Thermochemical production of sodium borohydride from sodium metaborate in a scaled-up reactor

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**Abstract**

Sodium borohydride (NaBH\textsubscript{4}) is a safe and practical hydrogen storage material for on-board hydrogen production. However, a significant obstacle in its practical use on-board hydrogen production system is its high cost. Hence, the reproduction of NaBH\textsubscript{4} from byproducts that precipitate after hydrolysis is an important strategy to make its use more cost effective. In this work, we focused on the optimization of thermochemical NaBH\textsubscript{4} reproduction reaction in a large-scaled reactor (~100 ml), and we investigated the effects of the reaction temperature (400–600 °C) and H\textsubscript{2} pressure (30–60 bar) on the NaBH\textsubscript{4} conversion yield using Mg as a reducing agent. The conversion yield of NaBO\textsubscript{2} to NaBH\textsubscript{4} increased with an increase in H\textsubscript{2} pressure to 55 bar and then decreased slightly at 60 bar. The yield increased with an increase in the reactor temperature from 400 to 600 °C. The maximum yield was 69% at 55 bar and 600 °C using homogenized reactants by ball-milling for 1 h under an Ar atmosphere. Though Ca as a reducing agent makes the thermochemical reproduction reaction more favorable, the NaBH\textsubscript{4} yield was low after 1 h of production at 55 bar and 600 °C. This result may be due to the fact that Ca is not as effective as Mg in catalyzing the conversion of hydrogen gas to protide (H\textsubscript{2}O), which can substitute oxygen actively in NaBO\textsubscript{2}.

1. **Introduction**

Hydrogen is one of the future energy sources with no emission and high power density, and its chemical energy can be converted to electrical energy using fuel cells. To use hydrogen energy effectively, it is important to develop a convenient and safe hydrogen storage system \cite{1}. In the past few decades, many researchers have devoted to develop and improve hydrogen storage systems such as high-pressure vessels \cite{2}, metal hydrides \cite{3}, and carbon materials \cite{4}. However, their hydrogen storage capacity, in terms of specific energy density, is still insufficient for commercial applications. Recently, chemical hydrides such as NaBH\textsubscript{4}, LiBH\textsubscript{4}, NaH and NaAlH\textsubscript{4} have received considerable attention as excellent hydrogen storage materials. Among them, sodium borohydride (NaBH\textsubscript{4}) has used the most due to its safe property and an economical cost compared with other chemical hydrides \cite{5–15}. NaBH\textsubscript{4} offers a high hydrogen storage density, up to 10.8 wt.%, and is able to produce hydrogen by a hydrolysis reaction according to (Eq. (1));

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} = \text{NaBO}_2 + 4\text{H}_2, \quad \Delta H = 217 \text{ kJ/mol}
\]
Because the hydrolysis reaction by NaBH₄ is significantly impeded by the presence of hydroxide ions, NaBH₄ can be stored safely and stably in an alkaline solution (pH > 11) at room temperature [5]. To generate H₂ from the alkaline NaBH₄ solution, a suitable catalyst is needed to promote the hydrolysis of NaBH₄. Noble metal-based catalysts using Ru and Pt have been reported to promote high catalytic activity for the hydrolysis of NaBH₄ [6–8]. However, noble metal-based catalysts are too expensive to be used on an industrial scale. Moreover, economical alternative catalysts with a similarly high catalytic activity such as Co powder, Co₇B, Ni₇B, Ni₇P, Co₇P, Co₇P–B and Co–Ni–P–B have been studied [10–15].

A significant obstacle in the practical use of this on-board hydrogen production system is the high cost. The cost of NaBH₄ is approximately $40–$55/kg, and the production cost of 1 kg H₂ is $240–$330 [16,17]. This production system is almost 100 times more costly than that of hydrogen produced from chemical hydrogen production using natural gas or coal oil. To solve this problem, many researchers have focused on the reproduction of NaBH₄ from byproduct NaBO₂, which remains after hydrogen production [16,18–22]. Among the various reproduction methods such as mechanical [18], electrical [19], and thermochemical process [16,20–22], the thermochemical processes using reducing agents under high H₂ pressure and temperature have shown the highest reproduction yield (efficiency) of more than 50% [16,21,22]. The thermochemical reaction is represented as follows:

\[
\text{NaBO}_2(\text{s}) + 2\text{H}_2(\text{g}) + x\text{Re}(\text{s}) \rightarrow \text{NaBH}_4(\text{s}) + \text{Re}_x\text{O}_2(\text{l}) 
\] (2)

In the above equation, Re denotes the reducing agents such as active metals (Mg, Ca, Na, Al, etc.) and metal hydrides (MgH₂, CaH₂, etc.). Kojima et al. [21] have used MgH₂ as a reducing agent and obtained NaBH₄ conversion yields greater than 95% under 550 °C and 7 MPa. However, when using Mg as a reducing agent, the yield was below 10%. The Gibbs free energy (ΔG) of the reaction (~342 kJ/mol) using Mg is lower than that of the reaction using MgH₂ (~270 kJ/mol). Therefore, it might be possible to use Mg as a reducing agent in the reaction through optimization of the reaction procedures and conditions. Suda et al. [22] and Li et al. [16] have reported that the conversion yield using Mg was above 90% at 31 bar and 600 °C. Mg can be an excellent catalyst to convert hydrogen gas into protide (H⁺), resulting in accelerated formation of NaBH₄ from NaBO₂ by active protide (H⁺). In the previous results, most of the researchers [16,21,22] have used a small amount of reactants (~mg) in a small-scaled reactor (below 5 ml) experimentally. However, to use this process practically, a scale-up of the system including reactor and reactants is necessary. In the larger scale system, the optimized production conditions might be different from those in previous results as a result of changes in kinetic factors with heat conduction and hydrogen diffusion. For practical, larger scale use of the thermochemical NaBH₄ reproduction system, the reaction conditions must be optimized, including temperature, H₂ pressure, reaction time, and process sequence. The ball-milling of reactants (NaBO₂ + Mg) can decrease the particle size, and thus increase their contact surface area. This outcome may increase the conversion yield even in a large-scaled reactor by facilitating deep penetration of hydrogen species into NaBO₂ and increasing the catalytic site of the reducing agents (Mg) to transfer from hydrogen to active protide (H⁺).

In this work, various reducing agents such as Mg and Ca, the ball-milling of reactants, and varying H₂ pressures and temperatures are investigated to determine their effect on the conversion yield of NaBH₄ in a scaled-up reactor (10–20 g reactants in a 100 ml-reactor).

2. Experimental methods

2.1. Setup of reactor

Fig. 1 presents a scheme of the homemade system for thermochemical hydride production to induce high temperature
and H₂ pressure in the reactor. The system is composed of inlet gas lines, outlet gas lines, a reactor, furnace, temperature sensors (located in the reactor inside, reactor outside, and furnace), pressure sensors, a BPR (back pressure regulator), two condensers with cooling water inlet (CWI) and outlet (CWO), a vacuum pump for removing the remained residual oxygen, and vent lines. In Fig. 1, the reactor has an internal volume of 100 ml and is constructed of Ni-based alloy (Inconel 600) that has high corrosion resistance at high temperatures. The upper limit for temperature and H₂ pressure are 700 °C and 70 bar, respectively.

2.2. Preparation of reactants

To produce NaBH₄ from NaBO₂ (byproduct after hydrolysis of Eq. (1)) thermochemically, anhydrous sodium metaborate (NaBO₂, Kosundo chemical) was prepared. As reducing agents, Mg powder with a particle size of approximately 100 μm and Ca powder with a particle size of approximately 100 μm particle size were prepared. To homogenize and increase the contact surface area between the reactant (NaBO₂) and the reducing agents, the ball-milling was conducted for 1 h under an Ar atmosphere.

2.3. Production conditions

Fig. 2 shows the change in reactor temperature and H₂ pressure as a function of time over the course of the reproduction process (in the case of 600 °C and 60 bar for 1 h). First, the reactor was evacuated for 30 min at 100 °C, and hydrogen gas was injected into the reactor to reach a constant pressure (60 bar in the case of Fig. 2). The H₂ pressures were varied from 30 to 60 bar. Afterward, the reactor temperature was increased to a constant value (600 °C in the case of Fig. 2) and held at that value for 1 h. After the initial heating, the reactor temperature was controlled from 300 to 600 °C for 1 h. To shut down the reactor, the heat and H₂ gas pressure were removed, and the products were obtained when the reactor temperature decreased to room temperature.

2.4. Product characterizations

The surface morphology of the reactants and products was analyzed using scanning electron microscopy (SEM). The composition of the products was analyzed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). NaBH₄ yields were assessed by measuring the total amount of hydrogen gas generated from the product. The product was inserted into a strong alkaline solution for stable storage. Then, a Co–P catalyst [14,15] was placed into the solution, and the hydrogen was generated quickly. The amount of H₂ generated during hydrolysis was measured automatically by a mass flow meter (MFM). In this method, most of the hydrogen was produced from the synthesized NaBH₄ rather than the intermediate product MgH₂ because MgH₂ hardly reacts [21] to form hydrogen. An equation for the calculation of NaBH₄ production yield is as follows:

\[
\text{NaBH}_4 \text{ yield} = \frac{16.3 PV_{H_2}}{RTW_s} \tag{3}
\]

\(V_{H_2}\) and \(W_s\) denote hydrogen generation volume (l) and the amount of NaBO₂ (g), respectively. \(P\) and \(T\) represent gas pressure (atm) and gas temperature (K), respectively. \(R\) represents the gas constant, and 16.3 is a constant calculated as follows:

\[
16.3 = 2(H_2 \text{ MW}) \times \frac{66(\text{NaBO}_2 \text{ MW})}{38(\text{NaBH}_4 \text{ MW})}/0.213 \tag{4}
\]

3. Results and discussion

3.1. Effects of hydrogen pressure and reactor temperature on the conversion yield

Fig. 3 shows the FT-IR spectrum of the product synthesized at 60 bar and 600 °C, from the process sequence demonstrated in Fig. 2. The two absorption peaks of 1120 and 2280 cm⁻¹ indicate the B–H deformation vibration and B–H stretching vibration, respectively. These peaks indicate the presence of NaBH₄ in the products [21]. It was reported that at 450–550 °C, dehydrogenation of the intermediate product MgH₂ (which is synthesized
at 400–430 °C occurs [16,21]. With an increase in the temperature above 450 °C, the formation of NaBH₄ begins. In the temperature range (450–530 °C) shown in region a of Fig. 2, a dramatic increase in the reactor temperature and instant decrease in H₂ pressure occurs and is likely due to the initiation of the exothermic reaction in Eq. (2) and hydrogenation of NaBO₂, respectively. Afterward, the temperature increased gradually to the set temperature of 600 °C (Fig. 2, region b). Upon reaching 600 °C, the temperature held constant for 1 h. However, as shown in region c of Fig. 2, a fluctuation in the temperature was detected for approximately 30 min. The elevated temperatures during this small fluctuation may be due to the exothermic hydrogenation reaction of NaBH₄ formation. Then, the conversion yield of the products was confirmed to be 63%. The temperature and pressure (and thus the NaBH₄ production yield) can be significantly affected by hydrogenation and dehydrogenation of NaBO₂, Mg, and NaBH₄. Therefore, the effects of reactor temperature and applied H₂ pressure on the NaBH₄ conversion yield were investigated. Fig. 4a shows the NaBH₄ conversion yield as a function of the reactor temperature at a constant applied pressure of 60 bar, using Mg as a reducing agent. With an increase in the temperature from 400 °C to 500 °C, the yield increased linearly. However, from 500 to 600 °C, the rate of increase was slightly lower. These results indicate that the production reaction does not depend largely on the temperature when operating above 500 °C, as the dehydrogenation of the intermediate phase (MgH₂) and the formation of NaBH₄ occur above approximately 500 °C [16,22]. Moreover, despite an increase in the reaction activity from 500 °C to 600 °C, the rate of yield is reduced in this temperature range because such high temperatures cause the newly synthesized NaBH₄ to decompose [21]. Therefore, especially when using a small-scaled reactor [21], the yield decreased from 500 to 600 °C. However, the reason why the yield increases from 500 to 600 °C in a large-scaled reactor is likely due to a decrease in the decomposition rate of NaBH₄ as a result of a decrease in the heat conduction rate.

Fig. 4b shows the effects of applied H₂ pressure on the NaBH₄ conversion yield at a reaction temperature of 600 °C. With increasing H₂ pressure, from 30 to 40 bar, the yield increased. However, from 40 to 50 bar, the yield remained constant at 54–55%. Then, the yield showed a maximum value of 63% at 55 bar. With a further increase to 60 bar, the conversion yield decreased to 56%. This decline was likely due to a decrease in dehydrogenation of the intermediate phase, MgH₂. That is different behavior from the previous results [16,21,22] obtained from a small-scaled reactor likely due to a decrease in hydrogen diffusion and penetration rates in a large-scaled reactor. Fig. 5 shows the XRD patterns of the products, which were synthesized at 600 °C under applied H₂ pressures of 55 bar (a) and 60 bar (b). In the two patterns, large peaks indicating NaBH₄ and MgO are presented, indicating that the reproduction reaction was successful. However, NaBO₂ also remained in the product. The intermediate material, MgH₂ was detected in the products synthesized at 60 bar and 600 °C. This finding may have resulted from the fact that decomposition of MgH₂ is difficult under H₂ pressures greater than 60 bar, and Fig. 5b offers good support of this hypothesis. From these results, it is clear that the optimal H₂ pressure and temperature were 55 bar and 500–600 °C, respectively.

### 3.2. Effects of ball-milling of reactants on the conversion yield

Fig. 6a and b presents the surface morphologies of reactants (NaBO₂ and Mg powder) before and after ball-milling for 1 h.
under Ar atmosphere. Before the ball-milling process, the particle sizes of Mg and NaBO₂ were 100–200 μm and 10–50 μm, respectively, as shown in Fig. 6a. After ball-milling, the size of all the particles decreased to below 1 μm, as shown in Fig. 6b. Hence, the ball-milling treatment is expected to homogenize and increases the contact surface area between the reactant (NaBO₂) and the reducing agents (Mg), resulting in increased NaBH₄ conversion yield even in a large-scaled reactor. After the NaBH₄ production process at 55 bar and 600 °C for 1 h, when using the ball-milled reactants (Fig. 6b), the conversion yield increased by 5%, compared to the process using reactants that were not ball-milled (Fig. 6a). The ball-milling effect on the NaBH₄ conversion yield was not large, indicating that the effect of homogenization of reactants is not a significant factor during the production of NaBH₄ in a large-scaled reactor. After the NaBH₄ production process at 55 bar and 600 °C for 1 h, when using the ball-milled reactants (Fig. 6b), the conversion yield increased by 5%, compared to the process using reactants that were not ball-milled (Fig. 6a). The ball-milling effect on the NaBH₄ conversion yield was not large, indicating that the effect of homogenization of reactants is not a significant factor during the production of NaBH₄ in a large-scaled reactor. Fig. 6c shows the SEM surface morphology of the product, which was synthesized from non-ball-milled reactants at 55 bar and 600 °C for 1 h. The atomic mapping images after the production process are also shown. Based on Fig. 6c, the products have a porous surface composed of agglomerated particles with diameters of 10–50 μm. Mg (of MgO) and Na (of NaBH₄) were detected in all regions of the particles. These findings indicate that NaBH₄ and MgO were sufficiently homogenized without ball-milling of the reactants.

3.3. Effects of Ca as a reducing agent on the NaBH₄ production

The Gibbs free energy of the reaction when using calcium (ΔG° (Ca)) as a reducing agent is −416 kJ/mol-NaBH₄. This value is lower than the Gibbs free energy for Mg as a reducing agent (ΔG° (Mg) = −342.02 kJ/mol), indicating that the chemical reaction using Ca is more thermodynamically favorable. Fig. 7a shows the XRD pattern of the products after the NaBH₄ production reaction (Eq. (2)) using Ca as a reducing agent. However, no peak for NaBH₄ was detected, suggesting that NaBH₄ was hardly synthesized. Instead of NaBH₄, a large amount of CaH₂ was synthesized and a large amount of NaBO₂ remained. The catalytic effect of Ca was likely not induced because of the small contact area. The production procedure
was performed after ball-milling the reactant mixtures of NaBO₂ and Ca. Nevertheless, NaBH₄ was not synthesized as shown in Fig. 7b, but the production of CaH₂ increased significantly, and the amount of NaBO₂ decreased. As the previous reports indicate [16,22], Mg can be an excellent catalyst to convert hydrogen gas into protide (H⁻), thus accelerating the formation of NaBH₄ from NaBO₂ by active protide (H⁻). Furthermore, it is presumed that Ca plays little to no catalytic role in converting hydrogen gas to protide (H⁻). Based on this result, the thermodynamic favorability of the reaction, as represented by the Gibbs free energy, is not a significant factor, but the catalytic effects of the reducing agent are likely more important to the production of NaBH₄ from the thermochemical reaction in Eq. (2).

4. Conclusions

In this work, we optimized the thermochemical NaBH₄ reproduction reaction in a large scale reactor (~ 100 ml), and investigated the effects of reaction temperature (400–600 °C) and H₂ pressure (30–60 bar) on the thermochemical recycling yield of sodium borohydride (NaBH₄) from sodium metaborate (NaBO₂). The conversion yield of NaBO₂ to NaBH₄ increased with an increase in H₂ pressure to 55 bar and decreased slightly at 60 bar. The yield increased with an increase in reactor temperature from 400 to 600 °C. The effects of reaction temperature and pressure on the conversion yields showed different behavior from the previously reported results using a small-scaled reactor likely due to difference of heat conduction and mass transfer. The maximum yield was 69% at 55 bar and 600 °C using homogenized reactants by 1 h-ball-milling under an Ar atmosphere. From atomic mapping results, NaBH₄ and MgO in the products were well homogenized, indicating that a scale-up of the NaBH₄ reproduction system may not decrease the conversion yield. Despite the fact that the thermochemical reproduction reaction is more thermodynamically favorable, using Ca as the reducing agent resulted in a low yield of NaBH₄ after 1 h of production at 55 bar and 600 °C. This result may be due to the fact that Ca is not as effective a catalyst as Mg in converting hydrogen gas to protide (H⁻), which can substitute oxygen actively in NaBO₂.

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REFERENCES