Supporting Information

for

Realizing Facile Regeneration of NaBH₄ by Mg-Al Alloy


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**Fig. S1** XRD patterns of the raw materials: $\text{Mg}_{17}\text{Al}_{12}$ (red line) and $\text{NaB(OH)}_4$ (blue line).
Fig. S2 XRD patterns of the 1, 2, 5, 10 and 20 h ball milled products of Mg$_{17}$Al$_{12}$ and NaB(OH)$_4$ (in a 4:17 mole ratio).
Fig. S3 XPS spectra of Al 2p of the 1 h ball milled products of pure Mg₁₇Al₁₂.
Fig. S4 (a) XRD pattern of the 5 h ball milled product of Al and NaB(OH)$_4$ with a mole ratio of 24:9.
Table S1. Reaction mechanism, yield, optimal reaction condition and cost calculation of raw materials for NaBH₄ produced by different approaches.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Reaction mechanism</th>
<th>Yield</th>
<th>Cost (US $/ ton)</th>
<th>Optimal reaction condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₁₇Al₁₂, NaB(OH)₄</td>
<td>Hydrogen in NaB(OH)₄ transforms to H⁻ via the reaction with Mg₁₇Al₁₂ and produce NaBH₄, MgO and Al₂O₃.</td>
<td>72%</td>
<td>14,550</td>
<td>Raw materials mole ratio is 4 : 17; ball milling time is 20 h.</td>
</tr>
<tr>
<td>MgH₂, NaBO₂</td>
<td>Hydrogen from MgH₂ transfer to NaBO₂ and produce NaBH₄ and MgO.</td>
<td>76%</td>
<td>280,630</td>
<td>Raw materials mole ratio is 2.8 : 1; ball milling time is 6 h.</td>
</tr>
<tr>
<td>NaH, B(OCH₃)₃ (commercial method)</td>
<td>Via a heating treatment, hydrogen from NaH substitutes the [(OCH₃)₃]⁻ and produce NaBH₄ and NaOCH₃.</td>
<td>99.5%</td>
<td>18,670</td>
<td>With a B(OCH₃)₃ excess of 6.5 folds.</td>
</tr>
<tr>
<td>Mg, NaB(OH)₄, NaBO₂</td>
<td>Hydrogen in NaB(OH)₄ transforms to H⁻ via the reaction with Mg and produces NaBH₄ and MgO.</td>
<td>68%</td>
<td>10,072</td>
<td>Raw materials mole ratio is 5.5 : 1; ball milling time is 15 h.</td>
</tr>
<tr>
<td>Al, H₂, NaOH, NaBO₂</td>
<td>Hydrogen from H₂ transforms to H⁻ via the reaction between Al and NaBO₂ and produces NaBH₄ and Al₂O₃. In this process Na₂O reacts with Al₂O₃ to produce porous NaAlO₂ for the continuously reaction.</td>
<td>65%</td>
<td>497,750</td>
<td>Mole ratio of Al, H₂, NaOH and NaBO₂ is 4: 6: 4: 3. The reaction is operating under 23 bar H₂ pressure at 853 K.</td>
</tr>
</tbody>
</table>

a) According to our manuscript, a NaBH₄ yield of 37% can be achieved by ball milling Mg₁₇Al₁₂ and NaBO₂·2H₂O with a 4: 35 mole ratio. Thus about 6 tons of Mg₁₇Al₁₂ can produce 1 ton NaBH₄. Since the price of Mg₁₇Al₁₂ is $2420/ ton, the total cost of raw materials is $14550; b) In the reaction between MgH₂ and NaBO₂, MgH₂ and NaBO₂ with a ratio of 2: 1 can generate NaBH₄ with a yield of 63% ¹. About 2.21 tons of MgH₂ can thus produce 1 ton NaBH₄. Because
the price of MgH$_2$ is $127,000/\text{ton}$, then the total cost of raw materials is $280,630; \text{ c) Supposed by a yield of 100\% in current industrial production, 4.23 tons of NaH are needed for production of 1 ton NaBH}_4. \text{ The price of NaH is $4413, then the total cost of raw materials is $18,670. All the price of raw materials is from the same commercial company}^{2} \text{ The commercial method for NaBH}_4 \text{ production is based on the Brown-Schlesinger process}^{3} \text{ and the Bayer process.}^{4,5} \text{ d) In the reaction between Al, H}_2, \text{ Na}_2\text{O and NaBO}_2 \text{ with a ratio of 4: 6: 4: 3 can generate NaBH}_4 \text{ with a yield of 65\%. Therefore, about 1.46 tons of Al and 2.17 tons of NaOH can produce 1 ton NaBH}_4. \text{ Because the price of Al is $2,065/\text{ton}, while NaOH is $450/\text{ton}, then the total cost of solid raw materials is $2515. In addition, 1822000 Nm}^3 \text{ hydrogen is used to produce NaBH}_4. \text{ Considering renewable hydrogen used in this method, the price of hydrogen is about $0.27/\text{Nm}^3, thus the cost of renewable hydrogen is $493,740. The total cost of the raw materials is $497,750.}

\text{The costs of the electricity consumption are not taken into account in this case, because the electricity price depends on many factors such as production time, location, electric power company, etc. In some locations e.g. California the electricity price produced from regenerative sources becomes negative at certain times.}^{9} \text{ This makes electricity costs of the process less important. Therefore we have not considered electricity costs for the calculation.}
References


