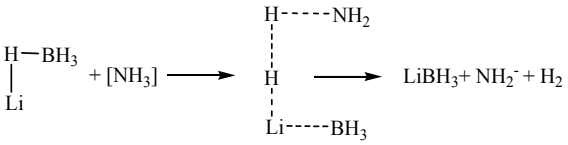
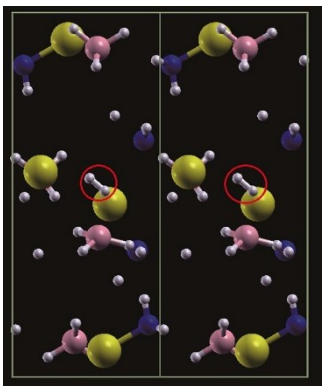
Table S1 The relationship between the temperature and the steps' setting

Temperature (K)	Steps (period)	
	ALB	AMgB
100 K	0-20000 (0-2 ps)	0-20000 (0-2 ps)
200 K	20001-40000 (2-4 ps)	20001-30000 (2-3 ps)
300 K	40001-60000 (4-6 ps)	30001-40000 (3-4 ps)
400 K	60001-80000 (6-8 ps)	40001-50000 (4-5 ps)
500 K	80001-100000 (8-10 ps)	50001-60000 (5-6 ps)
600 K	100001-130000 (10-13 ps)	60001-80000 (6-8 ps)
700 K	130001-150000 (13-15 ps)	
800 K	150001-180000 (15-18 ps)	
900 K	180001-210000 (18-21 ps)	

Table S2 The structures of intermediates and the first time they appear in the decomposition of ALB

(Yellow: Li, pink: B, blue: N, white: H)

Step	Intermediates	Time (ps)	Structures
TS1	$Li—NH_3 \longrightarrow Li\text{----}NH_3 \longrightarrow Li^+ + [NH_3]$	0.0245	
TS2	$Li^+ + [BH_4] \longrightarrow Li\text{----}BH_4 \longrightarrow Li—BH_4$	0.2815	
TS3	$n[LiBH_4] \longrightarrow {}^*\!\left[\text{---}Li\text{----}B(H_4)\text{----}Li\text{-----}B(H_4)\text{---}\right]^*$ $\longrightarrow {}^*\!\left[Li—B(H_4)—Li—B(H_4)\right]^*$	0.5555	
TS4	$[LiBH_4] + [NH_3] \longrightarrow \begin{matrix} BH_4 \\ \vert \\ Li\text{----}NH_3 \end{matrix} \longrightarrow \begin{matrix} BH_4 \\ \vert \\ Li—NH_3 \end{matrix}$	0.8035	

TS5		0.8295	
TS6		14.728	
TS7		16.458	
TS8		16.773	

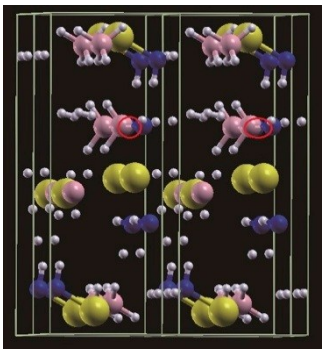
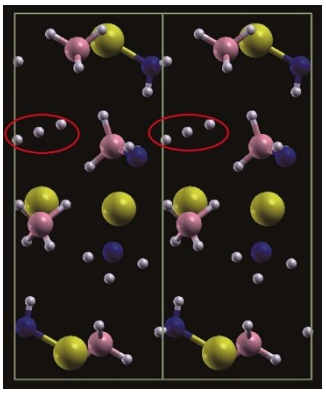
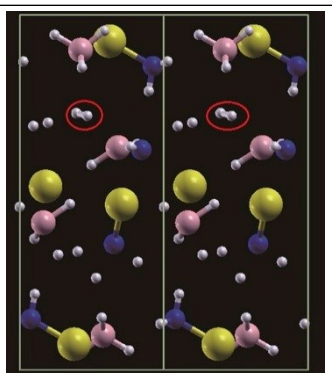
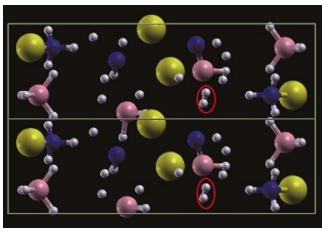
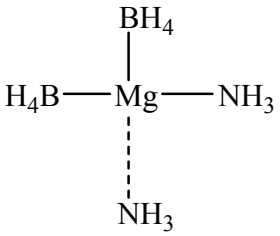
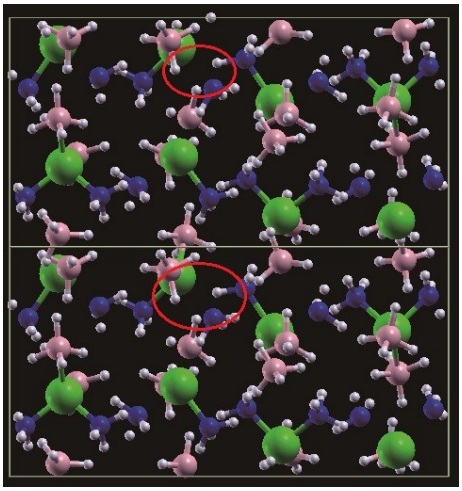
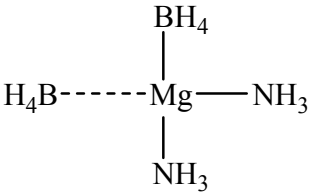
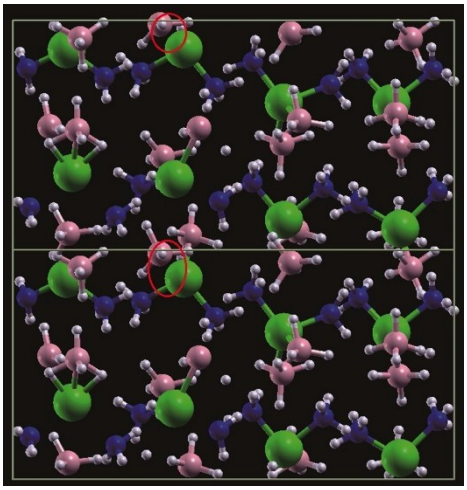
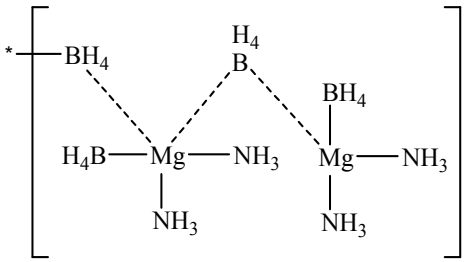
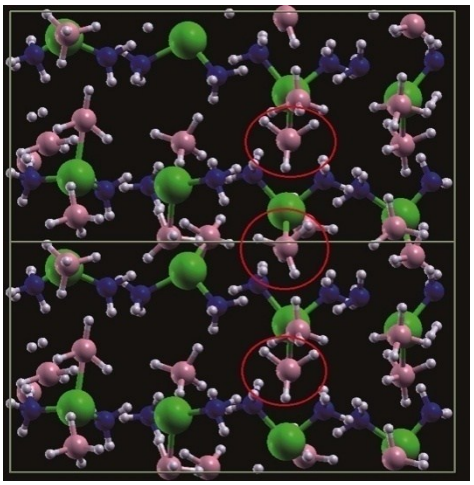
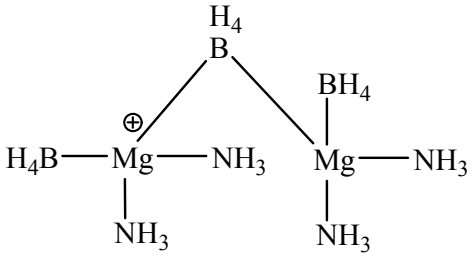
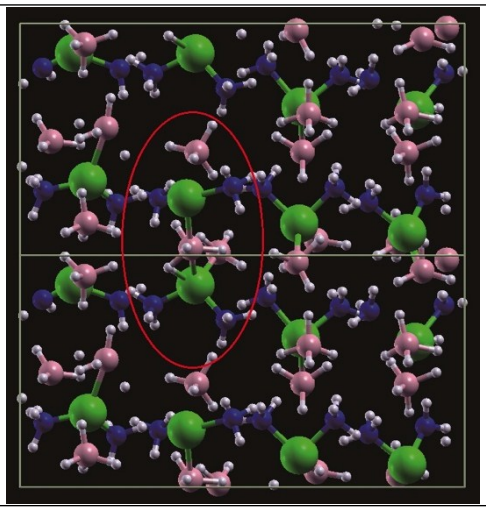
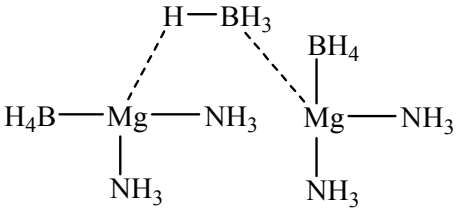
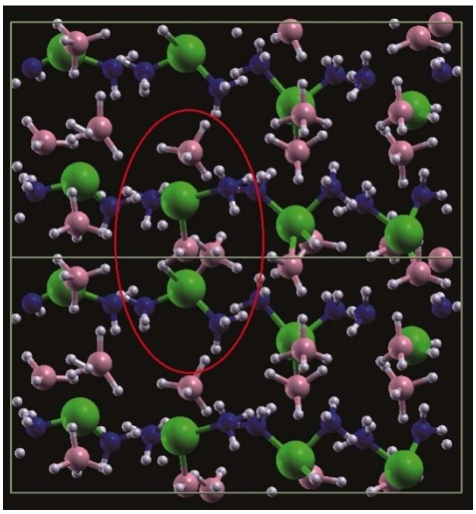
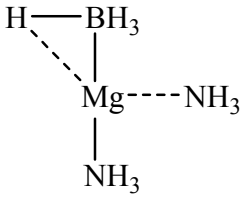
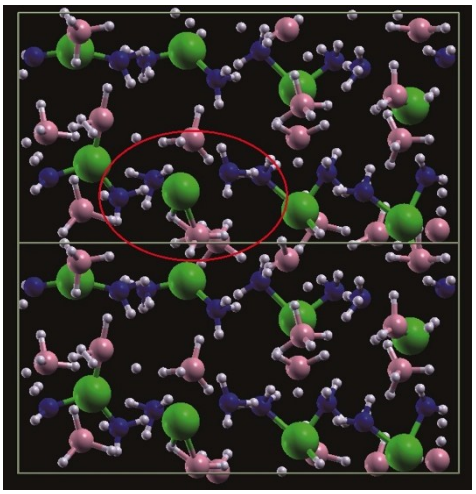
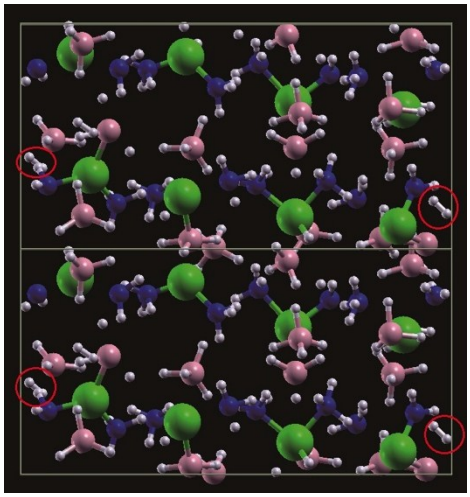
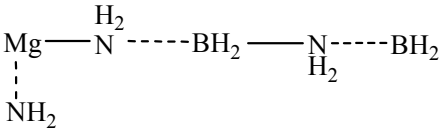
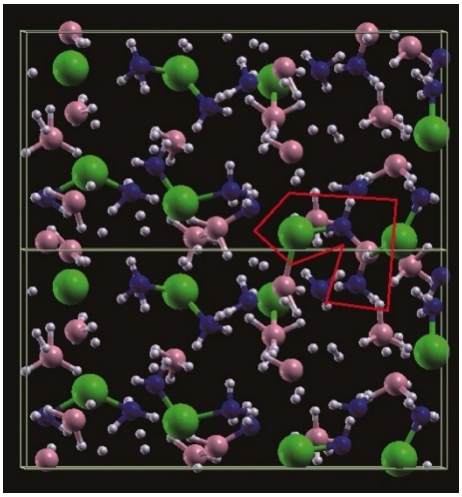
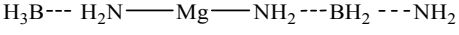
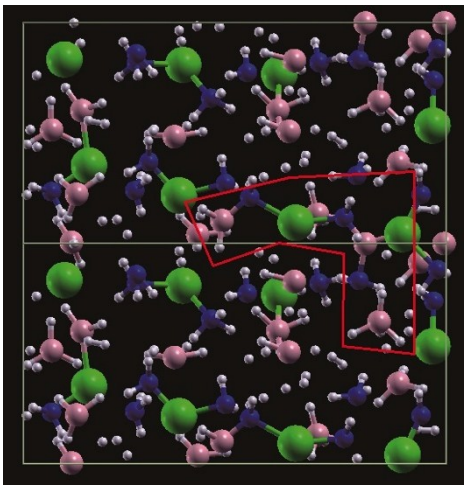
TS9	$LiBH_3 + NH_2^-$ → Li / H_3B----NH_2 → $LiNH_2BH_3$	17.309	
TS10	$LiNH_2BH_3 + H_2$ → Li----$NHBH_3$ / H----H----H → Li-N-BH_3 + H_2 + H / H	18.113	
TS11	H + Li-NH-BH_2 / H → Li-NH-BH_2 / H----H → Li-NH-BH_2 + H_2	18.280	
TS12	$2Li\text{-}NH\text{-}BH_2$ → Li-N-BH / H---H / Li-N-BH- → $2Li\text{-}N\text{-}BH + H_2$	19.882	

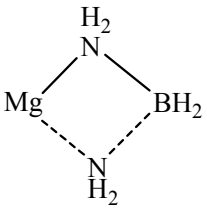
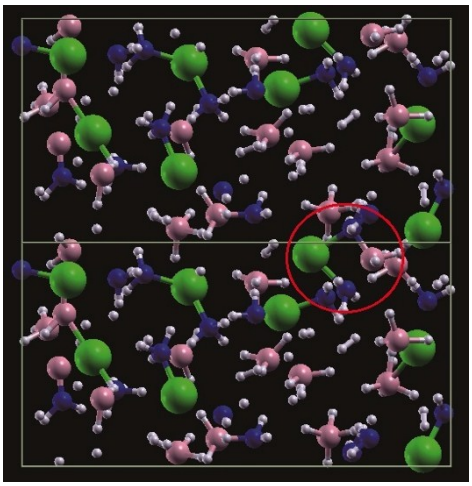
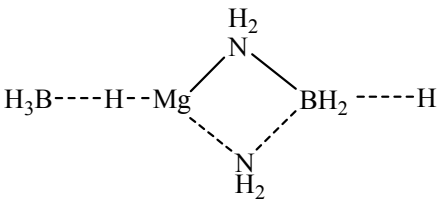
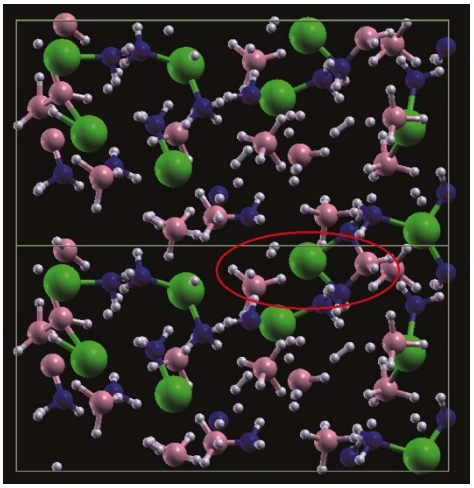
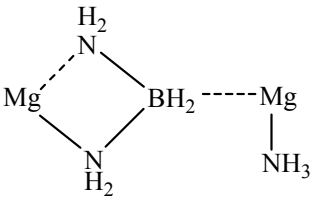
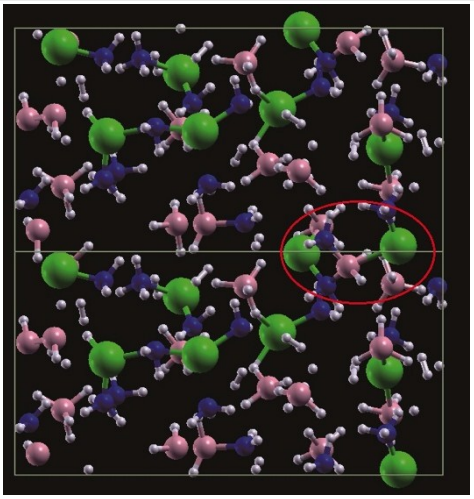
Table S3 The structures of intermediates and the first time they appear in the decomposition of AMgB

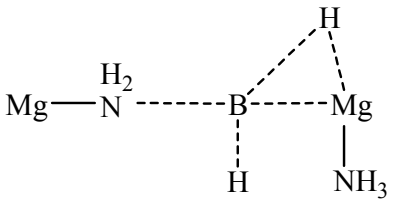
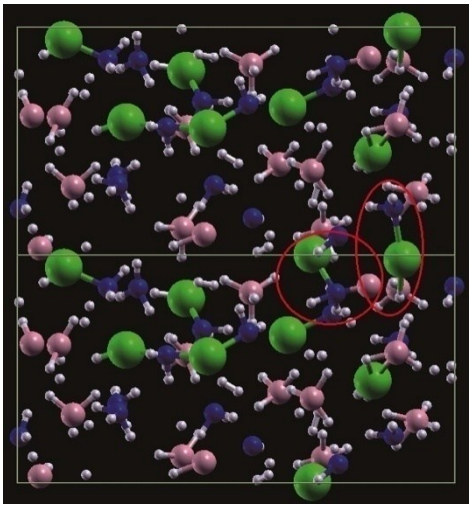
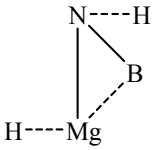
(Green: Mg, pink: B, blue: N, white: H)

Step	Intermediates	Time (ps)	Structures
TS1		3.331	
TS2		3.524	
TS3		3.6595	

TS4		3.7405	
TS5		3.75	
TS6		3.7655	

TS7	H_3B----H---H----NH_2	3.7995	
TS8		4.00	
TS9		4.0275	

TS10		4.15	
TS11		4.6625	
TS12		4.915	

TS13		5.1075	
TS14		6.1325