Supporting Information of

Synthesis of $NaBH_4$ as a hydrogen carrier from hydrated borax using a Mg-Al alloy

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Supplementary Data

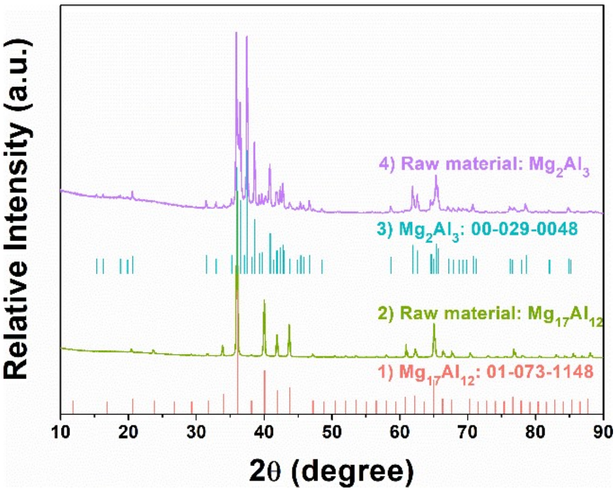

Figure S1. (a) XRD patterns of 1) standard PDF card of $Mg_{17}Al_{12}$, 2) raw $Mg_{17}Al_{12}$, 3) standard PDF card of Mg_2Al_3, and 4) raw Mg_2Al_3.

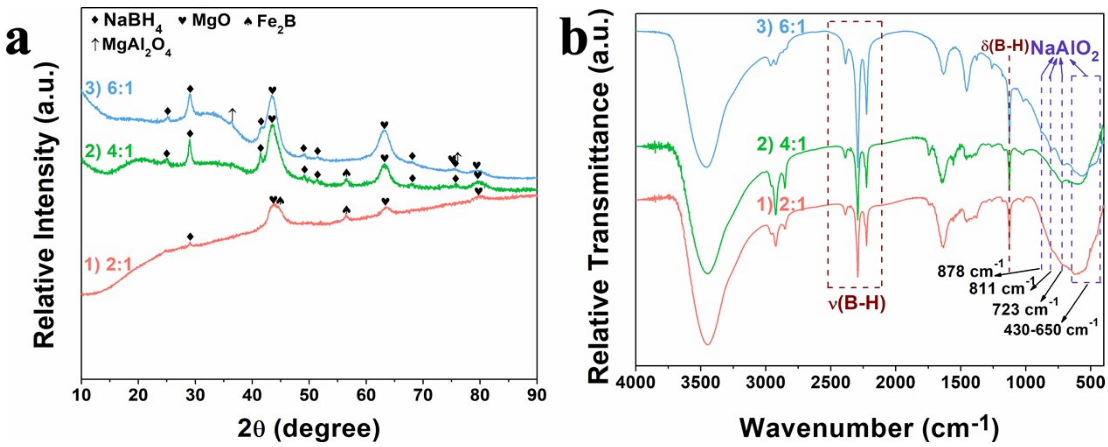

Figure S2. (a) XRD patterns and (b) FTIR spectra of products obtained after milling NaH and $Na_2B_4O_7 \cdot 10H_2O$ in different molar ratios for 20 h ($Na_2B_4O_7 \cdot 10H_2O$ and $Mg_{17}Al_{12}$ were fixed at 1:0.607). In Figure S2b, IR band at 811 cm^{-1} corresponds to the formation of O-O triangular species bonds and the bands at 617 and 558 cm^{-1} belong to the vibrations of Al-O bond in $NaAlO_2$ [1, 2].

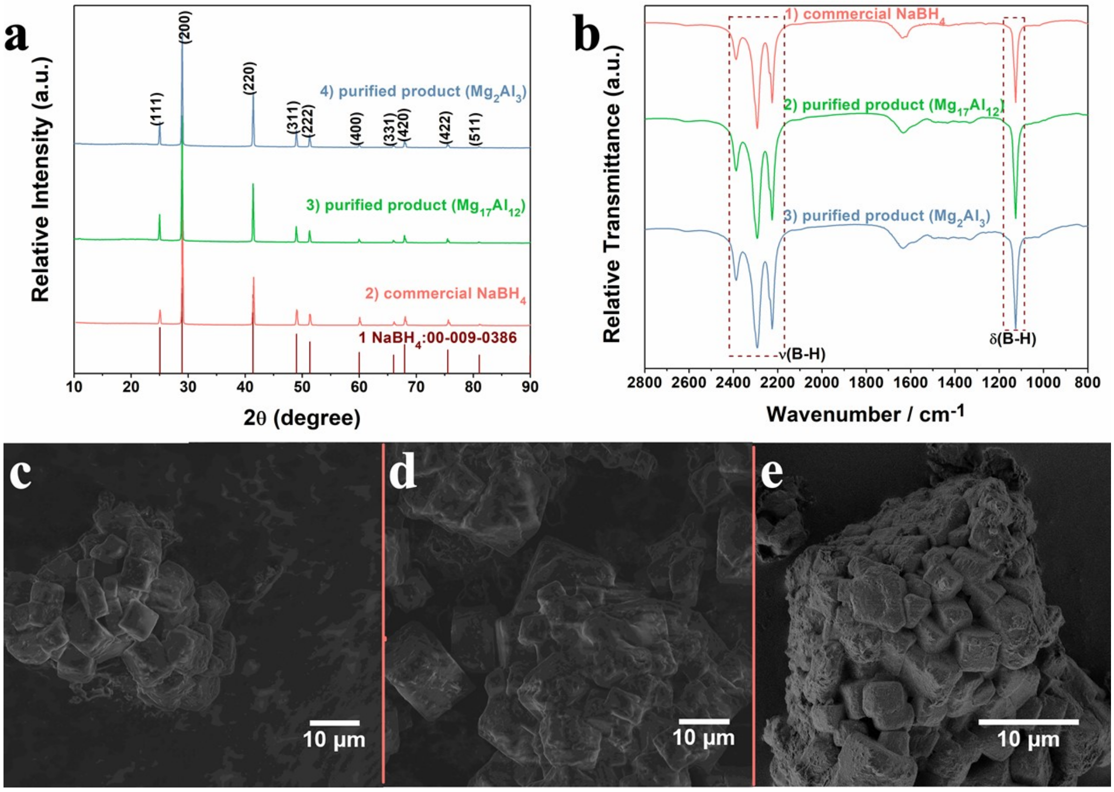

Figure S3. (a) XRD patterns of standard PDF card of $NaBH_4$, commercial $NaBH_4$ and purified product; (b) FTIR spectra of commercial $NaBH_4$ and purified product; SEM images of (c) purified product by using $Mg_{17}Al_{12}$ as reducing agent, (d) purified product by using Mg_2Al_3, and (e) commercial $NaBH_4$.

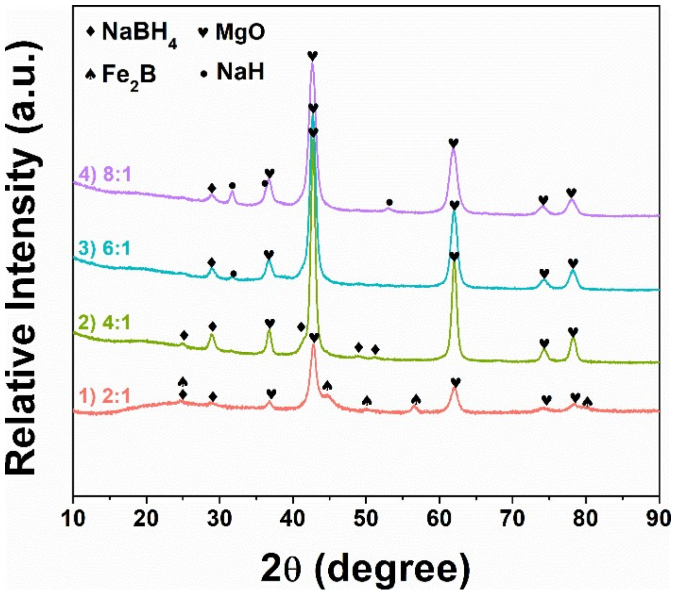

Figure S4. XRD patterns of products obtained after milling NaH and $Na_2B_4O_7\cdot 10H_2O$ in different molar ratios for 20 h ($Na_2B_4O_7\cdot 10H_2O$ and Mg were fixed at 1:21.25).

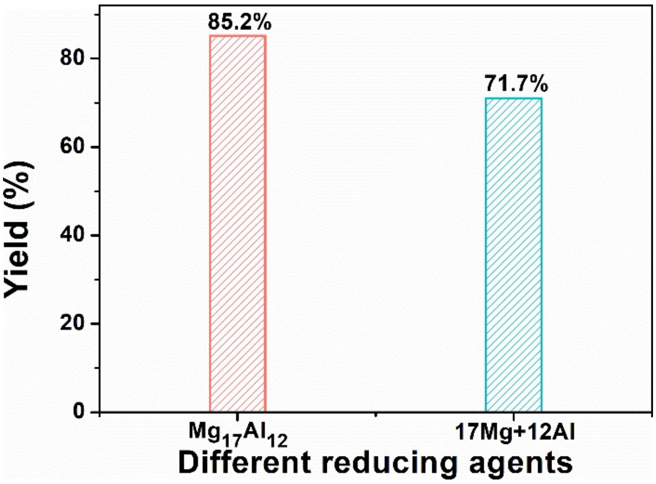

Figure S5. Yields of $NaBH_4$ of the products obtained after milling $Na_2B_4O_7 \cdot 10H_2O$, NaH, and $Mg_{17}Al_{12}$/(17Mg+12Al) mixtures (in 1:4:0.850 molar ratio) for 20 h at 1200 CPM.

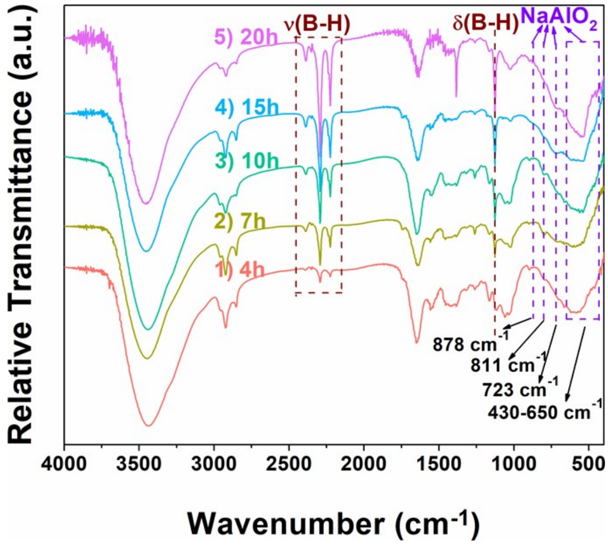

Figure S6. FTIR spectra of products obtained via ball milling $Mg_{17}Al_{12}$, $Na_2B_4O_7 \cdot 10H_2O$, and NaH in a molar ratio of 0.850:1:4 at 1200 CPM for different durations.

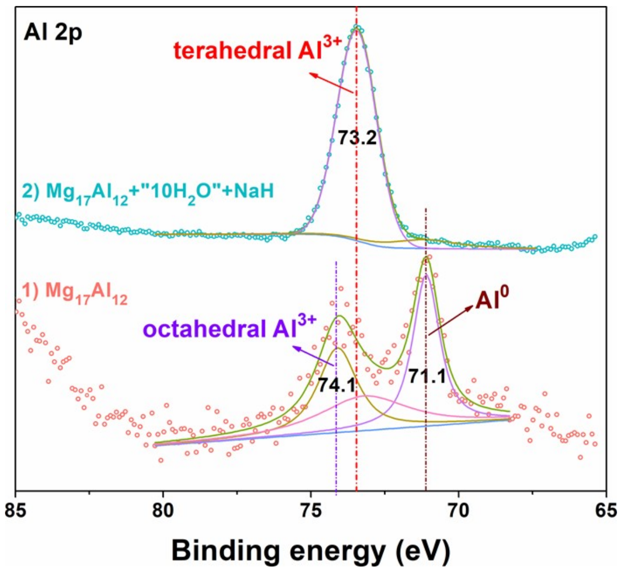

Figure S7. XPS of 1) raw commercial $Mg_{17}Al_{12}$ after milling 10 h at 1200 CPM and 2) products obtained after milling $Mg_{17}Al_{12}$, NaH, and $Na_2B_4O_7{\cdot}10H_2O$ in a molar ratio of 0.486:4:1 for 10 h at 1200 CPM.

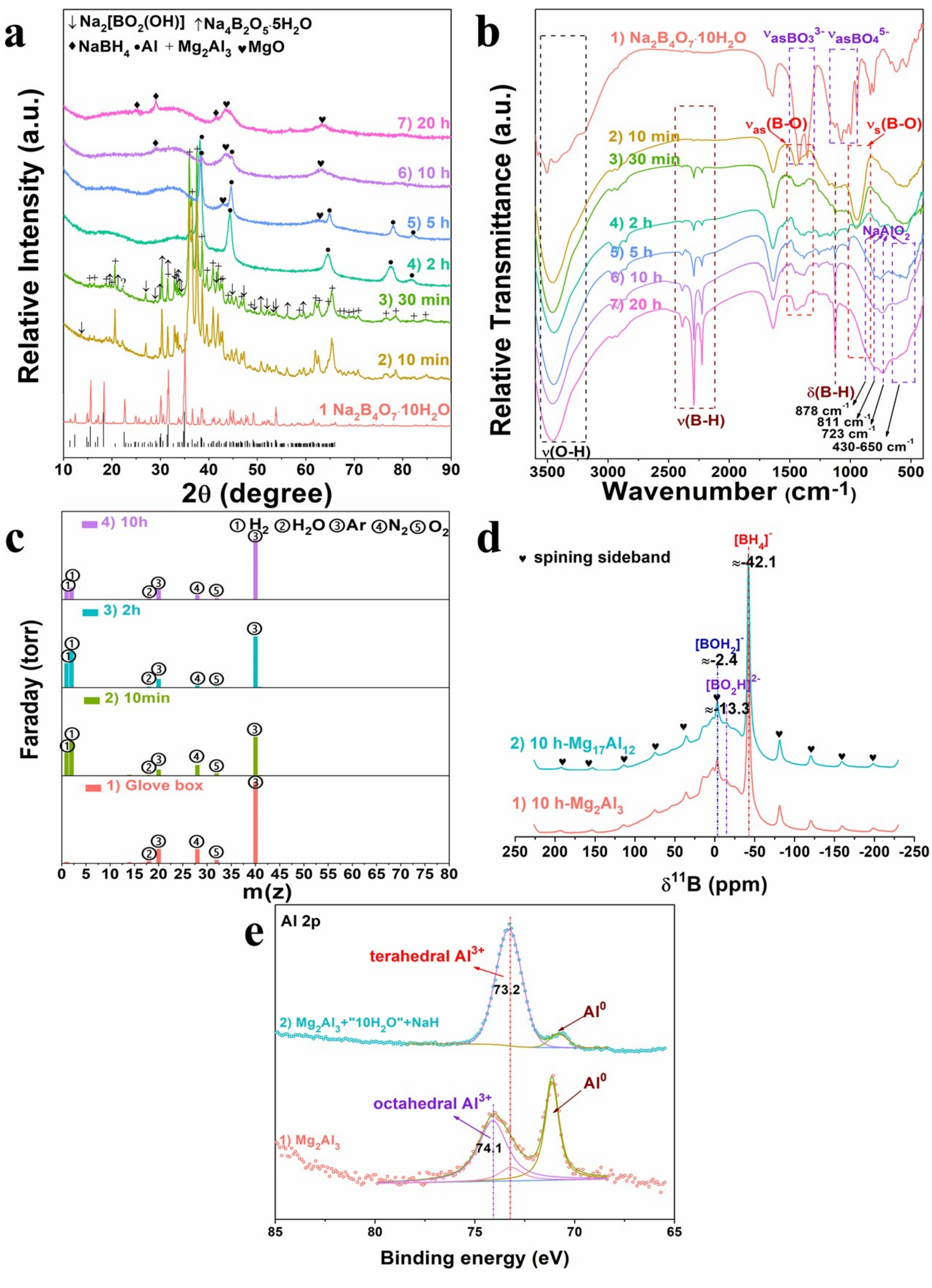

Figure S8. (a) XRD patterns and (b) FTIR spectra of 1) raw $Na_2B_4O_7 \cdot 10H_2O$; products obtained after ball milling Mg_2Al_3, NaH, and $Na_2B_4O_7 \cdot 10H_2O$ mixtures (in a 2.62:4:1 molar ratio) with different durations at 1200 CPM; (c) MS of the gaseous sample obtained after ball milling Mg_2Al_3, NaH, and $Na_2B_4O_7 \cdot 10H_2O$ mixtures (in a 2.62:4:1

molar ratio) with different durations at 1200 CPM; (d) solid-state ^{11}B NMR spectra of products obtained 1) after milling Mg_2Al_3, NaH, and $Na_2B_4O_7 \cdot 10H_2O$ in a molar ratio of 2.62:4:1 for 10 h at 1200 CPM and 2) after milling $Mg_{17}Al_{12}$, NaH, and $Na_2B_4O_7 \cdot 10H_2O$ in a molar ratio of 0.486:4:1 for 10 h at 1200 CPM; (e) XPS of 1) raw Mg_2Al_3 after milling 5 h at 1200 CPM and 2) products obtained after milling Mg_2Al_3, NaH, and $Na_2B_4O_7 \cdot 10H_2O$ in a molar ratio of 2.62:4:1 for 5 h at 1200 CPM.

Table S1. EDS results of products obtained after ball milling NaH and $Na_2B_4O_7 \cdot 10H_2O$ ("$10H_2O$") in different molar ratios for 20 h.

NaH: "$10H_2O$"	Al: "$10H_2O$" (14.16:1)		Mg: "$10H_2O$" (21.25:1)		$Mg_{17}Al_{12}$: "$10H_2O$" (0.607:1)	
	Fe (wt%)	Cr (wt%)	Fe(wt%)	Cr(wt%)	Fe(wt%)	Cr(wt%)
2:1	24.34	0.85	16.94	0.74	27.87	0.54
4:1	20.91	0.44	2.30	0.11	9.05	0.14
6:1	9.62	0.25	1.48	0.06	0.54	0.03
8:1	4.86	0.14	0.81	0.11		

Table S2. Yields of $NaBH_4$ synthesized by various methods.

Reactants	Method and conditions	Max yield (%)
$NaBO_2$:Mg (1:2)	anneal at 550°C, 7 MPa H_2	10 [3]
$NaBO_2·2H_2O$:Mg (1:4)	anneal at 600°C, 3 MPa H_2	12.3 [4]
$Na_2B_4O_7$:Mg (1:16)	anneal at 550°C, 25 bar H_2	46.5[a] [5]
$Na_2B_4O_7$:MgH_2 (1:9.5)	planetary ball 2750 rpm, 1 h, 1 atm Ar	43 [6]
$Na_2B_4O_7$:NaOH:MgH_2 (1:2:8)	planetary ball 2750 rpm, 1 h, 1 atm Ar	64 [6]
$Na_2B_4O_7$:Na_2O_2:MgH_2 (1:1:9.24)	planetary ball 2750 rpm, 1 h, 1 atm Ar	67 [6]
$Na_2B_4O_7$:Na_2CO_3:MgH_2 (1:1:9.24)	planetary ball 2750 rpm,1 h, 1 atm Ar	78 [6]
$NaBO_2$:MgH_2 (1:2.8)	shaker mill 1080 cpm, 6 h, 1 atm Ar	76 [7]
$NaBO_2$:MgH_2 (1:2.6)	shaker mill 1080 cpm, 11 h, 1 atm Ar	70 [8]
$NaBO_2$:MgH_2 (1:2.07)	shaker mill 1230 cpm, 2 h, 200 kPa Ar	71 [9]
$NaBO_2$:MgH_2 (1:2.7)	shaker mill 1200 cpm, 12 h, 3 MPa H_2, 0.15 mL CH_3OH	89 [10]
Na:B_2O_3:MgH_2 (2:1.2:5.2)	shaker mill 1080 cpm, 11 h,1 atm Ar	25 [11]
$NaBO_2·2H_2O$:MgH_2 (1:5)	shaker mill 1200 cpm,15 h, 1 atm Ar	90.0 [12]
$NaBO_2·2H_2O$:Mg (1:5)	shaker mill 1200 cpm, 15 h,1 atm Ar	68.55 [13]
$Na_2B_4O_7·10H_2O$:Na_2CO_3:Mg (1:1:24.75)	shaker mill 1000 cpm, 30 h, 1 atm Ar	78.9 [14]
$Na_2B_4O_7·10H_2O$:NaH:$Mg_{17}Al_{12}$ (1:4:0.850)	shaker mill 1200 cpm, 20 h, 1 atm Ar	85.2 (in this work)

[a] The yield was determined according to the following equation:

$$\text{Yield (NaBH}_4\text{)} = \frac{obtained\ mass\ NaBH4}{theoretical\ mass\ NaBH4} \times 100\%$$

The theoretical amount was based on a full conversion meaning that 1 mole $Na_2B_4O_7$ is converted to 4 mole of $NaBH_4$.

Table S3. Cost of raw materials

Method	Cost (US$/ ton)
Ball milling $Mg_{17}Al_{12}$, NaH, and $Na_2B_4O_7\cdot 5H_2O$	15,027 [a)]
Ball milling MgH_2 and $NaBO_2$	280670 [b)]
Ball milling MgH_2, Na_2CO_3, and $Na_2B_4O_7$	262,015 [c)]

The calculation does not include the cost of raw materials $Na_2B_4O_7$, $NaBO_2$ or $Na_2B_4O_7\cdot 10H_2O$, since they can be easily recycled from hydrolytic product of $NaBH_4$ or obtained from borax mineral. All the prices of raw materials are from a commercial company.

[a)] The calculation is based on the highest yield of 85.2% obtained via ball milling $Mg_{17}Al_{12}$, NaH, and $Na_2B_4O_7\cdot 5H_2O$ mixtures (in 0.850:4:1 molar ratio). 4.86 tons of $Mg_{17}Al_{12}$ and 0.74 tons of NaH are needed to produce 1 ton $NaBH_4$. For the price, it is $2,420/ton for $Mg_{17}Al_{12}$ and $4413/ton for NaH. Then the total cost of raw materials is $15,027;

[b)] The calculation is based on the highest yield of 63% obtained via ball milling MgH_2 and $NaBO_2$ mixtures (in 2:1 molar ratio) [7]. 2.21 tons of MgH_2 are needed to produce 1 ton of $NaBH_4$. For the price, it is $127,000/ton for MgH_2. The total cost of raw materials is $280,670;

[c)] The calculation is based on a 78% yield when MgH_2, Na_2CO_3, and $Na_2B_4O_7$ with a ratio of 9.24:1:1 is ball milled for 1 h [6]. 2.061 tons of MgH_2 and 0.898 tons of Na_2CO_3 are needed to produce 1 ton $NaBH_4$. The price of Na_2CO_3 is $298, so the total cost of raw materials is $262,015.

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