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Efficient Synthesis of Alkali Borohydrides from Mechanochemical Reduction of Borates Using Magnesium–Aluminum-Based Waste

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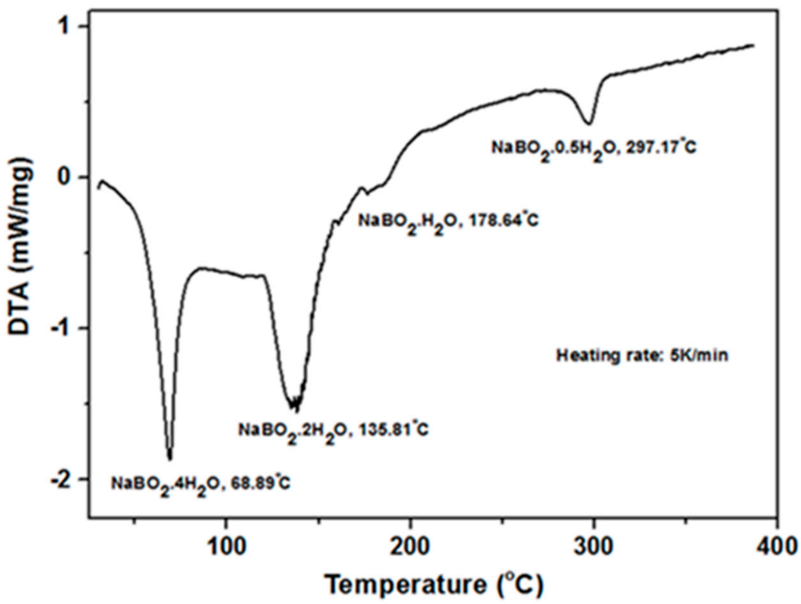

Figure S1. DTA of $NaBO_2{\cdot}4H_2O$, measured at argon atmosphere from room temperature to 380 °C with a heating rate of 5 °C/min.

Figure S2. The Mg–Al-based waste as received from the workshop.

Thermodynamic calculations

Reaction: $LiBO_2$ + 2.5Mg–Al-based waste under 70 bar H_2

Table S1 shows the calculated amounts (mol%) of the equilibrium species obtained from the mechanochemical synthesis of $LiBH_4$(s) from $LiBO_2$(s) and Mg–Al-based waste under 70 bar H_2. The mechanochemial synthesis leads to the formation of $LiBH_4$(s) and MgO(s). Moreover, the impurities in the Mg waste remain after the milling process, the main reaction based on the initial composition of the Mg–Al-based waste material and the calculated equilibrium composition can be described according to the thermodynamically favored reaction as shown in Figure S3 and Table S2.

Table S1. Calculated amounts (mol%) of equilibrium species. Conditions: 25–40 °C and 70 bar H_2 and 25–40 °C and 1 bar H_2. The amount of H_2(s) is not take into account in the calculated amounts.

Species	Starting Compositions	After Milling (25–40 °C and 70 bar H_2)
$LiBO_2$ (s)	28.57	-
Mg (s)	59.10	-
Al (s)	9.51	9.69
Ca (s)	0.03	0.03
Cu (s)	0.04	0.04
Mn (s)	0.04	0.05
Nd (s)	0.06	0.06
Zn (s)	2.48	2.53
Y (s)	0.05	0.05
Ag (s)	0.12	0.13
$LiBH_4$ (s)	-	29.14
LiH (s)	-	-
MgO (s)	-	58.28

Al_2O_3 (s)	-	-
H_3BO_2 (s)	-	-
L_2O (s)	-	-
MgB_4 (s)	-	-
MgB_{12} (s)	-	-

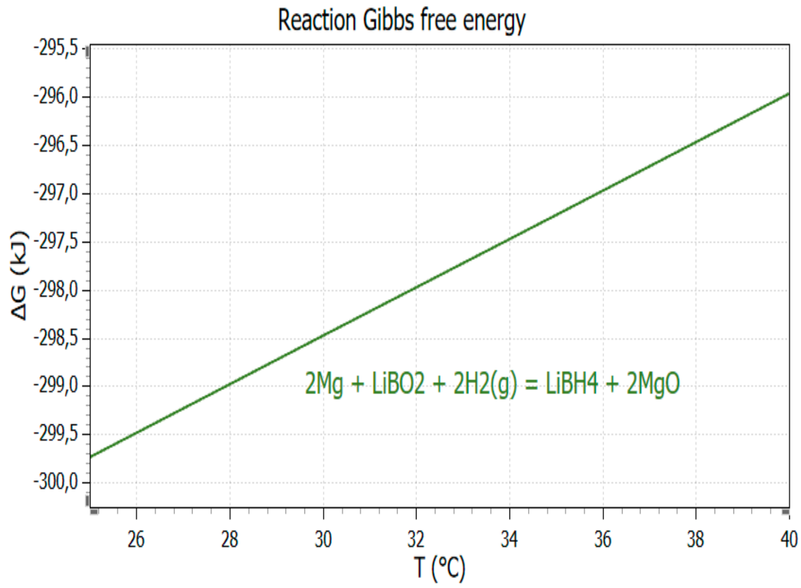

Figure S3. ΔG vs. T.

Table S2. Reaction under 70 bar H_2 condition.

Reaction Equation							
$2Mg + LiBO_2 + 2H_2(g) = LiBH_4 + 2MgO$							
Reaction Data							
T °C	**ΔH kJ**	**ΔS J/K**	**ΔG kJ**	**K**		**Log K**	
25,000	−374,441	−250,558	−299,737	$3{,}290 \times 10^{52}$		52,517	
30,000	−374,489	−250,716	−298,484	$2{,}723 \times 10^{51}$		51,435	
35,000	−374,531	−250,855	−297,230	$2{,}443 \times 10^{50}$		50,388	
40,000	−374,570	−250,979	−295,976	$2{,}366 \times 10^{49}$		49,374	
Species Data							
Formula	**M g/mol**	**Conc. wt%**	**Input Amounts mol**	**g**	**Volume**	**Unit**	**Extrapolated From T (K)**
Mg	24,305	47,474	2000	48,610	27,937	mL	-
$LiBO_2$	49,751	48,588	1000	49,751	35,613	mL	-
H_2(g)	2016	3938	2000	4032	44,827	L	-
$LiBH_4$	21,784	21,275	1000	21,784	32,708	mL	-
MgO	40,304	78,725	2000	80,609	22,516	mL	-

Reaction: $NaBO_2$ + 2.5Mg–Al-based waste under 70 bar H_2

Table S3 shows the calculated amounts (mol %) of the equilibrium species obtained from the mechanochemical synthesis of $NaBH_4$ (s) from $NaBO_2$ (s) and Mg–Al-based waste 70 bar H_2. The mechanochemial synthesis leads to the formation of $NaBH_4$ (s) and MgO (s) and the impurities in the Mg waste remain after the milling process. The main reaction based on the initial composition of the Mg–Al-based waste material and the calculated equilibrium composition can be described according to the thermodynamically favored reaction as shown in Figure S4 and Table S4.

Table S3. Calculated amounts (mol %) of equilibrium species. Conditions: 25–40 °C and 70 bar H_2. The amount of H_2 (s) is not take into account in the calculated amounts.

Species	Starting Compositions	After Milling (25–40 °C and 70 bar H_2)
$NaBO_2$ (s)	28.57	-
Mg (s)	59.10	-
Al (s)	9.51	9.69
Ca (s)	0.03	0.03
Cu (s)	0.04	0.04
Mn (s)	0.04	0.05
Nd (s)	0.06	0.06
Zn (s)	2.48	2.53
Y (s)	0.05	0.05
Ag (s)	0.12	0.13
$NaBH_4$ (s)	-	29.14
MgO (s)	-	58.28
Al_2O_3 (s)	-	-
NaH (s)	-	-
B (s)	-	-
Na (s)	-	-
MgB_2 (s) MgB_4 (s)	-	-

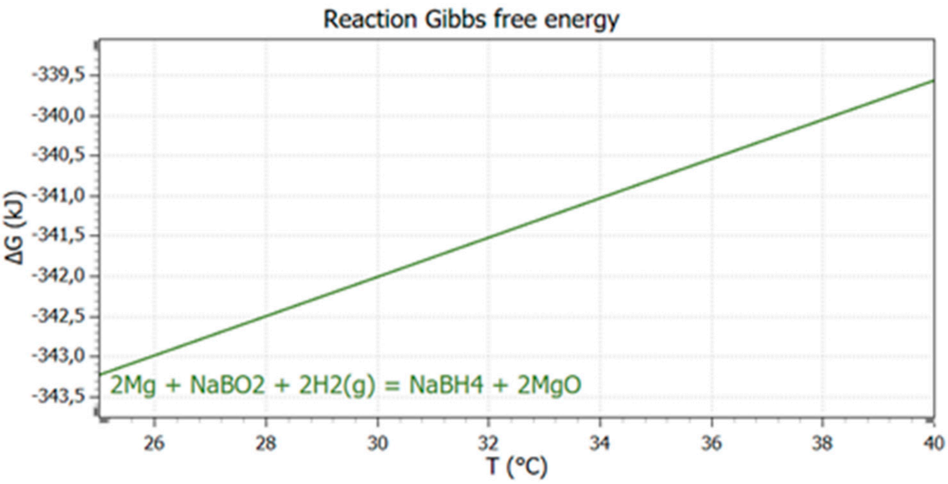

Figure S4. ΔG vs. T.

Table S4. Reaction under 70 bar H_2 condition.

Reaction Equation					
2Mg + $NaBO_2$ + 2H2(g) = $NaBH_4$ + 2MgO					
Reaction Data					
T °C	**ΔH kJ**	**ΔS J/K**	**ΔG kJ**	**K**	**Log K**
25,000	−416,189	−244,675	−343,239	1378×10^{60}	60,139
30,000	−416,250	−244,878	−342,016	8638×10^{58}	58,936
35,000	−416,308	−245,065	−340,791	5922×10^{57}	57,772
40,000	−416,361	−245,239	−339,565	4421×10^{56}	56,646

Species Data

Formula	**M**	**Conc.**	**Input Amounts**				**Extrapolated From T(K)**
	g/mol	**wt%**	**mol**	**g**	**Volume**	**Unit**	

Mg	24,305	41,041	2000	48,610	27,937	mL	-
$NaBO_2$	65,800	55,555	1000	65,800	26,704	mL	-
H_2 (g)	2016	3404	2000	4032	44,827	L	-
$NaBH_4$	37,833	31,942	1000	37,833	35,226	mL	-
MgO	40,304	68,058	2000	80,609	22,516	mL	-

Reaction: $NaBO_2 \cdot 4H_2O$ (s) + 7.25Mg–Al-based waste under 1 bar Ar

The results of the thermodynamic equilibrium calculations for $NaBO_2 \cdot 4H_2O$ (s) + Mg–Al-based waste under 1 bar Ar are shown in Table S5. The calculations hint that the formation of $NaBH_4$ (S) is thermodynamically favored under an Ar atmosphere and with the 1 $NaBO_2 \cdot 4H_2O$ (s) + 6Mg (total amount of Mg–Al-based waste: 7.25 mol). The products shown in Table S5 suggest the total conversion to $NaBH_4$ (s) and the formation of MgO (s) and H_2 (g) as byproducts. In Figure S5 and Table S6, the free energy as a function of the temperature and the reaction parameters are shown, respectively.

Table S5. Calculated amounts (mol %) of equilibrium species. Conditions: 25–40 °C and 1 bar Ar.

Species	Starting Compositions	After Milling (25–40 °C and 1 bar Ar)
$NaBO_2 \cdot 4H_2O$ (s)	12.11	-
Mg (s)	72.72	-
Al (s)	11.70	9.43
Ca (s)	0.03	0.03
Cu (s)	0.05	0.04
Mn (s)	0.05	0.04
Nd (s)	0.07	0.06
Zn (s)	3.05	2.46
Y (s)	0.06	0.01
Ag (s)	0.15	0.12
$NaBH_4$ (s)	-	9.76
H_2 (g)	-	19.51
Al_2O_3 (s)	-	-
MgO (s)	-	58.54

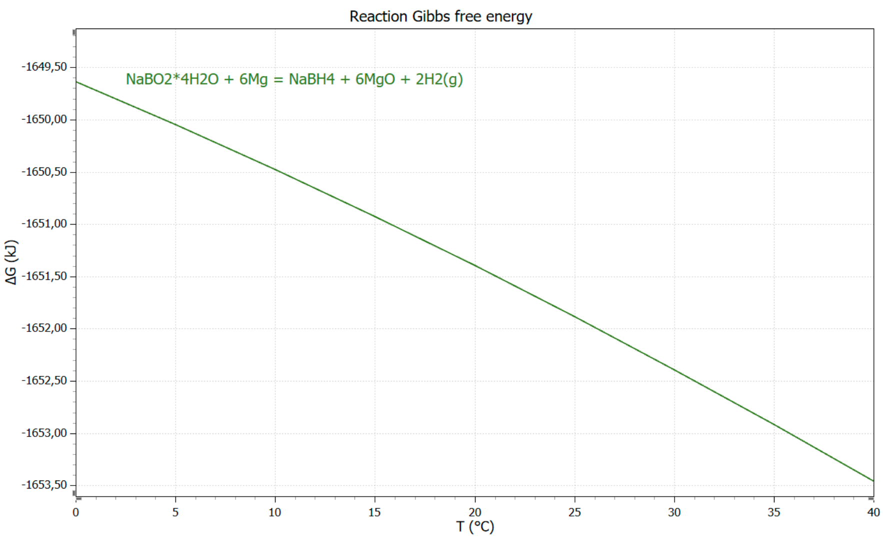

Figure S5. ΔG vs. T.

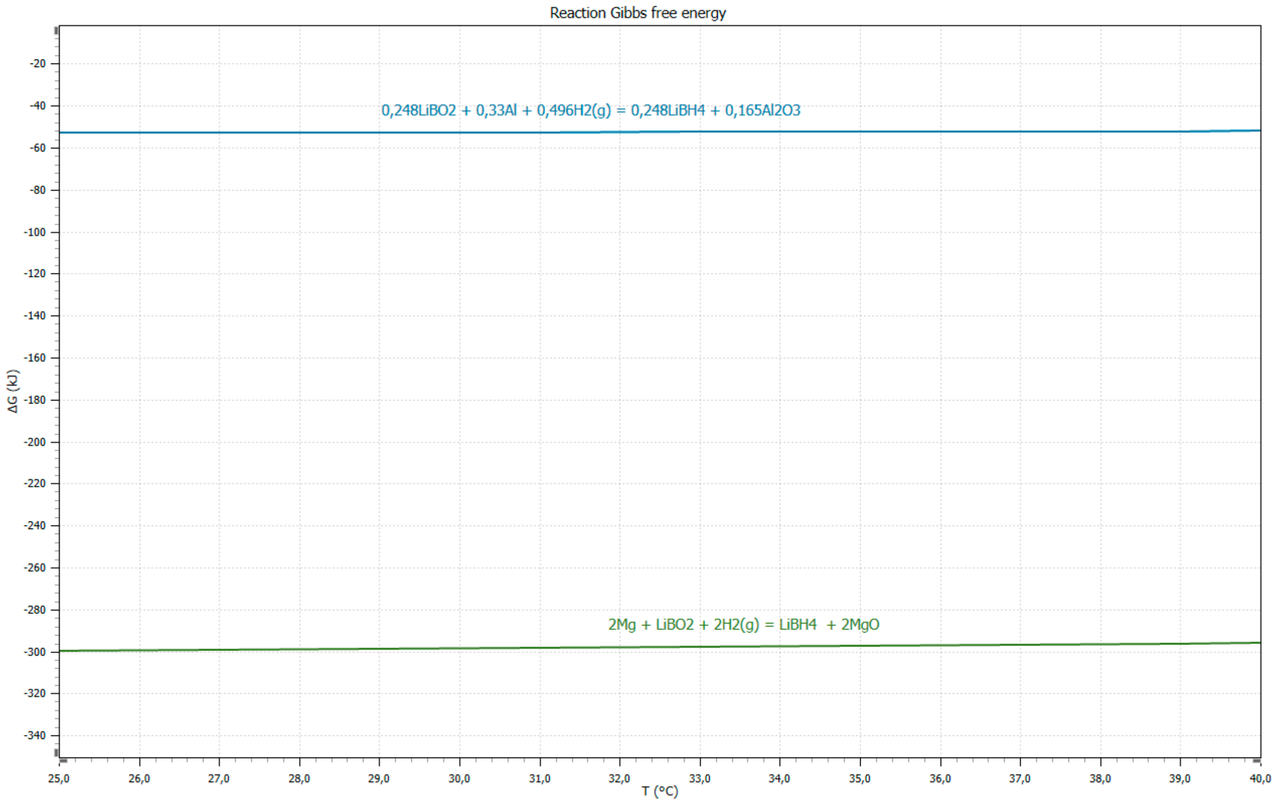

Figure S6. ΔG vs. T.

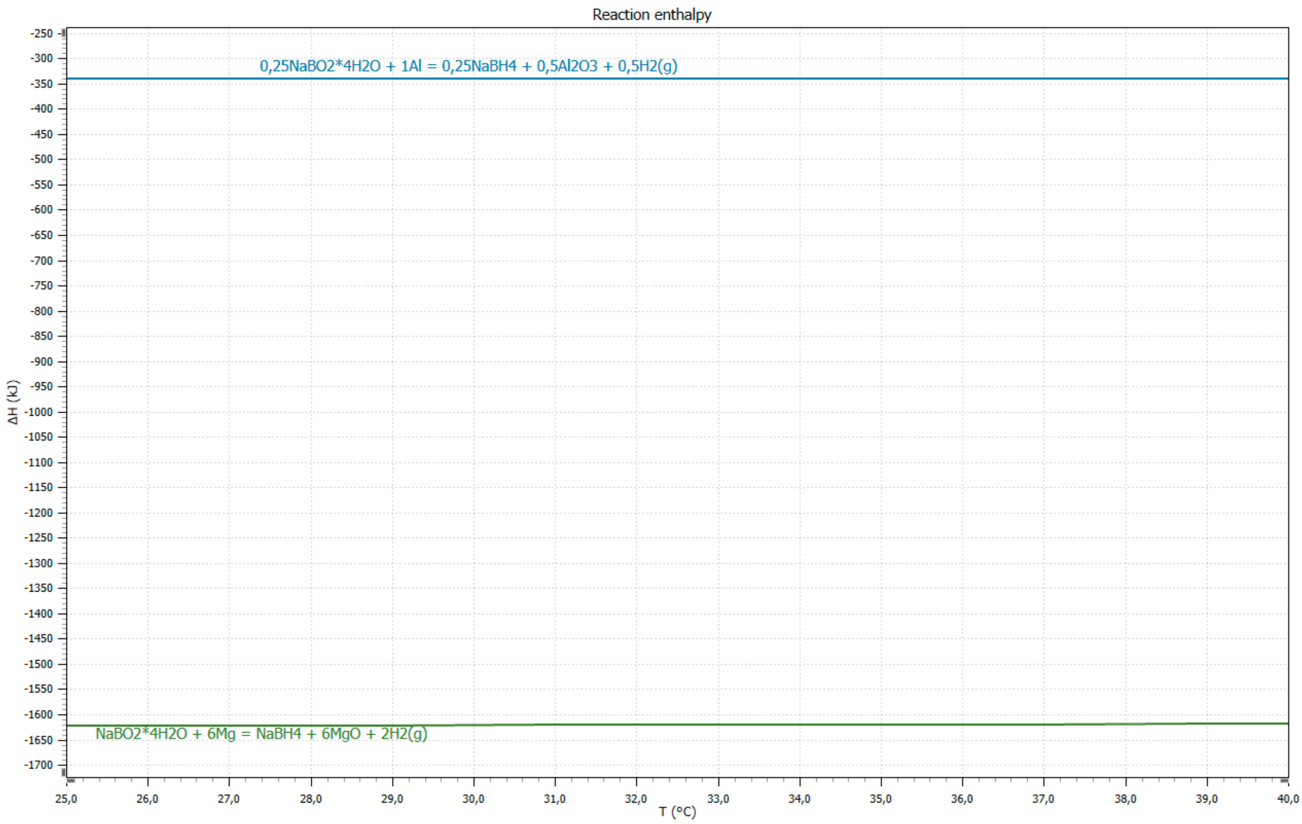

Figure S7. ΔG vs. T.

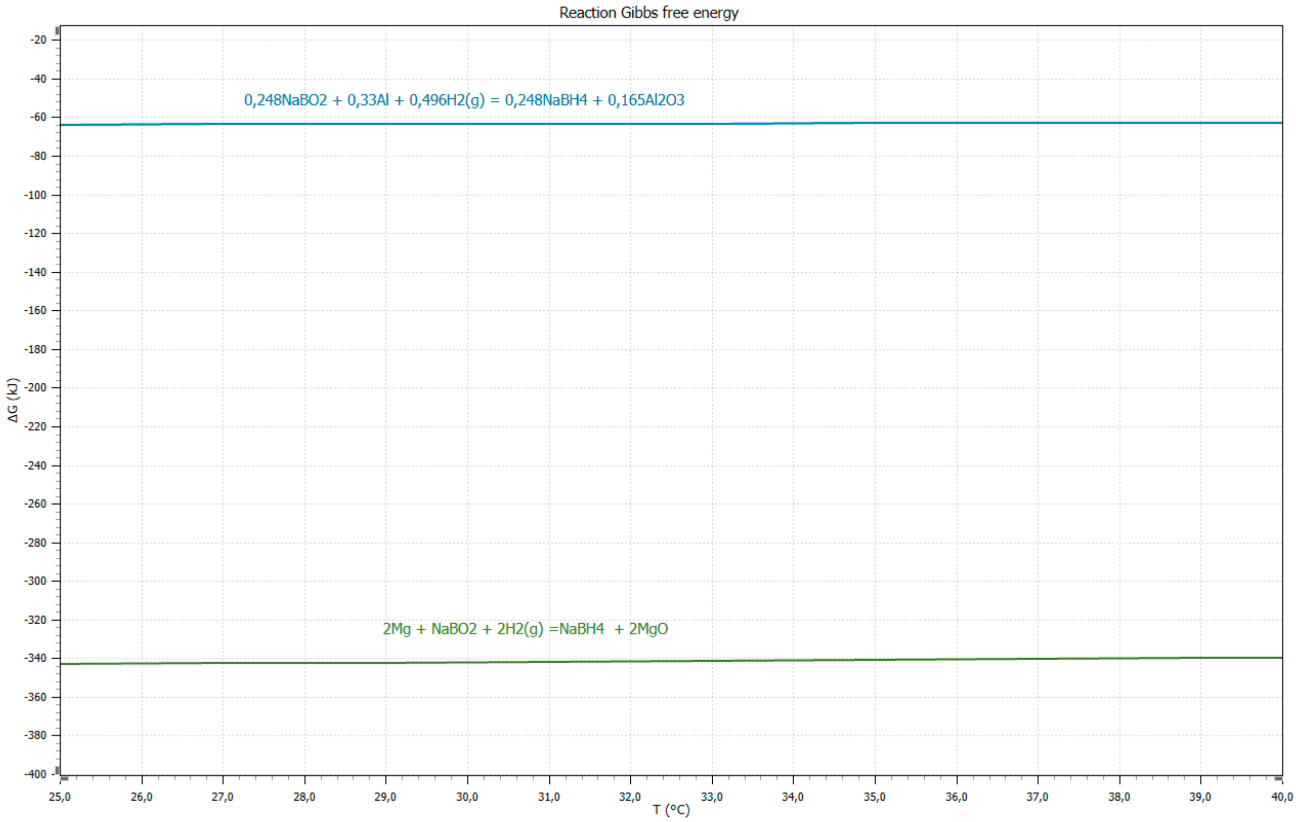

Figure S8. ΔG vs. T.

Table S6. Reaction under the milling conditions.

Reaction Equation							
$NaBO_2{\cdot}4H_2O + 6Mg = NaBH_4 + 6MgO + 2H_2(g)$							
Reaction Data							
T °C	**ΔH kJ**	**ΔS J/K**	**ΔG kJ**	**K**		**Log K**	
0000	−1627,585	80,724	−1649,635	1000x 10 [308]		308,000	
5000	−1626,559	84,445	−1650,048	1000 x 10 [308]		308,000	
10,000	−1625,517	88,159	−1650,479	3169x 10 [304]		304,501	
15,000	−1624,459	91,864	−1650,929	1990 x 10 [299]		299,299	
20,000	−1623,385	95,558	−1651,398	1894 x 10 [294]		294,277	
25,000	−1622,297	99,239	−1651,885	2678 x 10 [289]		289,428	
30,000	−1621,196	102,900	−1652,390	5510 x 10 [284]		284,741	
35,000	−1620,083	106,540	−1652,914	1621 x 10 [280]		280,210	
40,000	−1618,960	110,156	−1653,455	6700 x 10 [275]		275,826	
Species Data							
Formula	**M g/mol**	**Conc. wt-%**	**Input Amounts mol**	**g**	**Volume**	**Unit**	**Extrapolated From T(K)**
$NaBO_2{\cdot}4H_2O$	137,861	48,595	1000	137,861	0000	mL	-
Mg	24,305	51,405	6000	145,830	83,810	mL	-
$NaBH_4$	37,833	13,336	1000	37,833	35,226	mL	-
MgO	40,304	85,243	6000	241,826	67,549	mL	-
H_2 (g)	2016	1421	2000	4032	44,827	L	-

Table S7. Energy transferred to powder during milling.

System	F (rad/sec)	ΔE (J)	ρ_p (kg/m^3)	φ_b	ΔE^* (J)	P (W)	Milling Time (h)	P^* (Wh/g)
$LiBO_2$+2.5Mg–Al	28.125	0.04372	1953	0.9217	0.04030	31.7376	1	6.34753
							12	76.17031
							24	152.34062
							36	228.51094
$NaBO_2$+2.5Mg–Al	28.125	0.04372	2092	0.9225	0.04034	31.7643	1	6.35285
							12	76.23422
							24	152.46845
							36	228.70267

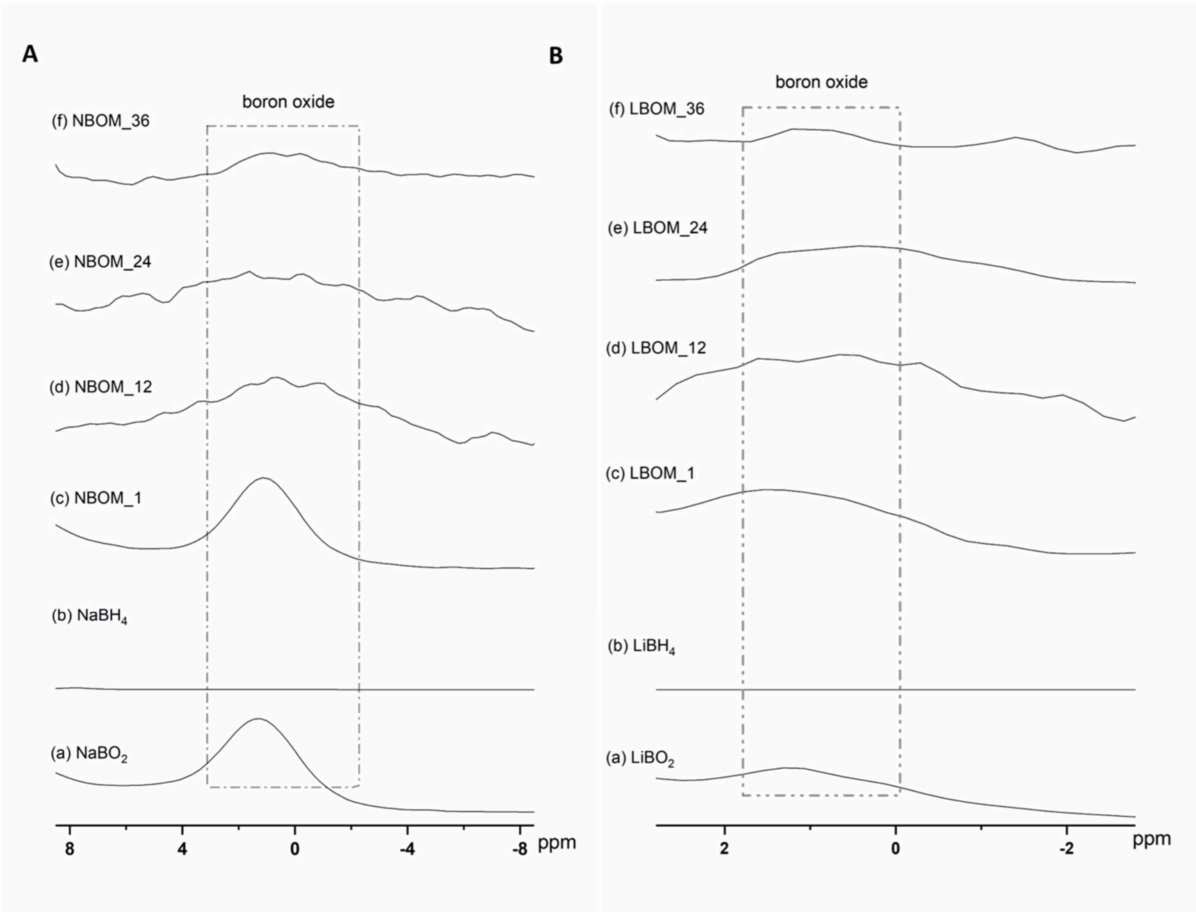

Figure S9. An inset of NMR spectra in range of 10 ppm to −10 ppm.

The Extraction Process

The synthesized borohydrides ($LiBH_4$ and $NaBH_4$) can be completely separated from the by-products (mainly MgO) by an extraction process. There are several solvents that can be used for extraction processes, i.e., isopropylamine (boiling point: 31–35 °C), ethylenediamine (boiling point: 116 °C), tetrahydrofuran (boiling point: 66 °C), ethylenglycoldimethylether (boiling point: 85 °C), 1,3–cyclohexanedione (boiling point: 105 °C), and diethylther (boiling point: 35 °C). In this study, it would be appropriate to use diethylether for $LiBH_4$ extraction and isopropylamine (or diethylether) for $NaBH_4$ extraction. The extraction process can be carried out by using a comercial device (Soxhlet extractor) (Figure S10). Once $LiBH_4$/and or $NaBH_4$ is extracted from the side-products (mainly MgO), subsequently the evaporation is performed to completely remove the solvents. Then, the purity of borohydrides is determined via hydrogen evolution apparatus (Figure S11).

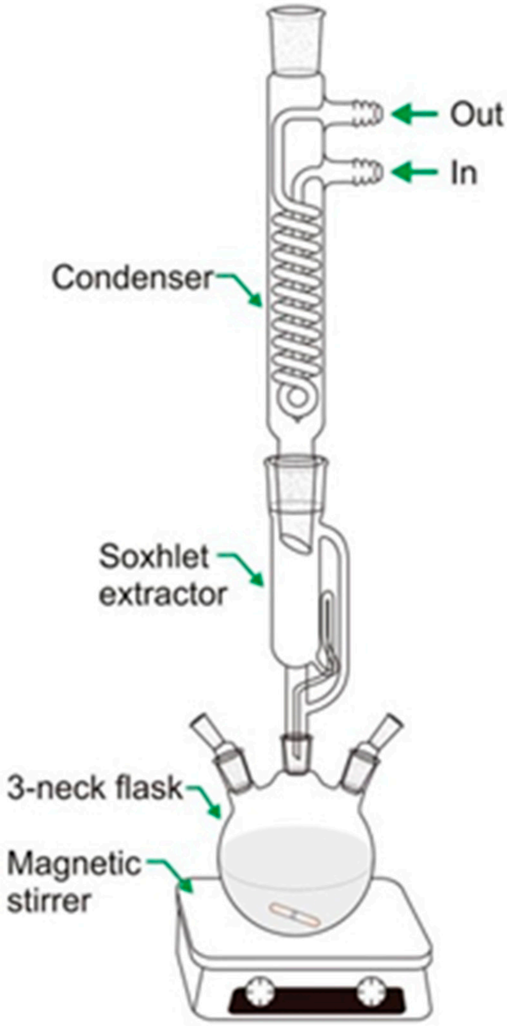

Figure S10. Schematic diagram of a Soxhlet extractor.

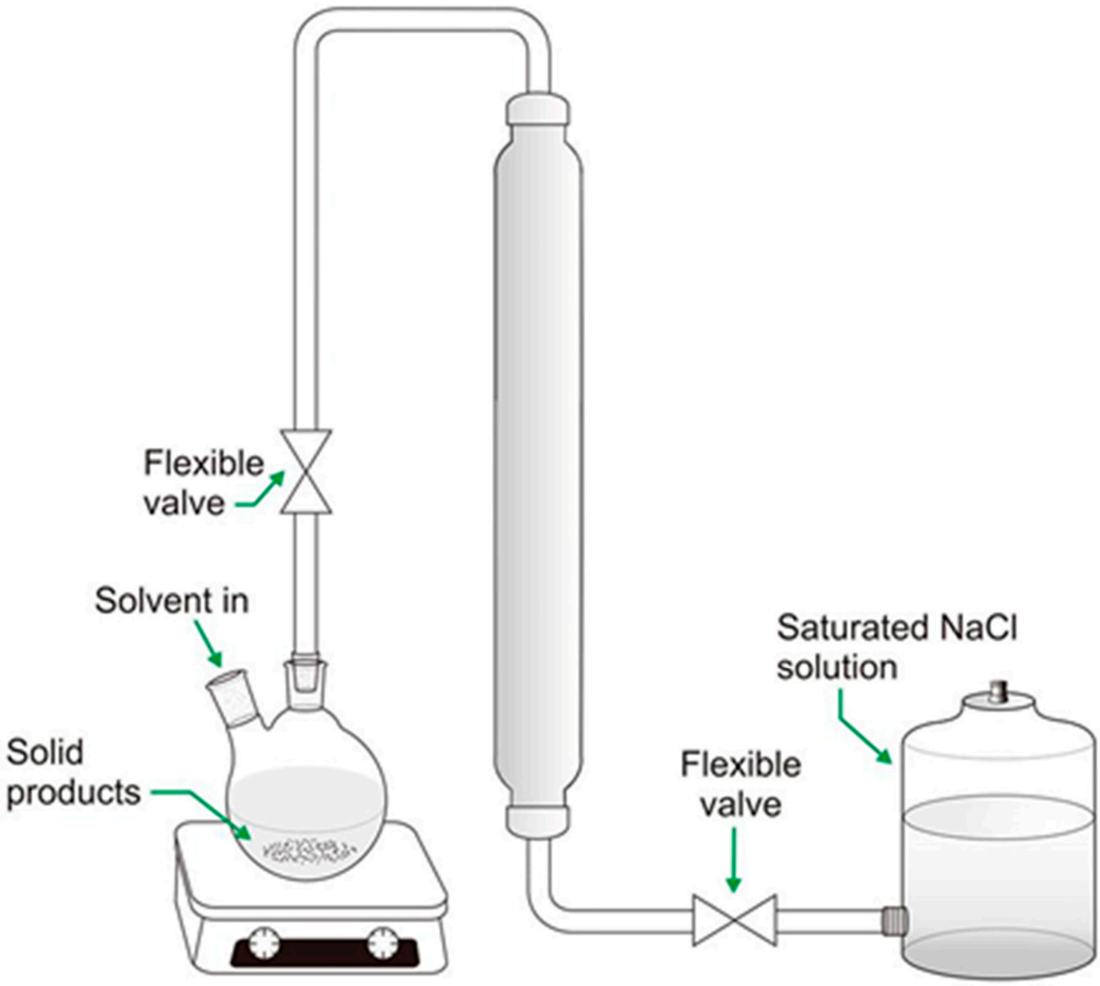

Figure S11. Schematic diagram of a hydrogen evolution apparatus.