Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Hydrogenation Properties of Lithium and Sodium Hydride – *closo*-borate, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$, Composites

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Table S1. Observed PXD reflections for the unidentified compound **1** (λ = 1.54056 Å).

1	2θ / °	14.16	14.58	15.18	15.51	16.52	16.84	19.24	19.36
	d / Å	6.25	6.07	5.83	5.71	5.36	5.26	4.61	4.58
	Int / %	62	49	64	34	64	100	27	27

Table S2. Observed PXD reflections for the unidentified compound **2** (λ = 1.54056 Å).

2	2θ / °	5.37	6.15	6.57	13.93	15.34	15.93
	d / Å	16.44	14.37	13.45	6.35	5.77	5.56
	Int / %	100	60	49	25	46	31

Table S3. Observed reflections of the unidentified compounds **3** and **4** (λ = 1.54056 Å).

3	2θ / °	12.28	13.63	14.11	14.41	18.39	18.99	22.49	26.42
	d / Å	7.20	6.49	6.27	6.14	4.82	4.67	3.95	3.37
	Int / %	26	19	28	62	47	100	14	26
4	2θ / °	11.98	13.98	14.63	18.47	21.93	28.21	30.69	
	d / Å	7.38	6.33	6.05	4.80	4.05	3.16	2.91	
	Int / %	45	67	37	100	31	33	43	

Table S4. ^{11}B NMR data for relevant *closo*-, *nido*-, *arachno*- and *hypho*-borates

BORATES	TYPES OF B	δ(^{11}B)	MULTIPLICITY	J_{BH}	B ATOM CHARGE	REFERENCE
***CLOSO*-BORATES**		-			-	.
$[B_6H_6]^{2-}$	1	-13.6	Doublet	122	-0.11	1
$[B_7H_7]^{2-}$	2 (5:2 ratio)	-0.2 -22.6	Doublet Doublet	119	-0.11	2
$[B_8H_8]^{2-}$	3 (1:2:1 ratio)	9.5 -3.6 -22.2	Doublet Doublet Doublet	n/a	n/a	3
$[B_9H_9]^{2-}$	2 (1:2 ratio)	-2.9 -20.5	Doublet Doublet	135 120	-0.10 -0.01	4
$[B_{10}H_{10}]^{2-}$	2 (1:4 ratio)	0.89 -30.85	Doublet Doublet	141 124	-0.08 -0.03	5
$[B_{10}H_{11}]^{-}$	3 (1:5:4 ratio)	26.1 -21.5 -24.8	Doublet Doublet Doublet	? ? ?	n/a	6
$[B_{11}H_{11}]^{2-}$	1	-16.95	Doublet	130	n/a	7
$[B_{12}H_{12}]^{2-}$	1	-15.63	Doublet	124	-0.02	8
***NIDO*-BORATES**						
$[B_5H_8]^{-}$	2 (4:1 ratio)	-13.6 -53.1	n/a	164 175	n/a	9
$[B_9H_{12}]^{-}$	6 (3:2:1:2:1)	-10.47 -14.74 -16.24 -35.00 -52.74	Doublet Doublet Doublet Doublet Doublet	137 175 148 153	n/a	10
$[B_{10}H_{13}]^{-}$	4 (2:1:5:2)	6.8 2.5 -5.0 -35.20	Doublet Doublet Doublet Doublet	140 135 135 150	n/a	11
$[B_{10}H_{12}]^{-}$	5 (1:2:5:1:1)	-1.44 -6.65 -25.9 -36.20 -40.60	Doublet Doublet Multiplet Doublet Doublet	162 132 134 132	n/a	12

Table S4 (continued). ^{11}B NMR data for relevant *closo*-, *nido*-, *arachno*- and *hypho*-borates

BORATES	TYPES OF B	δ(^{11}B)	MULTIPLICITY	J_{BH}	B ATOM CHARGE	REFERENCE
***ARACHNO*-BORATES**						
$[B_9H_{14}]^-$	3 (1:1:1)	-6.8 -19.2 -22.4	n/a	137 136 138	n/a	13
$[B_9H_{13}]^{2-}$	3 (1:1:1)	-4.55 -24.90 -29.00	Doublet Doublet Doublet	122 125 104	n/a	14
$[B_{10}H_{14}]^{2-}$	4 (1:2:1:1)	-8.09 -23.10 -36.62 -42.26	Doublet Doublet Triplet Doublet	124 130 103 129	n/a	15, 16
***HYPHO*-BORATES**						
$[B_5H_{12}]^-$	2 (4:1)	-15.9 -57.6	n/a	n/a	n/a	17

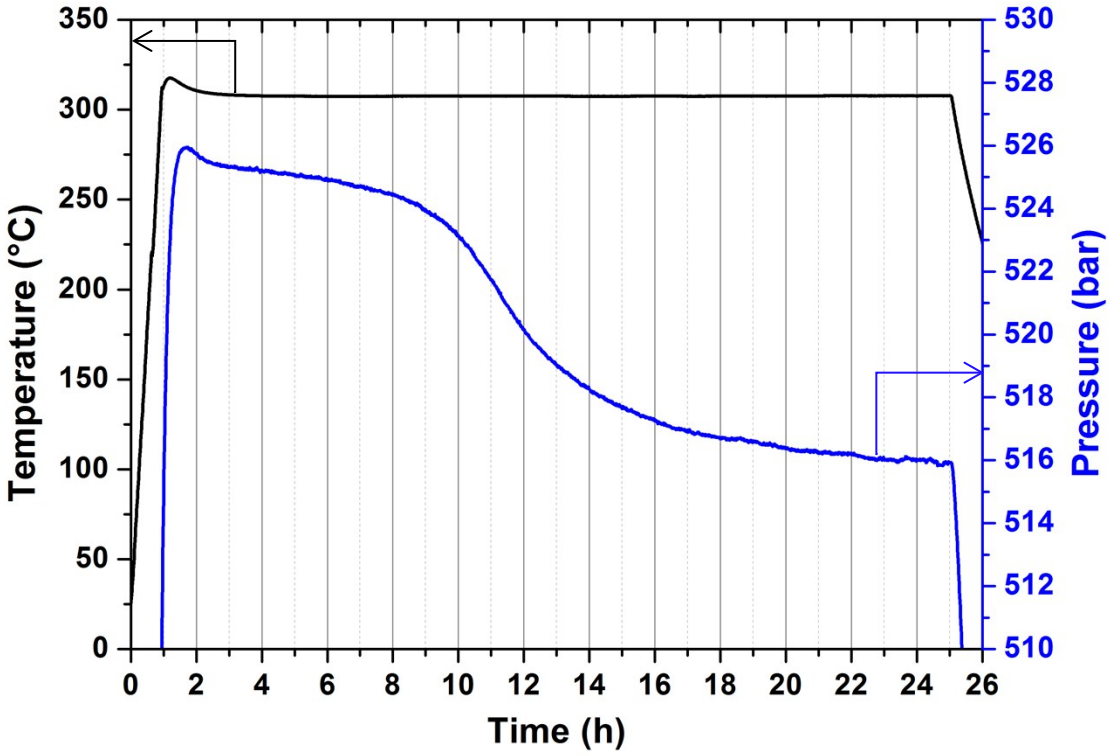

Figure S1. High-pressure hydrogen absorption experiment of $Li_2B_{10}H_{10}$–8 LiH (Li_2B_{10}-A) carried out by heating from *RT* to 307 °C ($\Delta T/\Delta t$ = 5 °C/min) and isothermal for 24 hours (black line) under $p(H_2)$ = 526 bar (blue line).

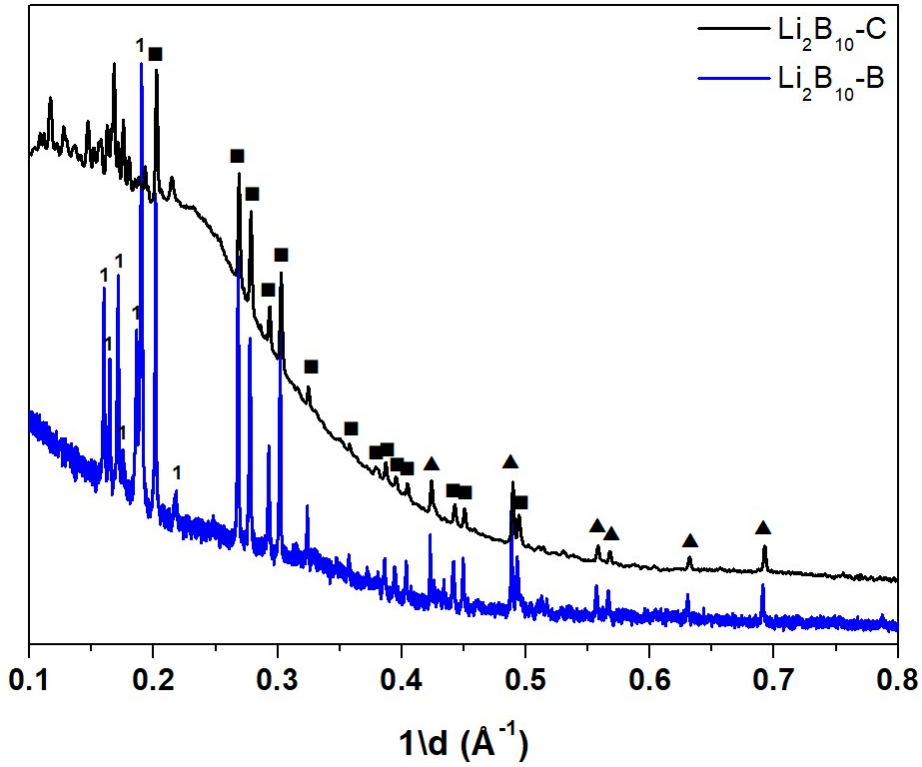

Figure S2. Powder X-ray diffraction patterns of Li_2B_{10}-B (bottom blue) and Li_2B_{10}-C (top black). Li_2B_{10}-B measured with λ = 1.5418 Å and Li_2B_{10}-C measured with λ = 0.20775 Å. Symbols: ■ *o*-$LiBH_4$, ● $Li_2B_{10}H_{10}$, ▲ LiH, and compound **1**.

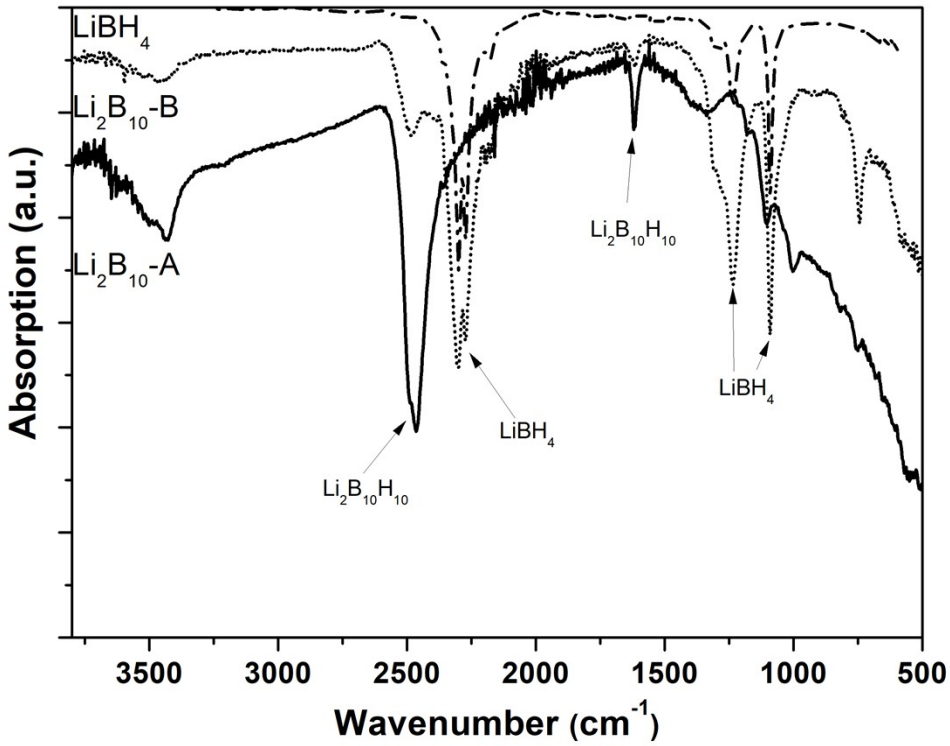

Figure S3. FT-IR spectra of Li_2B_{10}-A (solid black line), Li_2B_{10}-B (dotted grey line), and pure $LiBH_4$, (dashed line).

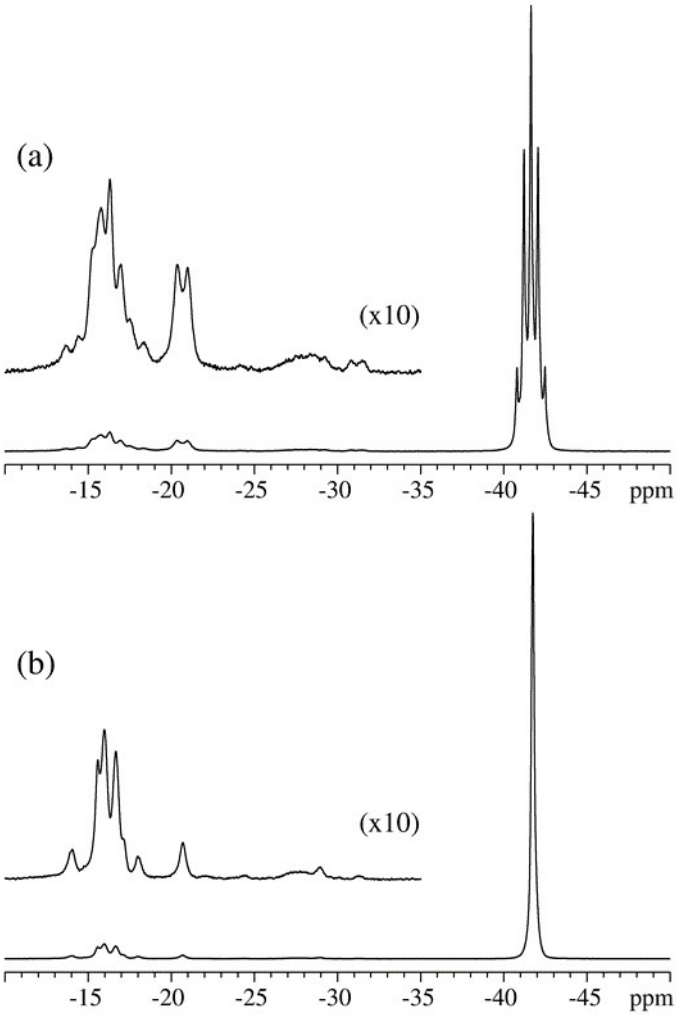

Figure S4. Solution ^{11}B NMR spectra (14.1 T) of Li_2B_{10}-B dissolved in THF obtained (a) without and (b) with ^{1}H decoupling.

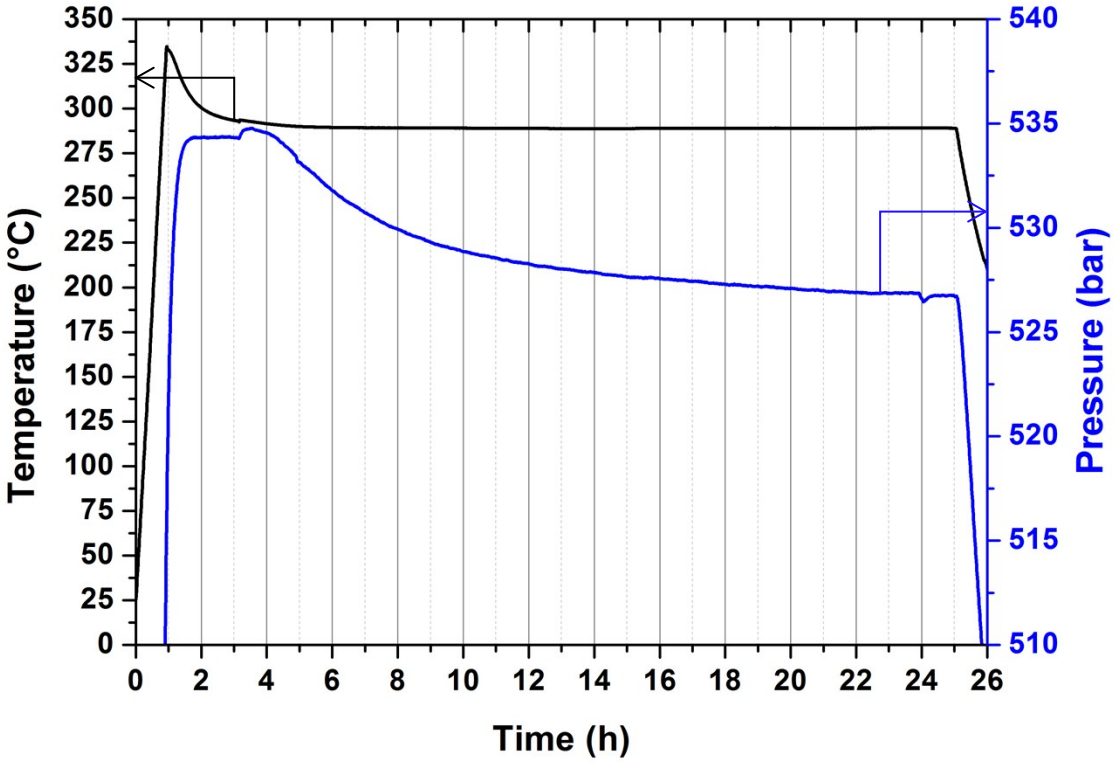

Figure S5. High-pressure hydrogen absorption experiment of $Na_2B_{10}H_{10}$–8 NaH (Na_2B_{10}-A) carried out by heating from *RT* to 300 °C ($\Delta T/\Delta t$ = 5 °C/min) and isothermal for 24 hours (black line) under $p(H_2)$ = 534 bar (blue line).

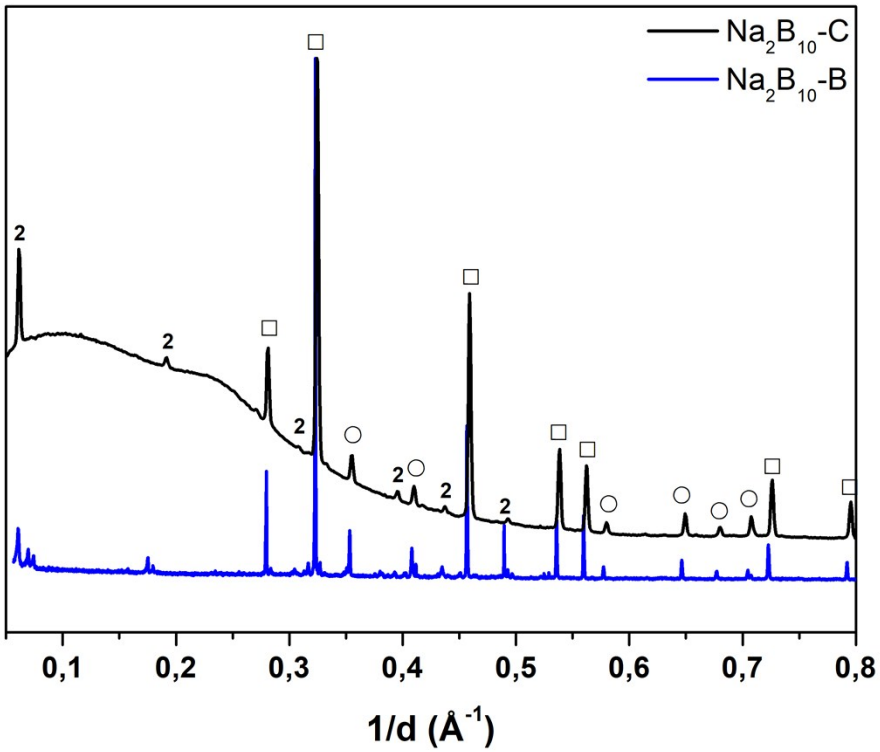

Figure S6. Powder X-ray diffraction patterns of Na_2B_{10}-B (blue) and Na_2B_{10}-C (black). Na_2B_{10}-B measured with $\lambda = 1.5418$ Å and Na_2B_{10}-C measured with $\lambda = 0.20775$ Å. Symbols: □ $NaBH_4$, ○ NaH, △ LT-$Na_2B_{10}H_{10}$ and compound **2**.

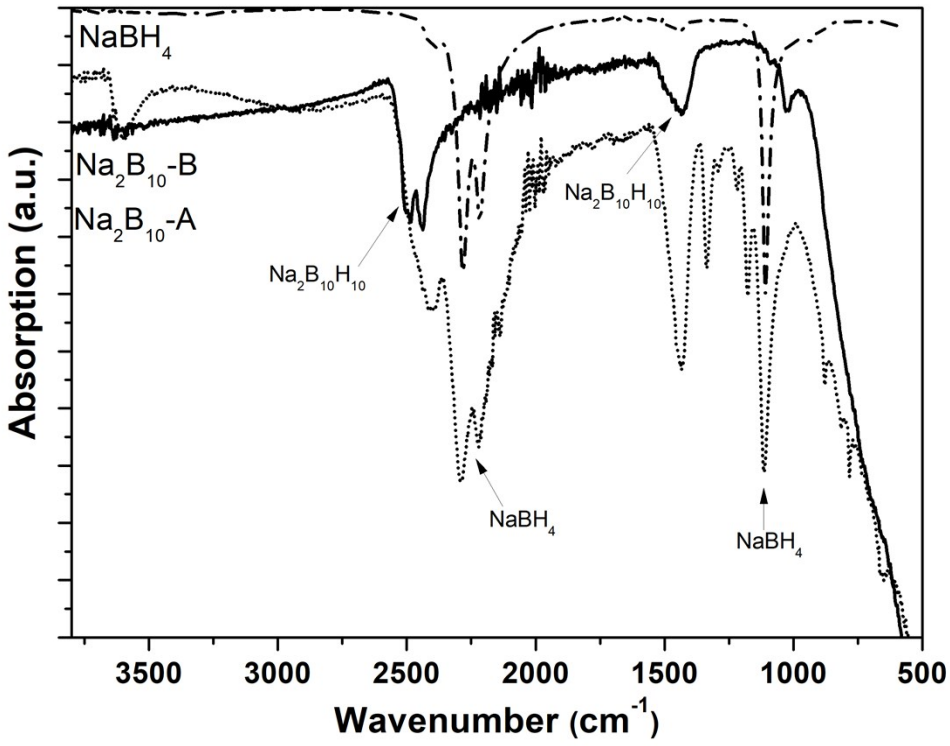

Figure S7. FT-IR spectra of Na_2B_{10}-A (solid black line), Na_2B_{10}-B (dotted line), and pure $NaBH_4$ (dashed line).

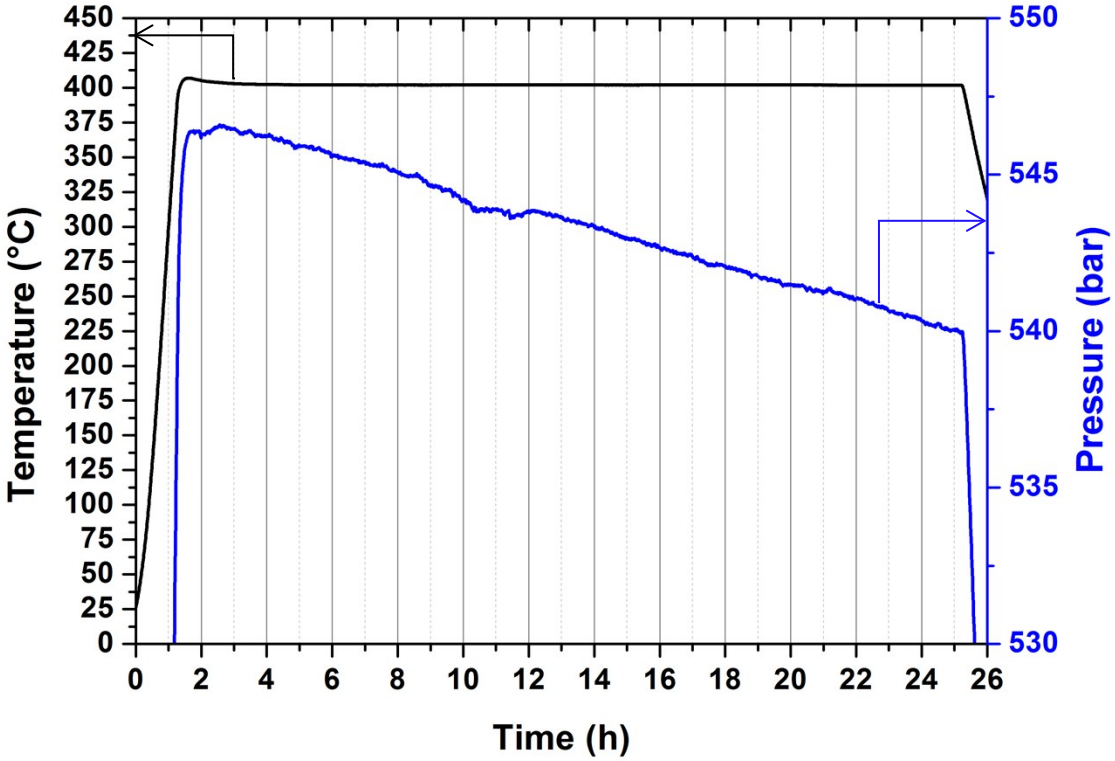

Figure S8. High-pressure hydrogen absorption experiment of $Li_2B_{12}H_{12}$–10 LiH (Li_2B_{12}-A) carried out by heating from *RT* to 400 °C ($\Delta T/\Delta t$ = 5 °C/min) and isothermal for 24 hours (black line) under $p(H_2)$ = 546 bar (blue line).

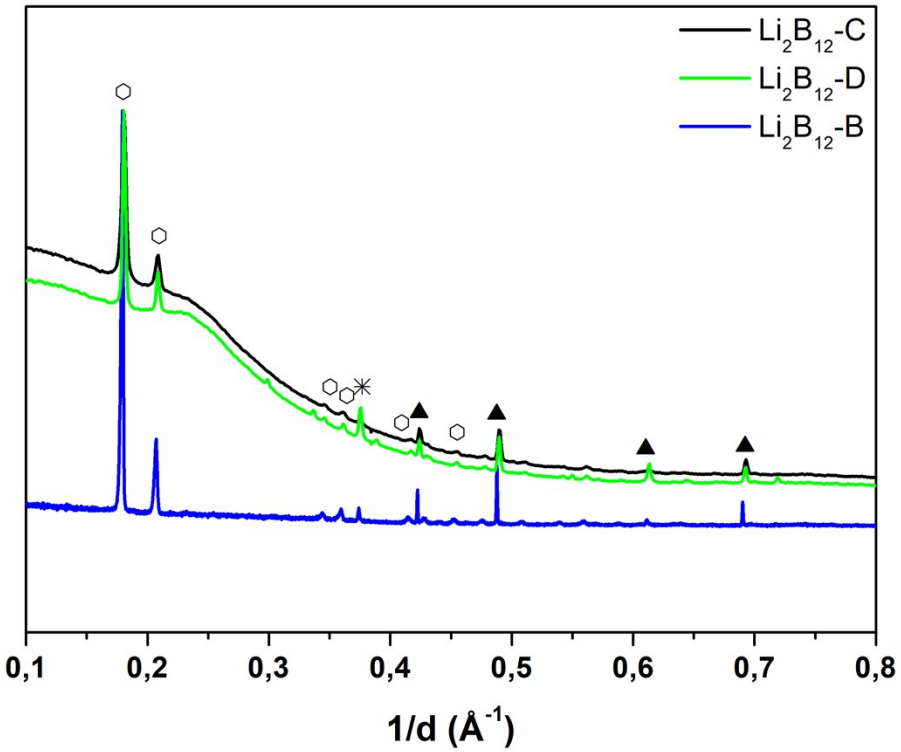

Figure S9. Powder X-ray diffraction patterns of Li_2B_{12}-B (bottom blue), Li_2B_{12}-D (middle green) and Li_2B_{12}-C (top black). Li_2B_{12}-B measured with λ = 1.5418 Å, Li_2B_{12}-C and Li_2B_{12}-D measured with λ = 0.20775 Å. LT-$Li_2B_{12}H_{12}$, ■ LiH, and ✳ Li_2O.

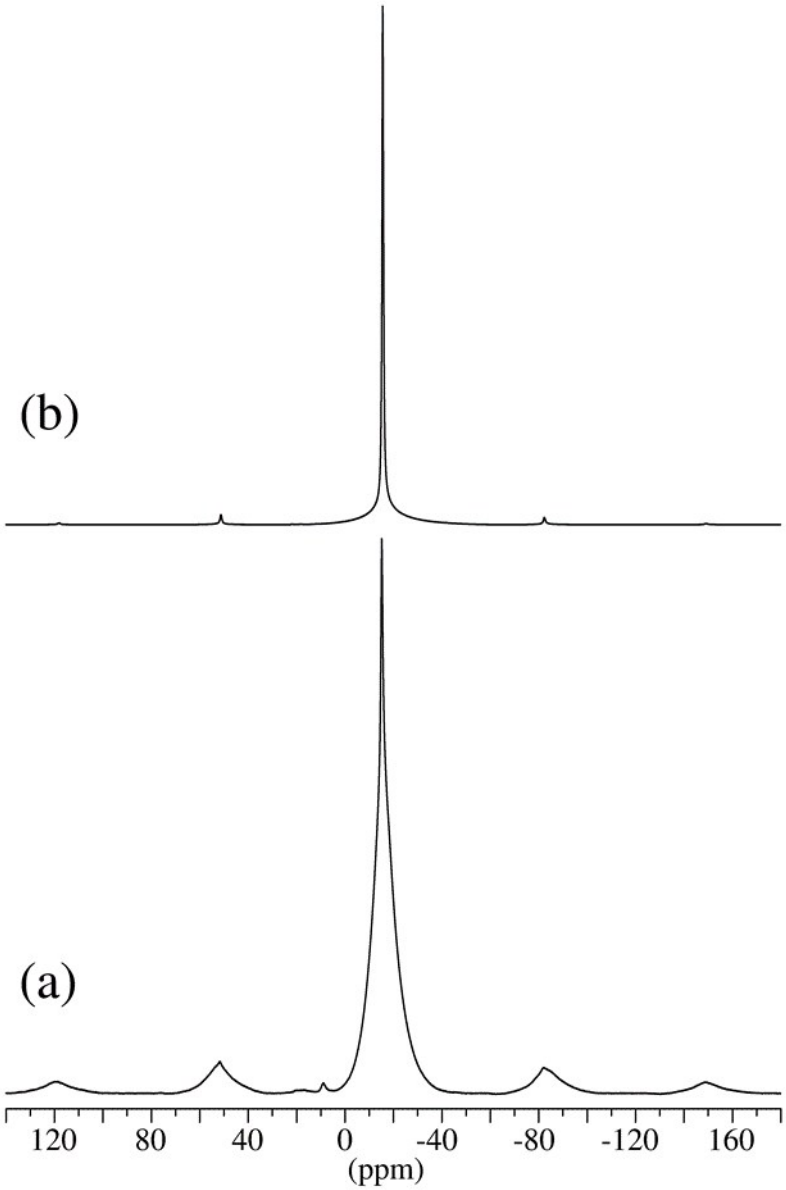

Figure S10. ^{11}B MAS NMR spectra (16.45 T, ν_R = 15.0 kHz) of the hydrogenated composites (a) Li_2B_{12}-B and (b) Na_2B_{12}-B, exhibiting centerband resonances at -15.2 ppm and -15.7 ppm, respectively.

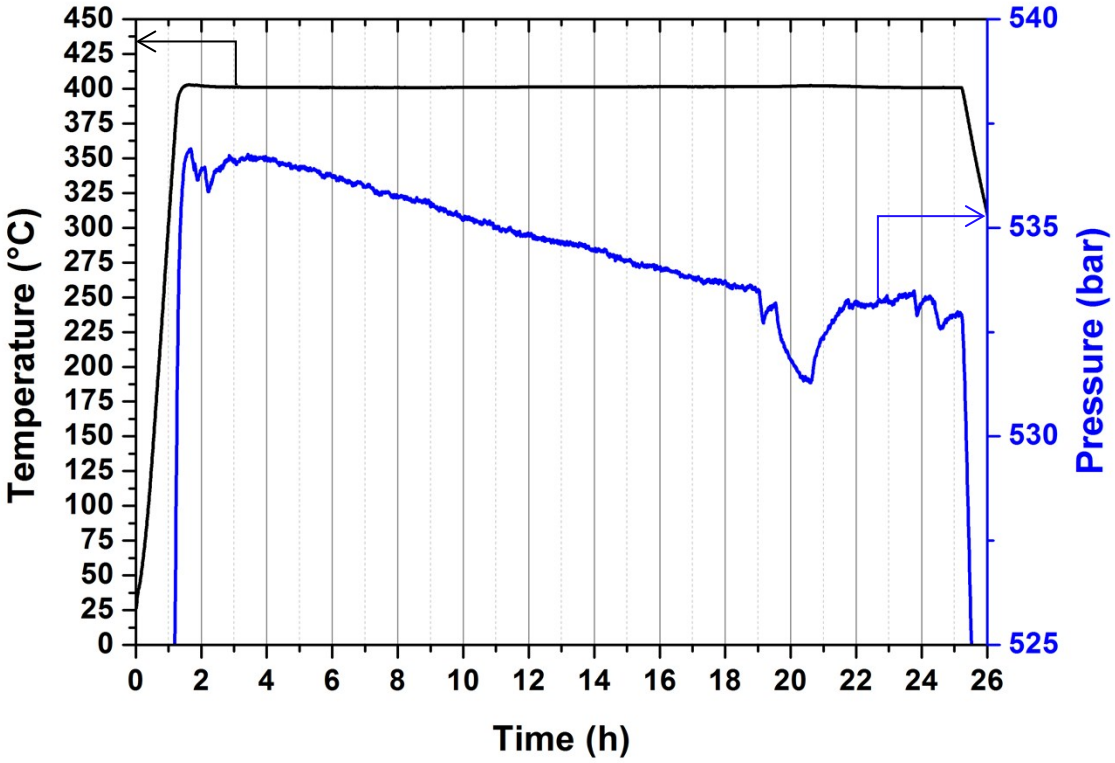

Figure S11. High-pressure hydrogen absorption experiment of $Na_2B_{12}H_{12}$–10 NaH (Na_2B_{12}-A) carried out by heating from *RT* to 400 °C ($\Delta T/\Delta t$ = 5 °C/min) and isothermal for 24 hours (black line) under $p(H_2)$ = 537 bar (blue line). Large pressure deviations are caused by room temperature fluctuations.

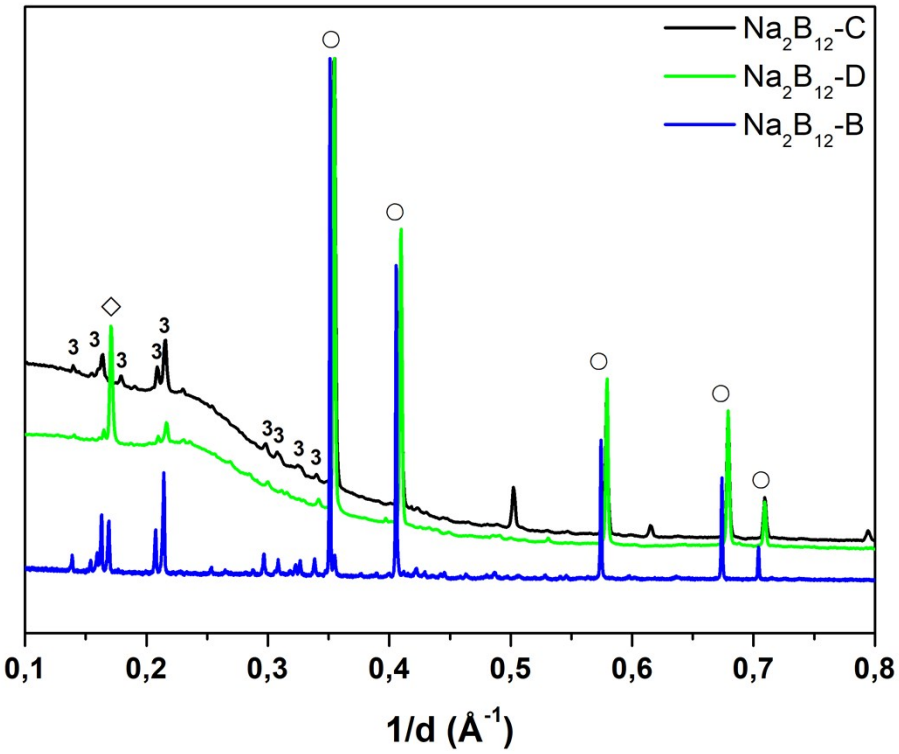

Figure S12. Powder X-ray diffraction patterns of Na_2B_{12}-B (bottom blue), Na_2B_{12}-D (middle green) and Na_2B_{12}-C (top black). Na_2B_{12}-B measured with $\lambda = 1.5418$ Å, Na_2B_{12}-C and Na_2B_{12}-D measured with $\lambda = 0.20775$ Å. Symbols: ◇ LT-$Na_2B_{12}H_{12}$, ■ NaH and compound **3**

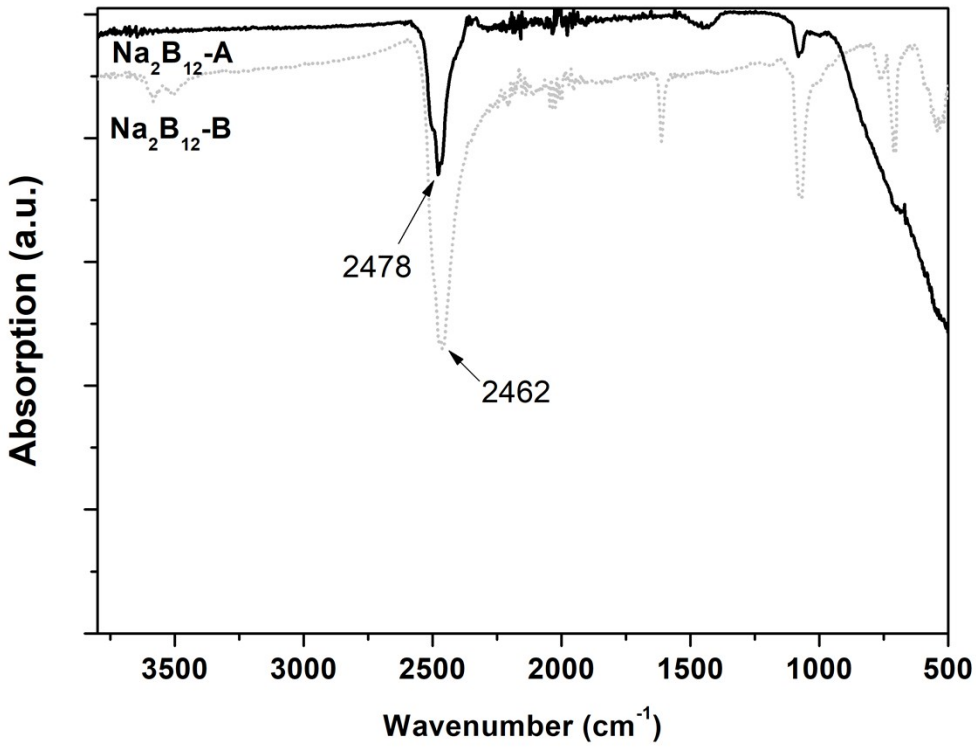

Figure S13. FT-IR spectra of Na_2B_{12}-A (solid black line) and Na_2B_{12}-B (grey dotted line).

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