A novel aided-cation strategy to advance the dehydrogenation of calcium borohydride monoammoniate

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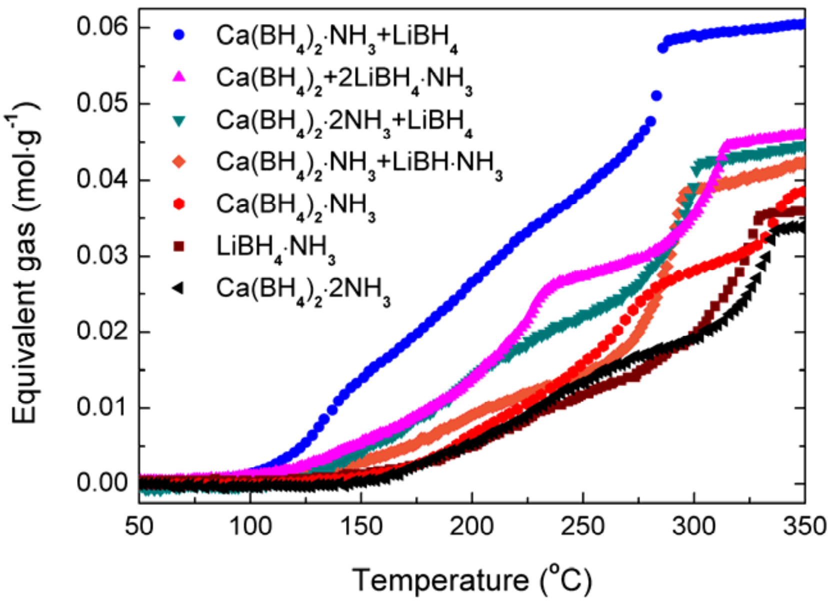

Figure S1. TPD results for ammonia complexes of $LiBH_4$ and $Ca(BH_4)_2$, and their composites of $Ca(BH_4)_2{\cdot}NH_3/LiBH_4$, $Ca(BH_4)_2/2LiBH_4{\cdot}NH_3$, $Ca(BH_4)_2{\cdot}2NH_3/LiBH_4$, $Ca(BH_4)_2{\cdot}NH_3/LiBH_4{\cdot}NH_3$ with a heating rate of 5 °C min^{-1} in argon.

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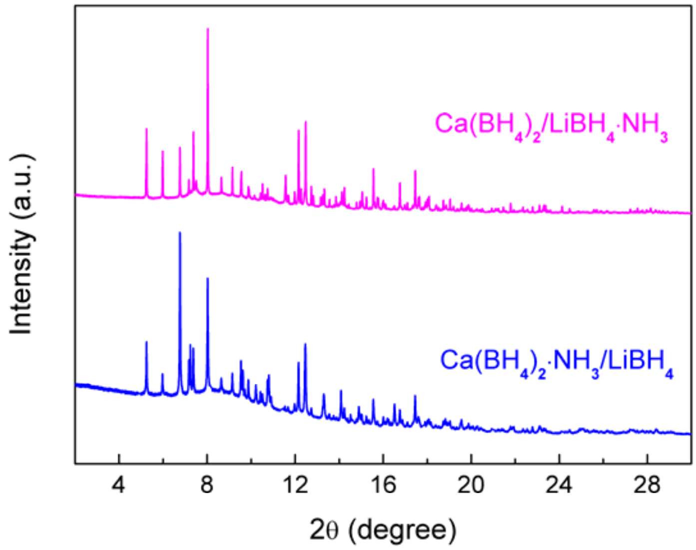

Figure S2. High-resolution X-ray diffraction patterns for $Ca(BH_4)_2 \cdot NH_3/LiBH_4$ and $Ca(BH_4)_2/LiBH_4 \cdot NH_3$ composites.

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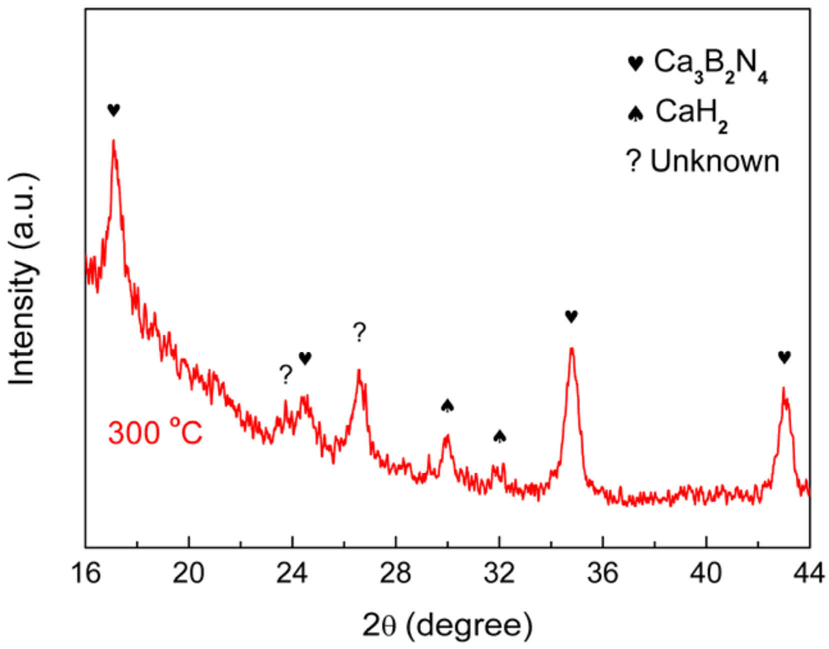

Figure S3. XRD pattern for the $Ca(BH_4)_2{\cdot}NH_3/LiBH_4$ composite heated to 300 ^oC in argon.

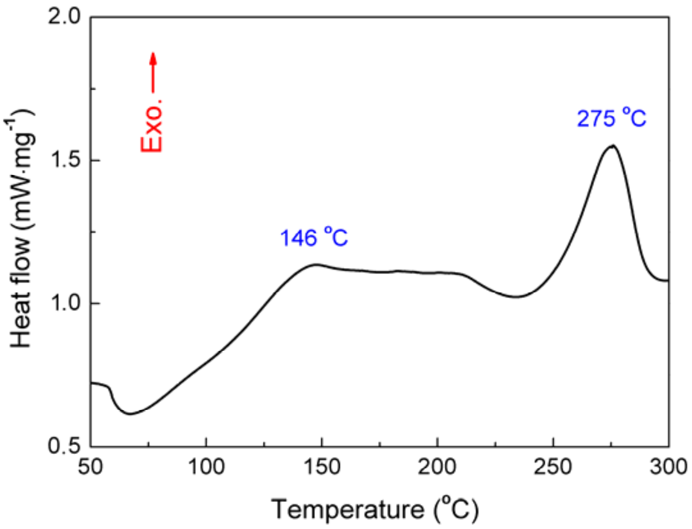

Figure S4. DSC result for the $Ca(BH_4)_2 \cdot NH_3/LiBH_4$ composite with a heating rate of 5 °C min^{-1}.

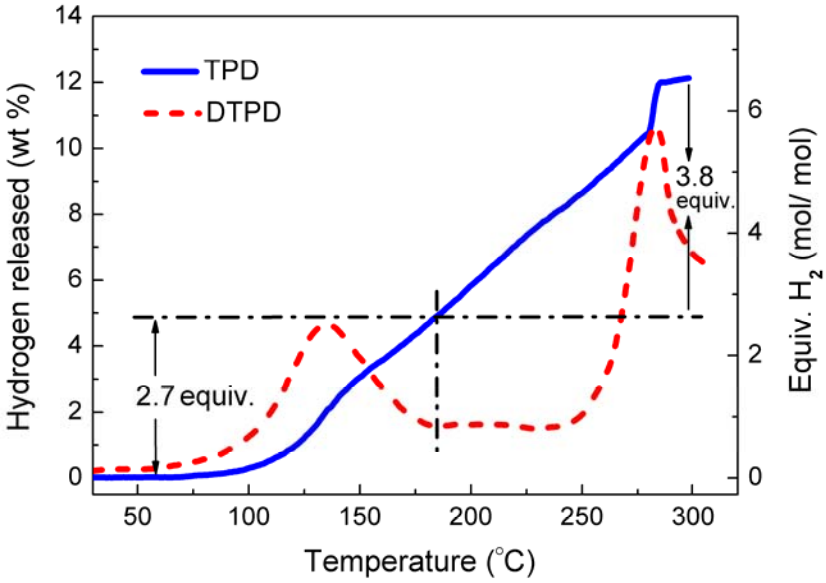

Figure S5. TPD result and its differential curve (DTPD) for the $Ca(BH_4)_2{\cdot}NH_3/LiBH_4$ composite with a heating rate of 5 °C min^{-1} in argon, which gives a total hydrogen release of 6.5 equiv..

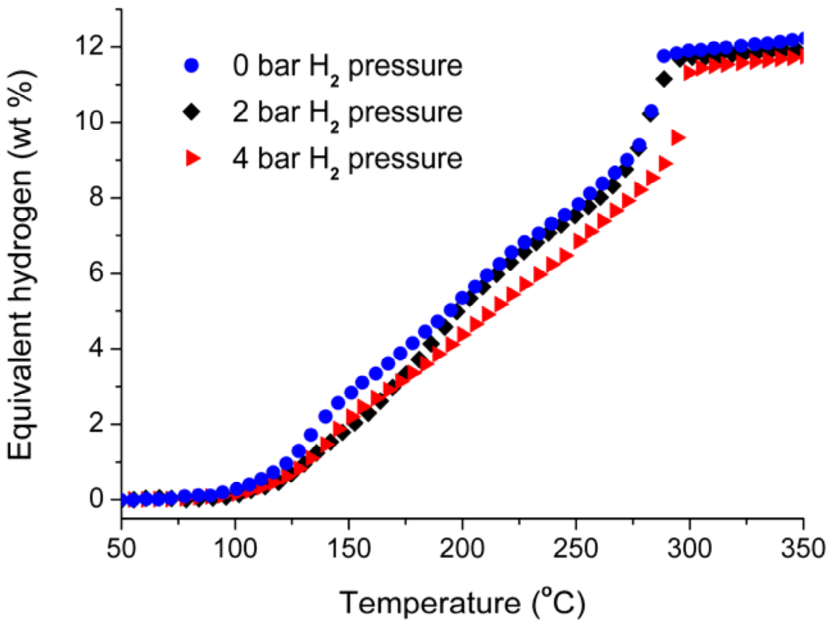

Figure S6. TPD results for the $Ca(BH_4)_2 \cdot NH_3/LiBH_4$ composite with a heating rate of 5 °C min^{-1}at 0, 2 and 4 bar hydrogen pressure, respectively.

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Table S1 Experimental and calculated structural parameters of $Ca(BH_4)_2{\cdot}NH_3$ (Space group $Pna2_1$, experimental unit cell a = 8.199959(50) Å, b = 11.846032(70) Å, c = 5.836681(30) Å, V = 566.9441 Å^3, calculation unit cell a = 8.4270 Å, b = 12.0103 Å, c = 5.6922 Å, V = 576.1121 Å^3).

Atom	Wyckoff Site	x		y		z	
		Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
Ca	4a	0.17213	0.16174	0.40028	0.40985	0.51900	0.51818
B1	4a	0.03703	0.05484	0.78745	0.78088	0.03079	0.00001
H1a	4a	0.07520	0.09283	0.84912	0.86569	0.19280	0.07081
H1b	4a	0.10327	0.08189	0.81332	0.78079	-0.15380	-0.18982
H1c	4a	0.07598	0.12440	0.69195	0.71376	0.08254	0.09684
H1d	4a	-0.10672	-0.08028	0.79666	0.76793	0.00258	0.02747
B2	4a	0.12699	0.14195	0.41511	0.43146	0.02552	0.03176
H2a	4a	0.22332	0.26062	0.47334	0.45512	0.12952	0.11765
H2b	4a	0.04894	0.08251	0.47521	0.51184	-0.10653	-0.03064
H2c	4a	0.19840	0.17126	0.34443	0.37061	-0.08696	-0.11155
H2d	4a	0.03628	0.05882	0.36597	0.38851	0.15738	0.15921
N3	4a	0.69750	0.69010	0.41656	0.40952	0.04765	0.05626
H3a	4a	0.78254	0.76966	0.35648	0.34884	0.01619	0.02300
H3b	4a	0.64893	0.68409	0.39646	0.42181	0.20886	0.22382
H3c	4a	0.60920	0.58134	0.40208	0.38731	-0.07454	-0.00198

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Table S2 Summary of H_2 evolution from ammonia complexes of $LiBH_4$ and $Ca(BH_4)_2$, and their composites of $Ca(BH_4)_2 \cdot NH_3/LiBH_4$, $Ca(BH_4)_2/LiBH_4 \cdot NH_3$, $Ca(BH_4)_2/2LiBH_4 \cdot NH_3$, $Ca(BH_4)_2 \cdot 2NH_3/LiBH_4$, $Ca(BH_4)_2 \cdot NH_3/LiBH_4 \cdot NH_3$.

Samples [a]	H_2 [b] capacity wt. %	H_2 [b] mol %	Mole H_2 [b] / Mole samples
$Ca(BH_4)_2 \cdot NH_3+LiBH_4$	12.1	99.8	6.6
$Ca(BH_4)_2+LiBH_4 \cdot NH_3$	11.1	97.0	6.0
$Ca(BH_4)_2+2LiBH_4 \cdot NH_3$	8.0	90.1	5.9
$Ca(BH_4)_2 \cdot 2NH_3+LiBH_4$	7.7	86.5	4.9
$Ca(BH_4)_2 \cdot NH_3+LiBH_4 \cdot NH_3$	7.0	82.0	4.4
$Ca(BH_4)_2 \cdot NH_3$	4.7	61.1	2.0
$LiBH_4 \cdot NH_3$	3.6	49.4	0.7
$Ca(BH_4)_2 \cdot 2NH_3$	3.0	44.1	1.6

[a] The samples were heated in 1 bar argon from 50 to 350 °C with a heating rate of 5 $°C \cdot min^{-1}$ for calculations of H_2 evolution.

[b] H_2 content in the released gas.