

# Preparation of sodium borohydride by the reaction of $\text{MgH}_2$ with dehydrated borax through ball milling at room temperature

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## Abstract

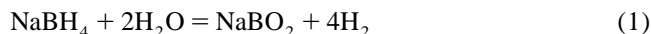
A convenient method was developed to synthesize  $\text{NaBH}_4$  by the reaction of  $\text{MgH}_2$  with  $\text{Na}_2\text{B}_4\text{O}_7$  through ball milling at room temperature. In order to improve the sodium borohydride yield, Na compounds were added to compensate the Na insufficiency in reactants when  $\text{MgH}_2$  instead of  $\text{NaH}$  was used as the reducing agent. It was found that  $\text{Na}_2\text{CO}_3$  addition was better than  $\text{NaOH}$  or  $\text{Na}_2\text{O}_2$  addition in increasing the borohydride yield.

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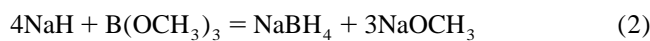
*Keywords:* Metal hydrides; Energy storage materials; Chemical synthesis; Crystal structure; X-ray diffraction

## 1. Introduction

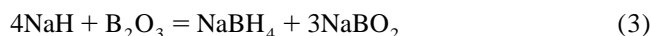
Borohydrides are well-known reducing agents. They often have quite specific uses in organic and inorganic chemistry, where they may also be the sources of  $\text{H}^-$  other than simple reductants. Recently they have attracted more attention as a hydrogen storage medium due to their high hydrogen storage capability. For example,  $\text{NaBH}_4$  contains 10.6 wt.% hydrogen which is much more than what most hydrogen storage alloys have. Furthermore, the hydrolysis of borohydride is of interest in hydrogen generation because half of the generated hydrogen is from the borohydride and the other half is from water.  $\text{NaBH}_4$  can generate 10.8 wt.% of hydrogen based on the following hydrolysis reaction.



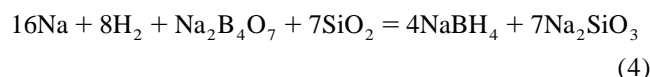
Its hydrogen generation rate, when using some catalysts, is rather high at room temperature compared with the hydrogen desorption rate of metal hydrides. However, only very few investigations have been done on borohydride synthesis since the 1950s, when Schlesinger et al. [1] proposed a rapid reaction at 225–275 °C of 1 mol of methyl borate with 4 mol of sodium hydride



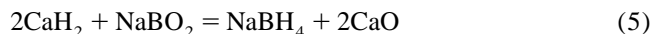
At higher temperatures (330–350 °C), sodium hydride and boric oxide react to produce up to 60% yields of sodium borohydride by the following reaction:



Sodium borohydride can also be synthesized by heating a mixture of dehydrated borax, quartz and sodium metal under hydrogen gas to higher temperatures of 450–500 °C through the following reaction [2].



Besides sodium hydride, calcium hydride has been used to react with  $\text{NaBO}_2$  to prepare  $\text{NaBH}_4$  in the same temperature range [3]



All these reactions mentioned above were conducted at higher temperatures. In this paper, a new method is proposed to prepare sodium borohydride through a mechano-chemical reaction at room temperature. The mechano-chemical reaction was conducted by ball milling the reactants in a planetary ball mill. Mg hydrides were used as the reducing agent to react with dehydrated borax, considering that  $\text{MgH}_2$  (7.60 wt.%) contains more hydro-

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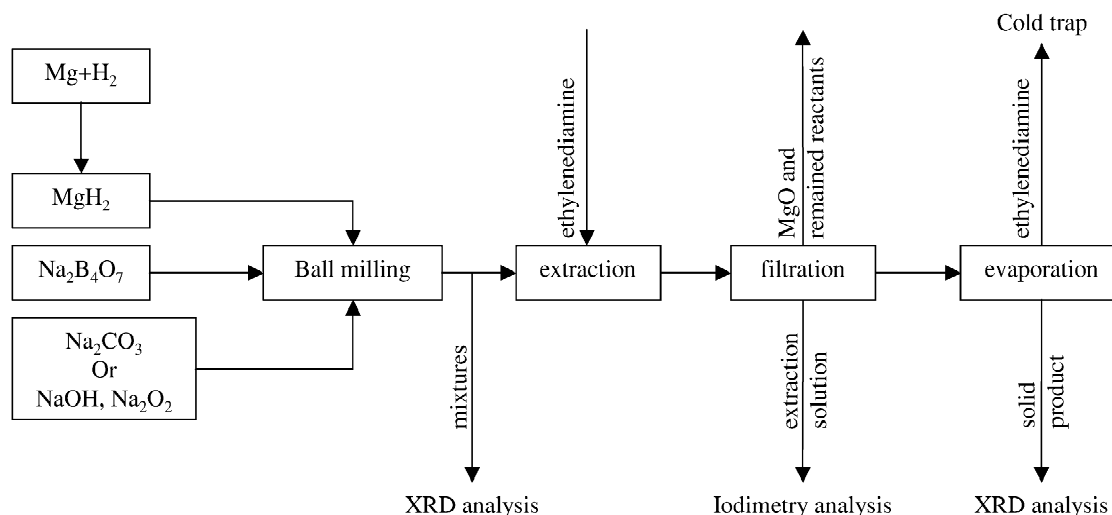


Fig. 1. Scheme of experimental procedures.

gen than NaH (4.17 wt.%) and CaH<sub>2</sub> (4.76 wt.%). Sequential experiments were planned to explore the possibility of borohydride synthesis at room temperature as shown in Fig. 1. On the other hand, in order to improve the conversion rate from Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> to NaBH<sub>4</sub>, some Na compounds were selected as additives to investigate their effects in improving borohydride formation.

## 2. Experimental

### 2.1. Preparation of Mg hydride

Mg powders with a purity of 99.95% (size: <75 μm) were hydrogenated at 350 °C under 1 MPa hydrogen pressure after degassing for 2 h. Mg hydrides with a hydrogenation rate of 60% were formed through 24-h hydrogenation. The absorbed hydrogen was measured by a volumetric method with a Sieverts apparatus. Figs. 2 and 3 show the XRD pattern and microstructure of the hydrogenated Mg sample, respectively.

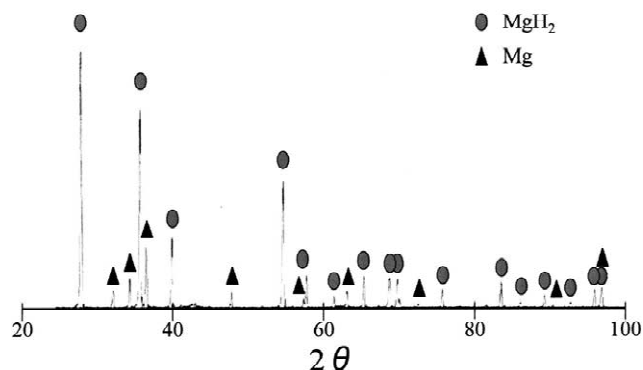


Fig. 2. XRD pattern of hydrogenated Mg.

### 2.2. Mechano-chemical reaction of dehydrated borax with Mg hydride

The mechano-chemical reaction was conducted by ball-milling a mixture of magnesium hydride, dehydrated borax and some Na compounds in a planetary ball mill at room temperature. The amount of MgH<sub>2</sub> varied from 0.835 g ( $3.175 \times 10^{-2}$  mol), i.e. 1.392 g of 60% MgH<sub>2</sub> to 4.821 g (0.183 mol), i.e. 8.035 g of 60% MgH<sub>2</sub>. The amount of dehydrated borax was fixed at 2.661 g ( $1.323 \times 10^{-2}$  mol). The amounts of Na compounds were fixed at 1.098 g ( $1.323 \times 10^{-2}$  mol) of Na<sub>2</sub>CO<sub>3</sub>, 1.058 g ( $2.645 \times 10^{-2}$  mol) of NaOH and 1.032 g ( $1.323 \times 10^{-2}$  mol) of Na<sub>2</sub>O<sub>2</sub>, respectively. The reaction components were put into a 45-ml grinding bowl with seven grinding balls having diameters of 13 mm. The grinding bowls and balls were made of stainless steel. Ball milling was then conducted at room temperature at 2750 rpm for 60 min. Fig. 4 shows the grinding bowl and the grinding mechanism.

The samples were subjected to a qualitative XRD

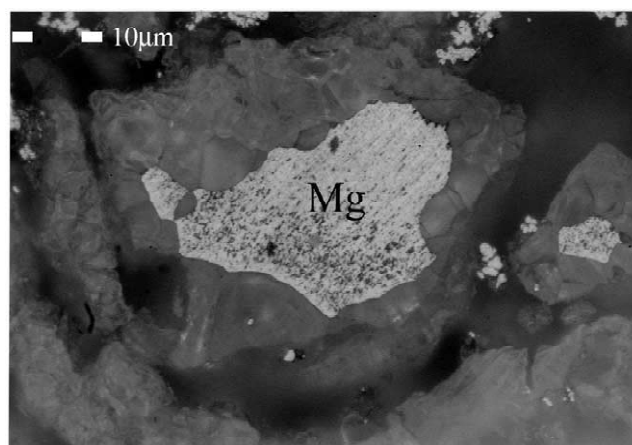


Fig. 3. Microstructure of hydrogenated Mg particle.

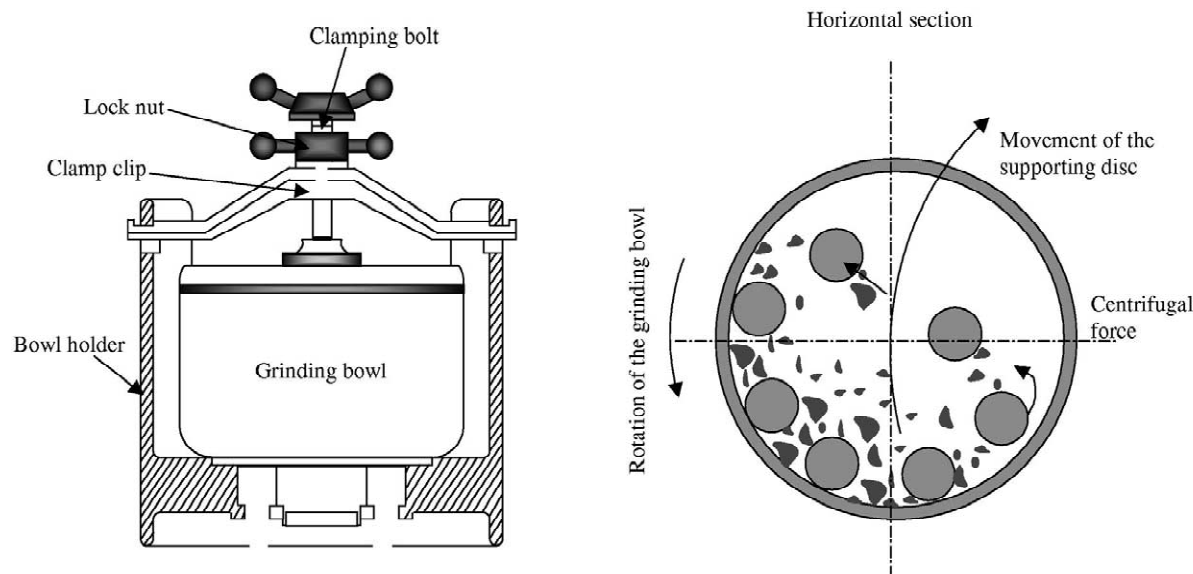


Fig. 4. Grinding bowl and grinding mechanism of the ball mill.

Table 1  
Purities of the used chemicals

Chemicals	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	Na <sub>2</sub> CO <sub>3</sub>	NaOH	Na <sub>2</sub> O <sub>2</sub>
Purity (%)	99	99	98	98

analysis after ball milling. The product (NaBH<sub>4</sub>) was extracted by anhydrous ethylenediamine with a purity of 99% under an Ar atmosphere. Hardened filter paper was used to separate the extraction solution from MgO and remaining reactants. The solid product (NaBH<sub>4</sub>) was obtained by evaporating the extraction solution under 0.05 MPa at room temperature. A cold trap was applied to capture the solvent vapor (ethylenediamine) at  $-10^{\circ}\text{C}$ . The obtained powders were subjected to XRD analysis for qualitative identification of the borohydride formation. The amount of formed NaBH<sub>4</sub> was quantitatively determined by iodimetric analysis [5]. The purities of the chemicals used are listed in Table 1.

### 3. Results and discussion

From published results [1–3], it is known that hydrides react with borates to form borohydride and oxide. According to the mass conservation law, when MgH<sub>2</sub> instead of

NaH was used as the reducing agent to react with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, it can be expected that the low Na content in the reactants would restrain the borohydride formation because the atomic ratio of Na and B in the reactant Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> is 1:2, but that in the product NaBH<sub>4</sub> is 1:1. Therefore, in order to improve the borohydride yield, some sodium compounds should be supplied to compensate for the Na insufficiency. Na<sub>2</sub>CO<sub>3</sub>, NaOH and Na<sub>2</sub>O<sub>2</sub> were selected as test materials. As a comparison, borohydride yields without Na compound additive were also investigated. The borohydride yield rate is referred to as the amount of sodium borohydride formed by 1 mol of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> to the theoretical value based on the corresponding reaction (see reactions (6)–(9) in Table 2). The Gibbs standard reaction energy ( $\Delta G^{\circ}$ ) is listed in Table 2. The calculation was done based on data of the Gibbs standard formation energy (298.15 K) [4]. From the thermodynamic calculation, it follows that all these reactions are possible in practice as regards thermodynamics.

Fig. 5 shows the XRD qualitative analysis of the sample after ball milling a mixture of MgH<sub>2</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and Na<sub>2</sub>CO<sub>3</sub> in a mole ratio of 9.24:1:1 based on reaction (6). The X-ray diagram verified the existence of NaBH<sub>4</sub> and MgO. Fig. 6 gives the XRD result of this sample after extraction, filtration and drying. The XRD peaks clearly show the existence of NaBH<sub>4</sub>. These results prove that

Table 2  
Expected reactions of sodium borohydride formation and the Gibbs standard reaction energy and maximum yield of NaBH<sub>4</sub>

Reaction	$\Delta G^{\circ}$ (kJ/mol NaBH <sub>4</sub> )	Max. yield (%)
$8\text{MgH}_2 + \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{CO}_3 = 4\text{NaBH}_4 + 8\text{MgO} + \text{CO}_2$ (6)	-254.4	78
$9\text{MgH}_2 + \text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaOH} = 4\text{NaBH}_4 + 9\text{MgO} + 2\text{H}_2$ (7)	-360.6	64
$9\text{MgH}_2 + \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{O}_2 = 4\text{NaBH}_4 + 9\text{MgO} + \text{H}_2$ (8)	-438.4	67
$4\text{MgH}_2 + \text{Na}_2\text{B}_4\text{O}_7 = 2\text{NaBH}_4 + 4\text{MgO} + \text{B}_2\text{O}_3$ (9)	-239.7	43

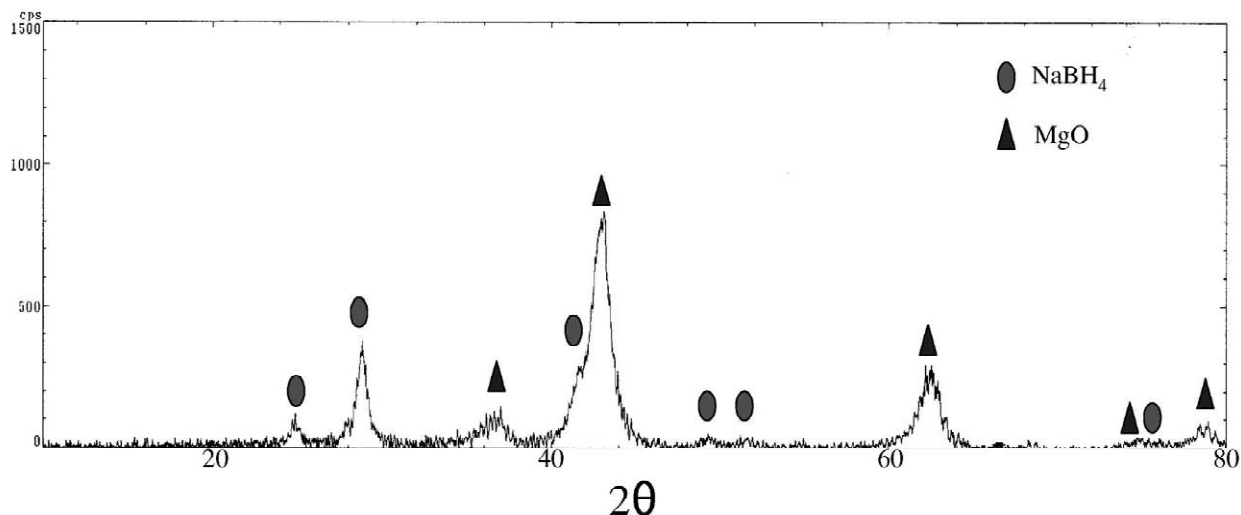


Fig. 5. XRD pattern of the sample after ball milling based on the reaction  $8\text{MgH}_2 + \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{CO}_3 = 4\text{NaBH}_4 + 8\text{MgO} + \text{CO}_2$ .

$\text{NaBH}_4$  can be synthesized by mechano-chemical reduction through ball milling at room temperature.

Fig. 7 shows the effect of the sodium compound addition on improving the  $\text{NaBH}_4$  formation. The experiments were performed through changing the  $\text{MgH}_2$  supply but the amounts of dehydrated borax and added sodium compound were fixed to the stoichiometric amounts based on reactions (6)–(9). It was found that the Na compound addition effectively promoted the  $\text{NaBH}_4$  formation compared with reaction (9).

Of all these additives,  $\text{Na}_2\text{CO}_3$  was the most effective in increasing the borohydride yield (Table 2). It is believed that  $\text{Na}_2\text{CO}_3$  is a stable salt with a very low reactivity to consume the product  $\text{NaBH}_4$ . However, when  $\text{Na}_2\text{O}_2$  was used as Na compensation agent, it was impossible to avoid oxidation of the formed  $\text{NaBH}_4$  due to its strong oxidizability. As to the NaOH addition,  $\text{Na}_2\text{B}_4\text{O}_7$  could react with NaOH to form  $\text{H}_2\text{O}$  and  $\text{NaBO}_2$  through the following reaction



The produced  $\text{H}_2\text{O}$  would consume some  $\text{NaBH}_4$  to generate  $\text{H}_2$  according to reaction (1) so that the borohydride yield was decreased. Therefore, in order to improve the borohydride formation through Na compensation, the selected Na compound should avoid reacting with the reactant ( $\text{Na}_2\text{B}_4\text{O}_7$ ) and the product ( $\text{NaBH}_4$ ).  $\text{Na}_2\text{CO}_3$  proved to be a successful example in our research.

It was noted that an excessive amount of  $\text{MgH}_2$  was needed to form the borohydride and improve the borohydride yield. This can be attributed to the fact that some  $\text{MgH}_2$  was desorbed due to high speed collisions with the balls during ball milling.

It was also noted that the amount of formed borohydride increased with increasing the amount of  $\text{MgH}_2$  supplied, but decreased when further increasing the amount of magnesium hydride after the borohydride yield reached an extreme value. It was beyond our expectation that the

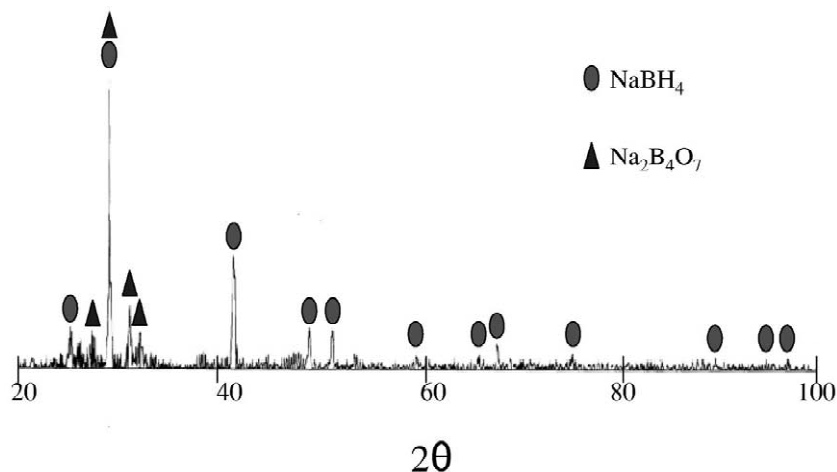


Fig. 6. XRD pattern of the product after vaporizing the extracted solution based on the reaction  $8\text{MgH}_2 + \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{CO}_3 = 4\text{NaBH}_4 + 8\text{MgO} + \text{CO}_2$ .

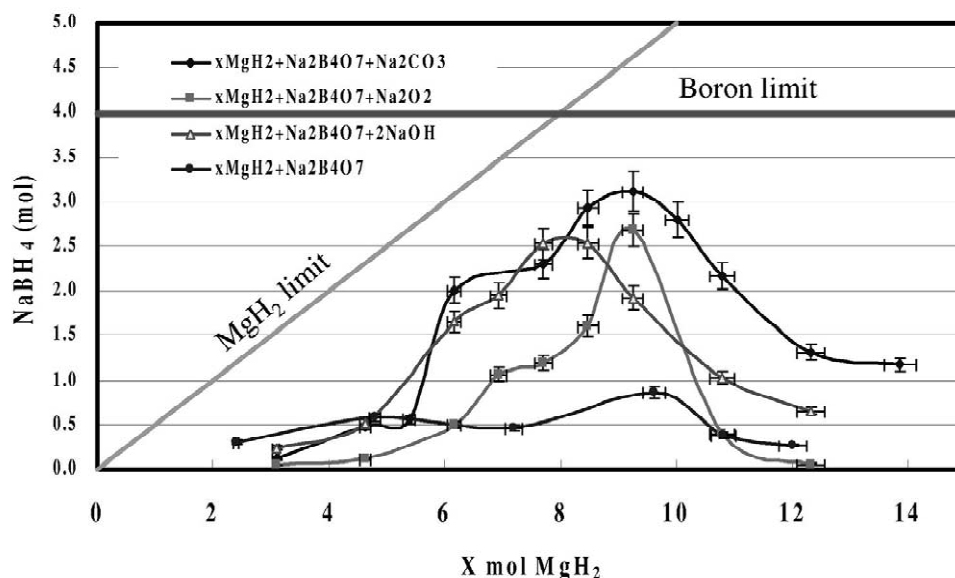


Fig. 7.  $\text{NaBH}_4$  formation when increasing the amount of  $\text{MgH}_2$ .

borohydride yield would remain constant after reaching its extreme value. When increasing the amount of  $\text{MgH}_2$ , it was found that the reactants easily stuck onto the walls of the bowl and the grinding balls, which resulted in decreasing the efficiency of the ball-milling for borohydride formation. In fact, in addition to their role as additives  $\text{Na}_2\text{B}_4\text{O}_7$  etc. also worked as a dispersant to avoid the sticking of the materials onto the walls of the bowl. It is suggested that the relative decrease in the amount of  $\text{Na}_2\text{B}_4\text{O}_7$  and Na compounds is the reason for the decrease in borohydride yield when excessive amounts of Mg hydrides are added.

#### 4. Conclusions

It has been proved that sodium borohydride can be formed from hydrated borax and magnesium hydride through ball milling at room temperature. The sodium borohydride yield can be improved by Na compensation through adding Na compounds as reactants.

#### Acknowledgements

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