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New insights on the mechanism of vapour phase hydrolysis of sodium borohydride in a fed-batch reactor

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ABSTRACT

This study aims to produce H_2 from sodium borohydride ($NaBH_4$) and to initiate its hydrolysis at elevated temperature in the absence of a catalyst. Experimental results indicated that the hydrogen generation yield increased up to %99 at 150 °C in the $NaBH_4$ concentration of %5 wt in the acidic medium. It can be concluded that experimental characterization of the by-products is quite important since they affected the reaction mechanism or pathway. When the experiments are carried out under aqueous condition, the primary by- product is sodium metaborate while it is boric acid under acidic condition. It is postulated that by-product boric acid decreased the mass transfer limitation due to its higher solubility that prevents the formation of shell and thus increases the contact area between $NaBH_4$ and vapor. A series of fed-batch reactions were performed to confirm the hypothesis, and the conversions of $NaBH_4$ reached 99% under the acidic condition.

Introduction

A lot of studies have been carried out on the reactions of boron-based chemical hydrides ($NaBH_4$, $LiBH_4$ etc.) as a chemical hydrogen storage materials [1–5]. Sodium borohydride (SBH) has been extensively investigated as a medium for the chemical storage of hydrogen [6–9]. The strength of $NaBH_4$ lies in its attractive properties: it is relatively safe, has the ability to dehydrogenate in mild conditions, and has a high gravimetric hydrogen sodium borohydride ($NaBH_4$, SBH, 10.8% wt H_2) density. SBH is known to be non-toxic, explosion-safe and relatively stable, and inexpensive, and thus has been introduced as being the storage solution for vehicular applications [7].

Hydrogen production from SBH has been achieved by thermolysis, catalytic hydrolysis, steam or vapor hydrolysis, and methanolysis [8–11]. Considering the chemical formula of SBH ($NaBH_4$), it is possible to form 2 mol of hydrogen from 1 mol of SBH. The important advantage of hydrolysis (Eq. (1)) is that it can produce 4 mol of hydrogen per 1 mol of SBH, two from SBH itself and two from water. Hence, the hydrolysis method is preferred rather than thermolysis and methanolysis. However, the hydrolysis reaction of SBH requires a relatively expensive catalysts made in noble mono or bimetallic metals and satisfies the requirement for the purity of the hydrogen fed to the PEM fuel cell. For example; Alumina nanofiber-stabilized ruthenium nanoparticles [12], Co-B

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catalysts [13] etc. In addition, another big issue is the deactivation problem that hydrolysis by-product, sodium metaborate covers the catalyst surface and reduces the active sites of the catalyst over the time [14].

$$NaBH_{4(s)} + 2H_2O_{(l)} \xrightarrow{\text{absence or presence of catalyst}} 4H_{2(g)} + NaBO_{2(s)} \quad (1)$$

In recent years, a few studies have focused on eliminating such problems by employing vapor phase hydrolysis reaction over 100 °C in the absence of any catalysts (Eq. (2)). This method is the ability to produce high purity hydrogen with high yield, and in a short time without using any catalysts. Vapor phase batch hydrolysis of $NaBH_4$ at elevated temperature and pressure was investigated [15]. In practice, this method is provided the elimination of the main factors which lead to excess water utilization when $NaBH_4$ hydrolysis is carried out in the liquid phase. When it is desired to retain reactants and products in the solution, then excess water is essential because of the low solubility of the chemical hydride (55 g $NaBH_4$/100 g H2O at 25 °C) and the metaborate byproducts, even less soluble in water (28 g $NaBO_2$/100 g H_2O at 25 °C) [9,15–18].

$$NaBH_{4(s)} + (2 + x)\, H_2O_{(g)} \rightarrow 4H_{2(g)} + NaBO_2 \cdot xH_2O_{(s)} \quad (2)$$

The vaporizing water prior to contact with SBH, called a 'solid-phase' presumably minimizes the water utilization at any instant. This approach could lead to byproducts with lower hydration state (x, excess hydration factor). Moreover, when vapor directly contacts solid $NaBH_4$, by-product accumulation may occur (sodium metaborate) due to its low solubility where the surface of the unreacted solid SBH is covered with the by-product, thus lead to decrease the overall yield of the process [9–15, 18].

Most of the studies conducted previously investigated solid-phase vapor hydrolysis. However, there is no research into vapor hydrolysis with liquid feeding, which was used for the first time in this study. Therefore, we present an alternative solution to combine the advantage of the liquid and vapor hydrolysis method. The objective of this study is to prove the vapor hydrolysis with liquid feeding, which is thought to be more convenient and controllable for large scale, practical usage and to applications their hydrogen generation performance for the fuel cell. We also supplied a systematic investigation for the vapor hydrolysis of SBH and some progress on the reaction rate with some additives like NaOH or HCl.

Experimental

Materials

Sodium borohydride ($NaBH_4$, SBH, 99%), NaOH (99%) and HCl (37%) were purchased from Fluka, Kimetsan and Merck, respectively. In addition, deionized water, pyrex, and glass materials were used.

Vapor hydrolysis of SBH experiments

Vapor hydrolysis experimental system was shown in Fig. 1. The system consisted of glass bead filled (1 mm diameter) cylindrical fixed bed reactor (dimensions 20 mm × 200 mm), an injection pump system and a gas burette system in which the hydrogen gas volume was measured. There were two injection pumps to feed the reactant solutions into the reactor, one of which belonged to $NaBH_4$ solution ($NaBH_4$, water, NaOH), and the other to acidic solution (HCl + water), if necessary. The feed solutions were sent to the bottom or inlet part of the vertical reactor. An oil bath was used to keep the reactor temperature constant. Heating-stirring plate (IKA-RCT branded) was used to adjust the temperature of the oil bath. Glass beads were employed to prevent the foaming from occurring during the reaction and the spilling over the reactor as well as providing a uniform temperature and increasing solid-vapor interaction. Outlet of the reactor or upper was attached to a condenser with an 8 mm diameter in order to recycle the vapor. A gas burette system (250 ml) was applied for quantifying the released hydrogen from the condenser. Before the hydrolysis reaction, the leakage test for all system was so important as to effectively manage the measurements.

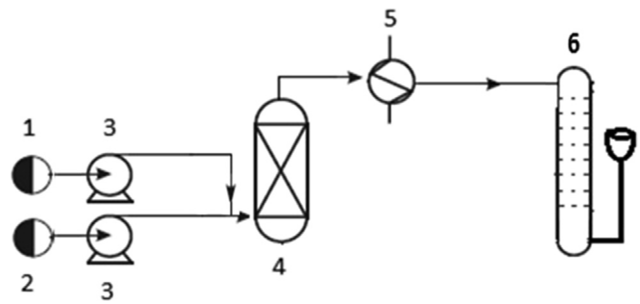

Fig. 1 – The experimental set-up: (1) and (2) reactant solutions, (3) injection pump, (4) packed column reactor, (5) reflux condenser, (6) gas burette system.

The vapor hydrolysis experiments of SBH consist of following three stages:

(1) **One feed system ($NaBH_4$-Water):** The experiments carried out under 100 °C and 3% wt. SBH and at higher than 7 % wt. SBH concentrations have demonstrated that hydrogen gas production was considerably decreased. For that reason, the vapor hydrolysis reaction was carried out at three different concentrations (3%, 5% and 7% wt. SBH solutions) and two different temperatures (130 °C and 150 °C). Once the reactor condition reached the desired temperature, the reaction was initiated by feeding 50 ml SBH solution with a flow rate of 0.66 ml/min through the injection valve. Releasing hydrogen gas against time was measured by gas burette system after the steam condensed. This measurement continued until the SBH solution ended and the water level in the gas burette system did not fluctuate.
(2) **One feed system ($NaBH_4$-NaOH-Water):** To investigate the effect of NaOH concentration, the experiments were conducted on the same system by using different NaOH concentration (0.5%, 1.0% and 7% wt) at constant SBH concentration (5% wt.).
(3) **Two feed system ($NaBH_4$-NaOH-Water) and (HCl-Water):** A second injection pump was used to scrutinize the effect of acidic medium for vapor hydrolysis