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The Hydroloysis of ammonia borane by using Amberlyst-15 supported catalysts for hydrogen generation

Derya Öncel Özgür [a], Tayyibe Şimşek [a], Göksel Özkan [a], Meryem Sena Akkuş [a], Gülay Özkan [b,*]

[a] Department of Chemical Engineering, Gazi University, 06570, Maltepe, Ankara, Turkey
[b] Department of Chemical Engineering, Ankara University, 06100, Tandoğan, Ankara, Turkey

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ABSTRACT

Resin catalysts have the advantage of having various properties and long lifetime due to their ability to be regenerated easily, which makes them attractive supports. In this paper, a comparative study was conducted to optimize the dehydrogenation reaction condition using two different types of support materials: alumina (Al_2O_3), and Amberlyst-15 and to improve the catalytic activity as well as preparing an efficient and low-cost system for practical application, ruthenium metal catalyst was incorporated on Amberlyst-15 resin (a sulfonic acid type based upon a styrene-divinylbenzene copolymer) to release H_2 via hydrolytic dehydrogenation of ammonia borane. Using ruthenium (Ru) catalysts based on Amberlyst-15 support material and comparing the results with Al_2O_3 as the common supporting material is considered to be studied for the first time. The effect of temperature (20–50 °C), the initial ammonia borane concentration (0.05–0.5 %wt), and catalyst amount (0.2–0.5 g) on the produced H_2 yield was also investigated. Ru@Amberlyst-15 nanoparticle was discovered to be an effective catalyst for hydrogen evolution via the hydrolysis of ammonia borane with a turnover frequency value (TOF) of 343.3 min^{-1}, while Ru@Al_2O_3 yielded a TOF of 87.5 min^{-1} at the room temperature. Therefore, it can be concluded that the Amberlyst-15 supporting effect on ruthenium metal leads an increase in the hydrogen production rate.

Introduction

Researchers are driven to find alternative and renewable energy solutions due to a rapid decrease in fossil fuel resources, increasing consumption of these resources, and mitigating global change. Hydrogen production is one of the most crucial alternative energy technologies for meeting future global energy need. It is environmentally clean and efficient, compared to conventional petroleum-based fuels [1–5]. However, it has many problems to be issued before its effective application in small portable devices and transportation vehicles. In this regard, some reaction systems and new hydrogen containing materials have been investigated. Among solid hydrogen materials, ammonia-borane is an environmentally friendly and dependable option. Hence, a number of recent studies have focused on improving an efficient hydrogen generation

* Corresponding author.
E-mail address: gozkan@eng.ankara.edu.tr (G. Özkan).

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procedure using ammonia-borane. To overcome the interrupted energy supply problem in fuel cells, researchers are forced to develop not only catalysts but also new storage materials and methods to enhance hydrogen generation for hydrogen-consuming fuel-cell [6].

Ammonia borane (denoted AB, NH_3BH_3) complex having remarkably high hydrogen content as high as 19.6 %wt, exceeding that of gasoline, has been considered as a promising material for on-board hydrogen storage [7–9]. AB dissolves in water and its solution is stable in ambient environments [10]. For this reason, it is unnecessary to use any additional base as a stabilizer in the hydrolytic dehydrogenation of ammonia borane solution as compared with borohydrides. However, AB, an outstanding structure including both N–H (protic) and B–H (hydridic) bonds [11,12] and a strong B–N bond which facilitated the splitting of the group into two part as ammonia and borane, releases hydrogen in the presence of appropriate catalyst under mild conditions. To release the stored hydrogen in AB, various ways could be applied such as thermoloysis in solid state [13,14] and, hydrolysis [8,15–17], or methanolysis [18–21] in solution. Although elevated temperature is required for thermoloysis pathway and it is comparatively difficult to govern its reaction, hydrolysis pathway (Eqn. (1)) in the presence of suitable catalyst can be liberated 3.0 equivalents of hydrogen under mild conditions, which appears to be the most appropriate method for on-board applications.

$$NH_3BH_3\ (aq) + 2H_2O(l) \xrightarrow{catalyst} NH_4^+\ (aq) + BO_2^-(aq) + 3H_2(g) \qquad (1)$$

Considerable research efforts were put forth to improve catalysts for the AB decomposition reaction. The hydrolytic dehydrogenation of AB has been achieved efficiently by using both noble metals such as Ru [22–34], Rh [22,35,36], Pt [22,34], and Pd [22,30,37–41] and non-noble metals such as Co [42–48], Ni [42,44,47], and Fe [49,50]. Among them, ruthenium-based catalysts have exhibited significantly higher activities. Catalyst supports apart from the metal nanoparticles are also a crucial issue to enhance the performance of metal catalysts. Numerous AB hydrolysis studies associated with improving the stability of Ru catalysts in the literature assign to the utilization of Al_2O_3 [51], hydroxyapatite [25], carbon black [31], multi-walled carbon nanotube [28], TiO_2 [23], and SiO_2 [29] as supports. Ambelyst-15 has elicited a great deal of interest as a catalyst support due to its mesoporous structures that facilitate mass transfer, have high adsorption capacity and ion exchange ability. This study addresses the synthesis of ruthenium supported Ambelyst-15 to utilize the hydrolysis of AB. They can be employed in the dissociation of AB to produce hydrogen with a hydrogen to AB ratio up to 3.0 under ambient conditions. In this article, Ru@Amberlyst-15, and Ru@Al_2O_3 were synthesized, and these catalysts were employed to figure out their kinetic properties and hydrogen generation rate.

Experimental

A commercial AB product of 97% purity (Aldrich-682098) and deionized water was used in this research. All other reagents were used as analytical grade and commercially supplied.

Several Ru catalysts were prepared with commercially available supports (Ambelyst-15, γ-Al_2O_3) by a simple impregnation method from an aqueous solution of $RuCl_3 \cdot 3H_2O$. If Al_2O_3 is used as a support, it is followed by a calcination step and then a reduction step for three hours under an H_2 atmosphere. BET surface areas were found by nitrogen adsorption at −196 °C on a Quantachrome Nova 2200e adsorption instrument. Besides, a scanning electron

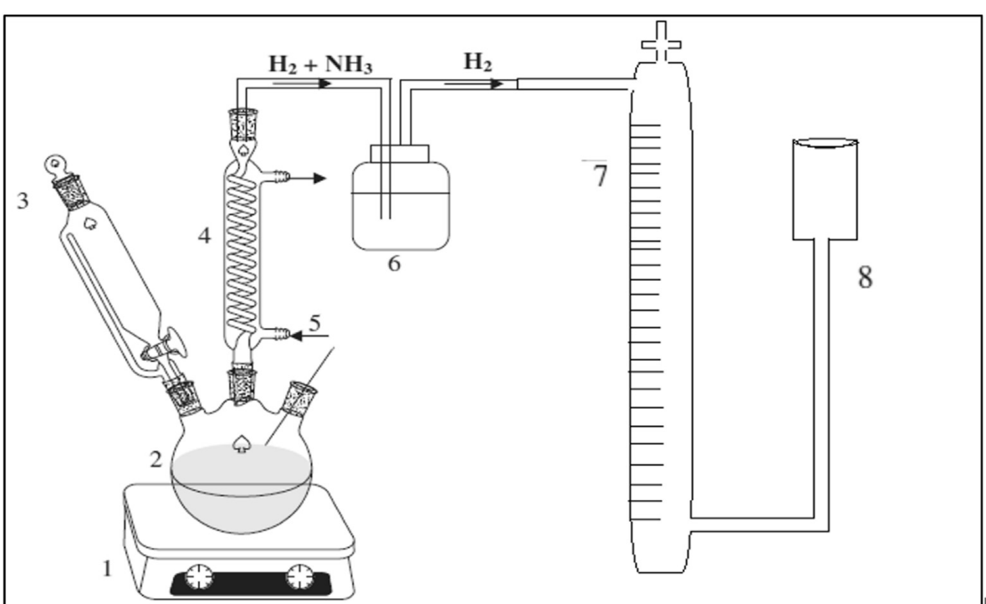

Fig. 1 – The reaction apparatus for hydrogen generation from AB. (1) hot plate, (2) fifty milliliters three-necked round-bottom flask, (3) additional funnel with a pressure equalized arm, (4) condenser, (5) coolant in and out, (6) washing bottle (7) gas burette, (8) leveling bottle.

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