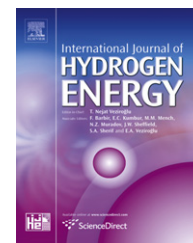


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Thermochemical production of sodium borohydride from sodium metaborate in a scaled-up reactor

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ABSTRACT

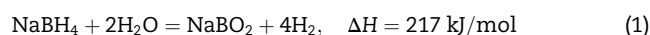
Sodium borohydride (NaBH₄) is a safe and practical hydrogen storage material for on-board hydrogen production. However, a significant obstacle in its practical use on-board hydrogen production system is its high cost. Hence, the reproduction of NaBH₄ from byproducts that precipitate after hydrolysis is an important strategy to make its use more cost effective. In this work, we focused on the optimization of thermochemical NaBH₄ reproduction reaction in a large-scaled reactor (~100 ml), and we investigated the effects of the reaction temperature (400–600 °C) and H₂ pressure (30–60 bar) on the NaBH₄ conversion yield using Mg as a reducing agent. The conversion yield of NaBO₂ to NaBH₄ increased with an increase in H₂ 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 NaBH₄ 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[−]), which can substitute oxygen actively in NaBO₂.

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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 [1]. In the past few decades, many researchers have devoted to develop and improve hydrogen storage systems such as high-pressure vessels [2], metal hydrides [3], and carbon materials [4]. However, their hydrogen storage capacity, in terms of specific energy density,

is still insufficient for commercial applications. Recently, chemical hydrides such as NaBH₄, LiBH₄, NaH and NaAlH₄ have received considerable attention as excellent hydrogen storage materials. Among them, sodium borohydride (NaBH₄) has used the most due to its safe property and an economical cost compared with other chemical hydrides [5–15]. NaBH₄ 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));



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Because the hydrolysis reaction by NaBH_4 is significantly impeded by the presence of hydroxide ions, NaBH_4 can be stored safely and stably in an alkaline solution ($\text{pH} > 11$) at room temperature [5]. To generate H_2 from the alkaline NaBH_4 solution, a suitable catalyst is needed to promote the hydrolysis of NaBH_4 . Noble metal-based catalysts using Ru and Pt have been reported to promote high catalytic activity for the hydrolysis of NaBH_4 [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, Co–B, Ni–B, Ni–P, Co–P, Co–P–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 NaBH_4 is approximately \$40–\$55/kg, and the production cost of 1 kg H_2 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 NaBH_4 from byproduct NaBO_2 , 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 H_2 pressure and temperature have shown the highest reproduction yield (efficiency) of more than 50 % [16,21,22]. The thermochemical reaction is represented as follows:



In the above equation, Re denotes the reducing agents such as active metals (Mg, Ca, Na, Al, etc.) and metal hydrides (MgH_2 , CaH_2 , etc.). Kojima et al. [21] have used MgH_2 as a reducing agent and obtained NaBH_4 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 MgH_2 (–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 NaBH_4 from NaBO_2 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 NaBH_4 reproduction system, the reaction conditions must be optimized, including temperature, H_2 pressure, reaction time, and process sequence. The ball-milling of reactants ($\text{NaBO}_2 + \text{Mg}$) 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 NaBO_2 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 H_2 pressures and temperatures are investigated to determine their effect on the conversion yield of NaBH_4 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

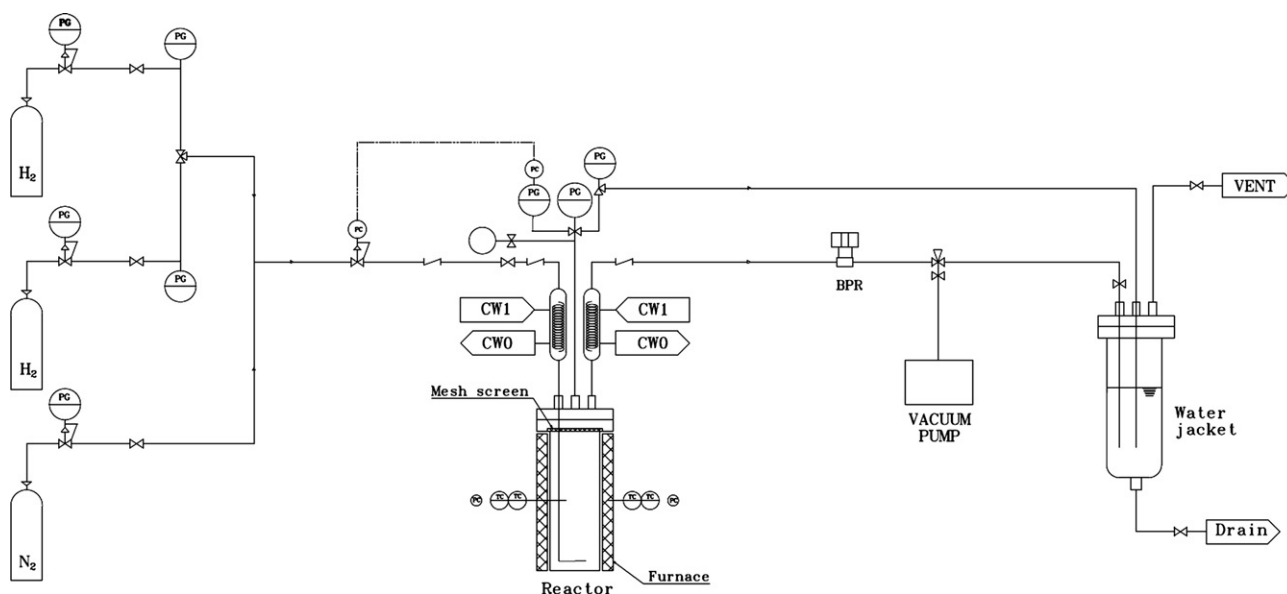


Fig. 1 – A scheme of the homemade thermochemical hydride production system.

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