Chemical Engineering Journal 424 (2021) 130445

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Thermal hydrolysis of solid-state sodium borohydride for noncatalytic hydrogen generation

Geo Jong Kim, Hyun Tae Hwang *

Department of Chemical and Materials Engineering, University of Kentucky, 4810 Alben Barkley Drive, Paducah, KY 42002, USA

ARTICLE INFO

Keywords:
Hydrogen storage
Chemical hydride
Sodium borohydride
Thermolysis
Hydrolysis

ABSTRACT

Hydrogen from sodium borohydride ($NaBH_4$, SBH) can be generated by thermolysis or hydrolysis. Unfortunately, thermolysis of SBH requires high temperatures (>300 °C), while hydrolysis is conducted in the presence of catalyst and self-hydrolysis can cause safety concerns due to unexpected generation of hydrogen. In order for hydrolysis of SBH to be practical, efficient and safe methods to produce hydrogen are required. Here, we propose a new process, thermal hydrolysis of SBH, to generate hydrogen via hydrolysis in the solid phase. In this new process, SBH generates hydrogen by hydrolysis with water produced by thermal decomposition of boric acid (BA). Self-hydrolysis causing safety issues no longer occurs because the SBH-BA mixture in the solid-state is stable at below 80 °C. When heating the mixture, a rapid hydrogen evolution was observed at ~ 120 °C and a maximum H_2 equivalent of 3.9 was achieved at 150 °C for SBH:BA = 1:4. BA is dehydrated to form metaboric acid with a release of 1 mol H_2O at 150 °C and an additional 0.5 mol water at 200 °C. With recent progress in regeneration of SBH spent fuels, this newly proposed method is promising for hydrogen storage in proton exchange membrane fuel cell applications.

1. Introduction

As the world population and economics grow, environmental pollution surges due to an increase in use of fossil fuels. As a result, many countries have set targets for carbon neutrality and are looking for new energy sources to replace fossil fuels. In this context, hydrogen has received a great attention as a sustainable and alternative energy source because it is clean fuel or energy carrier that produces only water when it reacts with oxygen in a fuel cell. In addition, it has high calorific value per mass (120 MJ/kg) [1,2]. Despite these favorable properties, safety concerns and low energy density by volume remain important challenges to use hydrogen in practice.

Various methods have been developed for storing hydrogen efficiently and safely. Among the current approaches, the most commonly used methods for storing hydrogen for fuel cell applications are compressed or liquid hydrogen tanks. However, a relatively large volume is required for the compressed tanks, while vaporization in the liquid hydrogen can cause loss of hydrogen and safety concerns [3,4].

Unlike the physical methods mentioned above, hydrides have attracted considerable interest because they offer high H_2 capacity and improved safety. Table 1 lists theoretical and practical maximum H_2 yields and prices for various hydrides [3,5–15]. Conventional and complex metal hydrides have been considered as potential hydrogen storage materials owing to their reversibility of hydrogen adsorption and desorption. However, they release hydrogen at relatively high temperatures, provide low hydrogen yield, and show slow kinetics. On the other hand, chemical hydrides have higher hydrogen capacity and release hydrogen faster even at lower temperatures. Unfortunately, spent products after dehydrogenation of the chemical hydrides must be regenerated.

Hydrogen can be generated from chemical hydrides via thermolysis or hydrolysis. Hydrolysis can be proceeded even at room temperature. Unfortunately, actual hydrogen yield by hydrolysis of chemical hydride is low because of limited solubility in water and added catalyst to enhance the hydrogen generation kinetics. In addition, self-hydrolysis can cause safety concerns due to unexpected generation of hydrogen. Finally, B-O bonds generated by hydrolysis of borohydride are not preferred in terms of the regeneration of the spent products.

Several selected hydrides including metal, complex metal, and chemical hydrides are listed in Table 1 and they offer thermolysis to release hydrogen via thermal decomposition. Thermolysis of hydrides provides potentially high hydrogen yield and produces more

* Corresponding author.
E-mail address: hyun-tae.hwang@uky.edu (H.T. Hwang).

https://doi.org/10.1016/j.cej.2021.130445
Received 17 March 2021; Received in revised form 11 May 2021; Accepted 18 May 2021
Available online 24 May 2021