



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Ammonia borane as hydrogen storage materials

Serdar Akbayrak^a, Saim Özkar^{b,*}

^a Department of Chemistry, Sinop University, 57000 Sinop, Turkey

^b Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey

ARTICLE INFO

Article history:

Received 15 December 2017

Received in revised form

24 February 2018

Accepted 28 February 2018

Available online xxx

Keywords:

Metal nanoparticles

Ammonia borane

Hydrolysis

Hydrogen generation

Heterogeneous catalysis

ABSTRACT

Ammonia borane is an appropriate solid hydrogen storage material because of its high hydrogen content of 19.6% wt., high stability under ambient conditions, nontoxicity, and high solubility in common solvents. Hydrolysis of ammonia borane appears to be the most efficient way of releasing hydrogen stored in it. Since ammonia borane is relatively stable against hydrolysis in aqueous solution, its hydrolytic dehydrogenation can be achieved at an appreciable rate only in the presence of suitable catalyst at room temperature. Metal(0) nanoparticles have high initial catalytic activity in releasing H₂ from ammonia borane. Thermodynamically unstable metal(0) nanoparticles can kinetically be stabilized against agglomeration either by using ligands in solution or by supporting on the surface of solid materials with large surface area in solid state. Examples of both type of stabilization are presented from our own studies. The results show that metal(0) nanoparticles dispersed in solution or supported on suitable solid materials with large surface area can catalyze the release of H₂ from ammonia borane at room temperature. Dispersion of metal(0) nanoparticles, stabilized in liquid phase by anions or polymers, seems advantageous as providing more active sites compared to the metal nanoparticles supported on a solid surface. However, the supported metal nanoparticles are found to be more stable against agglomeration than the ones dispersed in liquid phase. Therefore, metal nanoparticles supported on solid materials have usually longer lifetime than the ones dispersed in solution. Examples are given from the own literature to show how to improve the catalytic activity and durability of metal nanoparticles by selecting suitable stabilizer or supporting materials for certain metal. For the time being, nanoceria supported rhodium(0) nanoparticles are the most active catalyst providing a turnover frequency of 2010 min⁻¹ in releasing H₂ from ammonia borane at room temperature.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

There is a growing interest for the ecofriendly renewable energy carriers for energy-related applications due to the increase in the energy consumption. In this concern, hydrogen has been considered as energy carrier because of its

sustainability nature, abundance and high energy density [1]. The use of hydrogen as energy carrier is anticipated to facilitate the transition from fossil fuels to the renewable energy sources, on the way towards a sustainable energy future [2]. However, the safe and efficient storage of H₂ is the major obstacle in its wide applications [3]. Therefore, much attention has been paid to the development of new materials which can

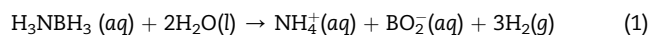
* Corresponding author.

E-mail address: sozkar@metu.edu.tr (S. Özkar).

<https://doi.org/10.1016/j.ijhydene.2018.02.190>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

provide hydrogen with high gravimetric and volumetric densities with suitable thermodynamic and kinetic properties [4]. The most effective and safest way of storing hydrogen is to use solid media such as sorbent materials [5] or hydrides [6]. Chemical hydrides provide a higher energy density for hydrogen storage as compared to the gas or liquid H₂ tank systems. Recent reports have shown that B–N adducts need to be considered as hydrogen storage materials because of their high content of hydrogen with multiple nature, the protic N–H and hydridic B–H hydrogen [4]. B–N adducts such as ammonia borane, dimethyl ammonia borane, hydrazine borane are considered as ideal hydrogen storage materials due to their high H₂ content [4]. Among these B–N adducts, ammonia borane (H₃N·BH₃, AB) is one of the most promising hydrogen storage materials because of its high hydrogen content (19.6% wt.), high stability under ambient conditions, nontoxicity, and high solubility in common solvents such as water and methanol [7]. The efficient release of hydrogen stored in the storage materials is another challenge in the hydrogen economy. Hydrogen can be released from ammonia borane by thermolysis or solvolysis in the presence of suitable catalysts. The former process has some drawbacks: i) it requires long induction time (~3 h) and high temperature, ii) various by-products, such as ammonia (NH₃) and borazine (B₃N₃H₆) can be formed during reaction [8]. Hydrolysis or methanolysis are two practical ways of hydrogen generation from ammonia borane for hydrogen fuel cell applications at ambient temperature. Hydrolysis can release 3 mol H₂ per mole of AB (Eq. (1)).



Ammonia borane is relatively stable against hydrolysis in aqueous solution (Eq. (1)). Therefore, the hydrolytic dehydrogenation of AB can be achieved at an appreciable rate only in the presence of suitable catalyst at room temperature. The hydrolysis reaction can be followed by ¹¹B-NMR spectroscopy. During the hydrolytic dehydrogenation reaction the quartet around $\delta = -24.0$ ppm for NH₃BH₃ is gradually converted to the singlet around $\delta = 10.0$ ppm for the BO₂⁻ ion [9].

Although many studies have been reported on the development of efficient catalysts for the hydrolytic dehydrogenation of AB, it is still a big challenge to develop highly active and long-lived catalyst in this reaction. Transition metal nanoparticles (NPs) have been widely used as catalysts in releasing H₂ from AB (Eq. (1)) [10]. Since the metal nanoparticles tend to agglomerate causing a significant loss in catalytic activity they need to be stabilized either by using surfactants or ligands in solution or by using supporting materials with large surface area in solid state. The results reported in literature will be given together to show (i) that metal(0) nanoparticles dispersed in solution or supported on suitable solid materials with large surface area can catalyze the release of H₂ from AB at room temperature and (ii) how to improve the catalytic activity and durability of metal(0) nanoparticles by selecting suitable stabilizer or supporting materials for a certain metal or by modifying them appropriately. Since a wide range of methods for the preparation of metal(0) nanoparticles, either dispersed in solution or supported on solid materials with large surface area, have been reported, it will be difficult to

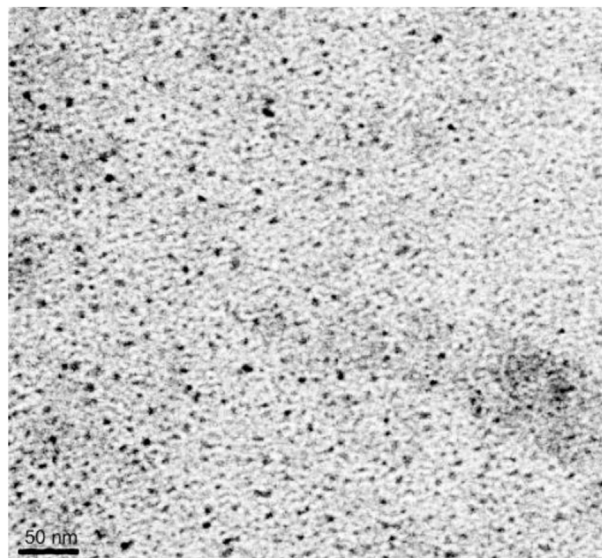


Fig. 1 – TEM image of the water soluble laurate-stabilized Rh(0) NPs obtained from the reduction of rhodium(III) ions by dimethylamine borane in the presence of laurate anion in aqueous solution. Reproduced with permission from Ref. [11]. Copyright [2009], Elsevier.

make a conclusion on the best catalyst for the hydrolytic dehydrogenation of AB. However, one has to keep in mind the well-known phenomenon that activity and stability of metal nanoparticles can be improved by preventing their agglomeration using suitable stabilizing agents. Herein, we compile the results of our recent works on the metal(0) nanoparticles which have been stabilized by anionic or polymeric stabilizers in solution or supported on the surface of solid materials as catalysts in hydrolytic dehydrogenation of AB.

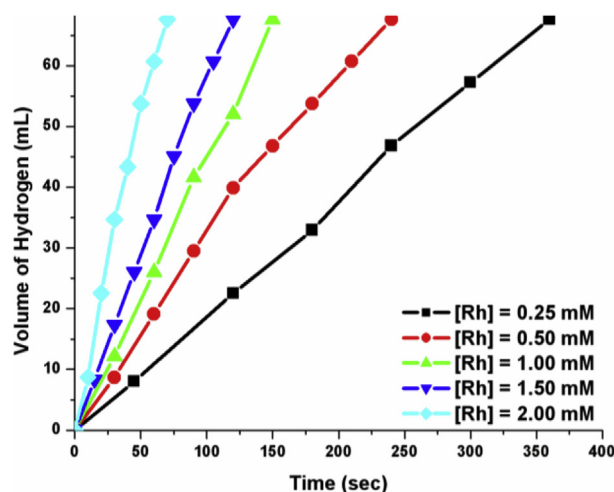


Fig. 2 – Volume of H₂ (mL) versus time (s) plot for the hydrolytic dehydrogenation of AB (100 mM) catalyzed by laurate-stabilized Rh(0) NPs in aqueous solution at 25.0 ± 0.1 °C with different rhodium concentrations: [Rh] = 0.25, 0.50, 1.0, 1.5, and 2.0 mM. Reproduced with permission from Ref. [11]. Copyright [2009], Elsevier.

Download English Version:

<https://daneshyari.com/en/article/11011596>

Download Persian Version:

<https://daneshyari.com/article/11011596>

[Daneshyari.com](https://daneshyari.com)