JOURNAL of THE TURKISH CHEMICAL SOCIETY
SECTION: B
CHEMICAL ENGINEERING
TURKISH CHEMICAL SOCIETY

Simulation of Hydrogen Production from Hydrolysis of Ammonia Borane for Hydrogen Fuel Cell Applications through Aspen HYSYS

Sefa Aras[1], **Derya Ünlü**[1*]

[1] Bursa Technical University, Chemical Engineering Department, Bursa, 16310, Turkey

Abstract: Hydrogen is an efficient, clean, and sustainable energy carrier with high energy density and zero emission, which can find important applications in fuel cells. Hydrolysis of ammonia borane is an enormous alternative to produce hydrogen. In this study, the hydrogen production via hydrolysis of ammonia borane for hydrogen fuel cell applications was investigated by using ASPEN HYSYS. Firstly, the thermodynamic method and suitable reactor were specified with depending on hydrogen production rate. The influences of reaction temperature and feed mass flow rate of water on the hydrogen production rate were studied. Hydrogen was acquired in the act of mixture with ammonia, boric acid, and unreacted water at the end of the reaction. First of all, solid boric acid was removed from the product mixture. Hydrogen would be purified from ammonia and water by using the separatory equipment. The goal of this study is to obtain the high production rate and high purity of hydrogen for hydrogen fuel cell applications. The optimum operation parameters were determined as 30°C of reaction temperature and 0.1 of feed water concentration. 99.9% purity of hydrogen was obtained at 30°C. The obtained results show that ASPEN HYSYS could be successfully applied for the determination of optimum reaction conditions and appropriate equipment for high production rate and purity hydrogen production from hydrolysis of ammonia borane.

Keywords: Ammonia borane, Aspen HYSYS, Hydrogen, Simulation

Submitted: June 04, 2022. **Accepted:** July 15, 2022.

Cite this: Aras S, Ünlü D. Simulation of Hydrogen Production from Hydrolysis of Ammonia Borane for Hydrogen Fuel Cell Applications through Aspen HYSYS. JOTSB. 2022;5(2):59–66.

***Corresponding author. E-mail:** derya.unlu@btu.edu.tr.

INTRODUCTION

In parallel with technological developments and population growth, the energy requirements of countries are increasing gradually. In this respect, energy has strategic importance worldwide. Energy is directly related to the economic development of countries as well as their security. The researches for new and alternative energy sources and integration with existing energy systems are important steps for sustainability (1-2). Fossil-based fuel reserves are gradually decreased and caused environmental pollution (3-5). Hydrogen production is a suitable environmental solution. Because, hydrogen-based energy systems which are high-quality, efficient, clean, reliable, and sustainable, sufficiently meets the conditions expected from an energy source (6-7).

Hydrogen is considered the clean fuel of the future due to its advantages such as high energy density ($142x10^3$ kJ / kg) and electronegative properties. In addition to these, the reasons such as high heat conversion, energy power, and no harmful wastes when burned with oxygen, being natural and renewable, unlimited, being used in industry, houses and vehicles, makes it advantageous among the alternative energy sources (7-9).

Fuel cells use hydrogen to convert chemical energy into electrical energy. Depending on evolvement of fuel cells, studies about storage and production of hydrogen are also being performed (10-11).

The biggest advantage of systems using chemical hydrides for hydrogen production is that hydrogen is not storable, but generable when needed. By using this system, all risks and difficulties of hydrogen storage are eliminated. Among the chemical hydrides, sodium boron hydride and ammonia borane have promising potential for using hydrogen energy in vehicles as solid hydrogen storage materials. When these two materials are compared, ammonia borane contains more hydrogen than sodium boron hydride (sodium boron hydride contains 10.8 wt.% H_2, ammonia borane contains 19.6 wt. % H_2). Also, the aqueous solution of sodium boron hydride is unstable and a base is added to the solution for stabilization. In contrast, ammonia borane has higher solubility and a more stable structure in an aqueous solution. Non-toxic, safe storage, high solubility in water, high stability in aqueous solution, and dehydrogenation in low temperature are other advantages of ammonia borane. Due to such prominent properties, it is possible to use ammonia borane as a high-density hydrogen generator in portable fuel cells (12-16).

Hydrogen generation is carried out by hydrolysis of ammonia borane. 1 mol of ammonia borane reacts and 3 mol of hydrogen occurs (16). The hydrolysis reaction of ammonia borane was given in the following equation.

$$NH_3BH_{3\,(aq)} + 3\,H_2O \dashrightarrow NH_4^+ + BO_2^- + 3\,H_{2\,(g)} \quad (1)$$

By using this method, rapid and controllable hydrogen production is possible. Hydrogen production by hydrolysis method in catalytic systems directly depends on the active substance and surface area of the catalyst. The biggest advantage of this method is that hydrogen can be produced quickly and at low temperatures (17-18).

In literature, there are lots of experimental studies about the hydrolysis of ammonia borane. According to the author's knowledge, this is the first study on simulation of hydrogen production from hydrolysis of ammonia borane by using Aspen HYSYS. In this research, suitable reactor for the reaction was selected and designed in Aspen HYSYS. The convenient thermodynamic method for the reaction was specified. After that, the details of simulation were given. The optimum reaction conditions such as reaction temperature and feed flow rate of water were determined. By the determination of optimum process conditions, hydrogen synthesis from hydrolysis of ammonia borane process design was simulated.

SIMULATION MODELING

Hydrogen production from hydrolysis of ammonia borane was investigated with ASPEN HYSYS. The scheme of simulation of the hydrogen production process is shown in Figure 1.

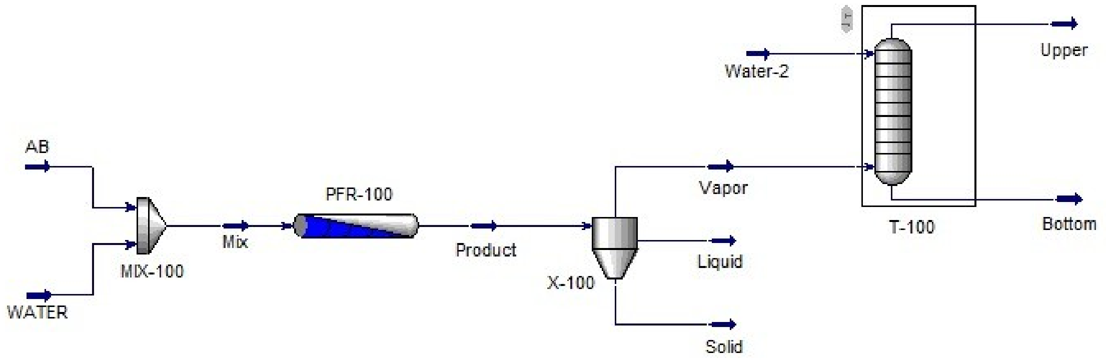

Figure 1: Scheme of simulation of hydrogen production.

The list of equipment was given in Table 1.

Table 1: Equipment list in simulation.

Equipment Code	Equipment Description	Duty
MIX-100	Mixer	Mixing of feed components
PFR-100	Plug flow reactor	Hydrogen production from hydrolysis of ammonia borane
T-100	Absorption column	Purification of hydrogen

Water and ammonia borane at different feed flow rates were fed to the mixer and stirred. After the mixer, the mixture of water-ammonia borane entered the plug flow reactor. The hydrogen synthesis from hydrolysis of ammonia borane was operated in a plug flow reactor. At the end of the reaction; hydrogen, boric acid, unreacted water were obtained. The reaction products were initially sent to the simple solid separator. Boric acid was removed from the mixture in this equipment. Vapor phase, which contained hydrogen, water, and ammonia, was sent to the absorption column. Finally, hydrogen was purified by using an absorption column and obtained as pure.

RESULTS AND DISCUSSION

Selection of Reactor Type

The appropriate reactor type was determined according to the hydrogen production rate. Hydrolysis reaction of ammonia borane was carried out by using a conversion reactor and a plug flow reactor. Determination of appropriate reactor type was investigated on hydrogen production rate (n_{H2}/n_{AB}) with the changing temperature.

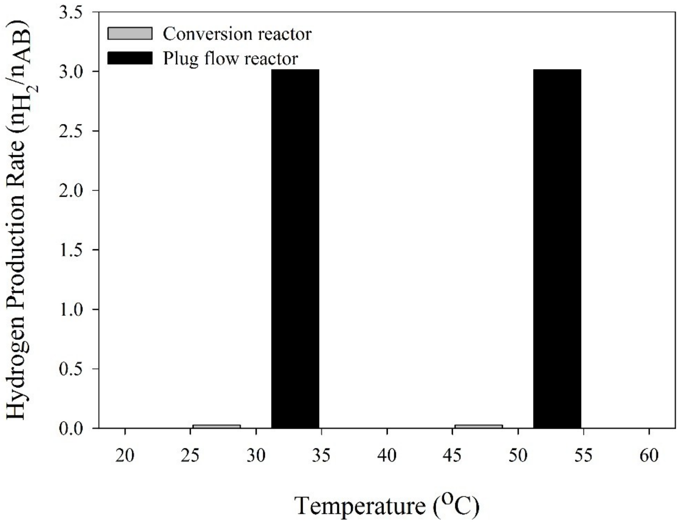

Figure 2: Selection of reactor type in different temperature.

Figure 2 shows the hydrogen production rate in conversion and plug flow reactor. Hydrogen production rate in the plug flow reactor is higher than that of the hydrogen production rate in the conversion reactor. This result is related to the working principle of reactors. Plug flow reactor is based on reaction mechanism and used catalyst features. As ammonia borane and water flown and reacted along the reactor, hence, the axial change in concentration value observed. The conversion reactor is only based on conversion and stoichiometric ratio. Conversion values are defined to the reactor by the user. Reaction continues until the particular conversion has been acquired. However, PFR calculates the reaction yield according to reaction mechanism and catalytic properties. In experimental studies, catalyst has an important effect for the reaction. From all reasons above, PFR was used to simulate hydrogen production. Due to the more production of hydrogen, a plug flow reactor was used for all processes. The reaction is exothermic, so there is no effect of temperature increment on the hydrogen production rate.

While the obtained hydrogen production rate was 0.0270 in the conversion reactor, this value was 3.014 for the plug flow reactor.

Selection of Thermodynamic Model

Thermodynamic methods are utilized to show the phase equilibrium and energy level of components in the systems. There are five types of property methods in ASPEN HYSYS. The equations of state, activity models, Chao-Seader based empirical methods, vapor pressure models, and miscellaneous methods are available as thermodynamic models. The equations of state are generally recommended for oil, gas, and petrochemical applications. It can be used for single, two, and three-phased systems. The model calculates the properties with high efficiency. The Activity Models is mostly preferred for non-ideal systems. The Chao-Seader is an older and semi-empirical method. Vapor Pressure model is to be utilized for ideal mixtures at low pressure values. The Miscellaneous methods are preferred if the groups previously mentioned do not fit.

In this study, equations of state and activity models were tested. Soave-Redlich-Kwong (SRK), Peng Robinson (PENG-ROB), Peng-Robinson Stryjek Vera (PRSV) in equations of state and Non-Random-Two-Liquid (NRTL), Wilson, UNIversal QUAsi Chemical (UNIQUAC) in activity models are applied. The activity methods are resulted in low hydrogen composition according to the EOS. Besides that, byproduct amounts increased while the activity models were used due to the formation of low hydrogen amount. Especially, formation of more ammonia is an undesired state for fuel cell applications. Therefore, the low amount byproduct formation was chosen. The obtained results were given in Table 2.

Table 2: The selection of thermodynamic method.

Property Package	Model	Hydrogen Composition
Equations of State	PENG-ROB	0.9347
	SRK	0.9306
	PRSV	0.9229
Activity Models	NRTL	0.8647
	WILSON	0.8456
	UNIQUAC	0.8586

All thermodynamic methods were examined in 30 °C of reaction temperature, 0.01 kg/h of water mass flow rate and 1 bar of pressure. According to Table 2, Peng Robinson method was selected was chosen as an appropriate thermodynamic model. Also, hydrogen synthesis reaction from hydrolysis of ammonia borane results in the formation of solid, liquid, and vapor phase products. Therefore, the usage of equations of state is appropriate for this process. Because these methods can be used for single, two and three phase systems. Among equations of state models, the Peng Robinson model has been chosen as an appropriate thermodynamic model.

Simulation Details of Hydrogen Production from Hydrolysis of Ammonia Borane

Hydrogen production from hydrolysis of ammonia borane has not been examined previously in the ASPEN HYSYS simulation programme. No study is available in the literature on the Hydrogen production from hydrolysis of ammonia borane by using ASPEN HYSYS. According to the author’s knowledge, this is the first study on ASPEN HYSYS simulation of hydrogen production from hydrolysis of ammonia borane.

According to the stoichiometric ratio, excess water was fed to the reactor. Also, usage of diluted ammonia borane in reaction has some advantages such as the formation of low byproduct, the decrement of the increase in ambient temperature due to the exothermic reaction. 1 mol of ammonia borane reacts and 3 mol of hydrogen occurs (16, 19). At the first stage of the process, water and ammonia borane were stirred in a mixer at 30 °C and 1 bar. Ammonia borane is a solid component, mixed with water and was dissolved, liquid mixture was achieved. The mixed stream was obtained and sent to plug flow reactor. Plug Flow Reactor (PFR) which is shown in Figure 3 is used for hydrogen generation.

Figure 3: Plug flow reactor.

Plug flow reactor was operated 30 °C and 1 bar. The usage of appropriate catalyst plays a significant part on the hydrogen generation rate. The used catalyst was a ruthenium based catalyst. The researches in literature confirmed that ruthenium-based catalysts are one of the most productive catalysts for the ammonia borane hydrolysis reaction (20-24). The features of the used catalyst can be seen in Table 3. These values are also defined in simulation programme.

Table 3: The catalyst data.

Particle Diameter	3.8e-009 m
Particle Sphericity	1
Solid Density	0.5 kg/m^3
Bulk Density	0.15 kg/m^3
Solid Heat Capacity	10 kj/kg°C

The feed molar flow rates of ammonia borane and water are 1.5x10^{-6} and 5.55x10^{-3} kmol/h. The conversion of ammonia borane was 100%. There is no ammonia borane in product stream. The produced hydrogen molar flow rate is 5.542x10^{-3} kmol/h. The hydrogen production rate (nH_2/nAB) was calculated as 0.19. The molar composition of the product stream was given in Table 4.

Table 4: The molar composition of the product stream.

Components	Mole Fraction
H_3BO_3	0.0003
Hydrogen	0.0008
H_2O	0.9986
AB	0.0003
NH_3	0.0027

The products of hydrogen synthesis reaction are H_3BO_3, NH_3, H_2 and unreacted water. The H_3BO_3 was obtained as a solid phase at the end of the reaction. Therefore, the removal of H_3BO_3 gains importance for the obtain pure hydrogen. For this purpose, solid separator was used. The simple solid separator equipment is shown in Figure 4.

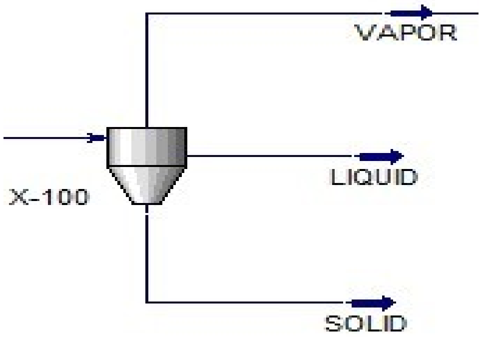

Figure 4: Simple solid separator.

The solid phase was completely separated. Due to the no hydrogen in a liquid phase, the vapor phase was sent to the separator. The molar composition of each stream in the exit side was given in Table 5.

Table 5: The molar composition of the product stream.

Components	Solid	Vapor	Liquid
H_3BO_3	1	0.0000	0.0000
Hydrogen	0.0000	0.9915	0.0000
H_2O	0.0000	0.0077	0.9973
AB	0.0000	0.000	0.000
NH_3	0.0000	0.0008	0.0027

Vapor stream includes Hydrogen, H_2O and NH_3 components. Hydrogen should be purified from water and NH_3. Therefore, the separator should be used in the process. For that purpose, an absorption column was used and a high purify of hydrogen was obtained. The used absorption column is shown in Figure 5.

The additional water stream was given in the absorption column. Ammonia was dissolved easily in water, and separated from hydrogen. 99.15 wt. % hydrogen purity was obtained in the upper stream.

Investigation of Reaction Parameters

Effect of temperature

To investigate the effect of temperature on the hydrogen production reaction from hydrolysis of ammonia borane, the temperature range was chosen as 20-50 °C with 10 °C of increment. The observed mass fraction of hydrogen and ammonia were given in Figure 6.

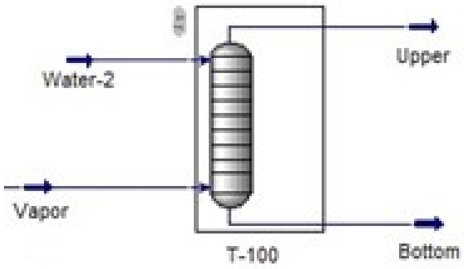

Figure 5: Absorption column.

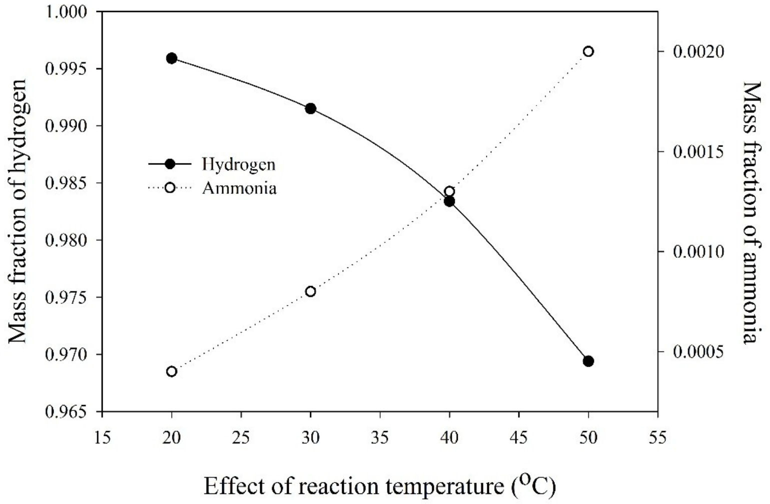

Figure 6: Effect of reaction temperature.

The hydrogen production from hydrolysis of ammonia borane is an exothermic reaction. Therefore, an increase in temperature results in low hydrogen concentration (7, 17, 25). With the raise in reaction temperature from 20 °C to 50 °C, the mass fraction of hydrogen decreases from 0.9959 to 0.9694. Besides, the mass composition of ammonia increased from 0.0004 to 0.0022. The maximum H_2 mass composition was acquired at 20 °C. This is the expected result.

Effect of feed mass flow rate of water

To investigate the effect of the feed mass flow rate of water on the mass fraction of hydrogen and ammonia in the hydrolysis of ammonia borane, the water at different ratios were fed to the system. The dependence of the feed mass flow rate of water on the mass fraction of hydrogen and ammonia is investigated by varying the mass flow rate of water from 0.001 kg/h to 0.1 kg/h, and the results are shown in Figure 7.

With the increase of the feed mass flow rate of water, the mass fraction of hydrogen increased. When the feed mass flow rate of water was 0.1 kg/h, the highest hydrogen composition was obtained. As the water concentration increased in the feed mixture, ammonia borane in the feed mixture was diluted. In experimental studies, diluted ammonia borane was used for the reaction.

As the increment of dilution of the ammonia borane, the formation of ammonia had been decreased. This result was supported by the literature. It can be explained that the use of dilute Ammonia borane solution reduces the increase in ambient temperature as a result of the exothermic reaction, thus reducing the formation of ammonia (26-27).

As seen in Figure 7, when the feed mass flow rate of water was increased from 0.001 to 0.1 kg/h, the mass fraction of hydrogen increased from 0.9806 to 1. Under the same conditions, ammonia concentration decreased from 0.0004 to 0.

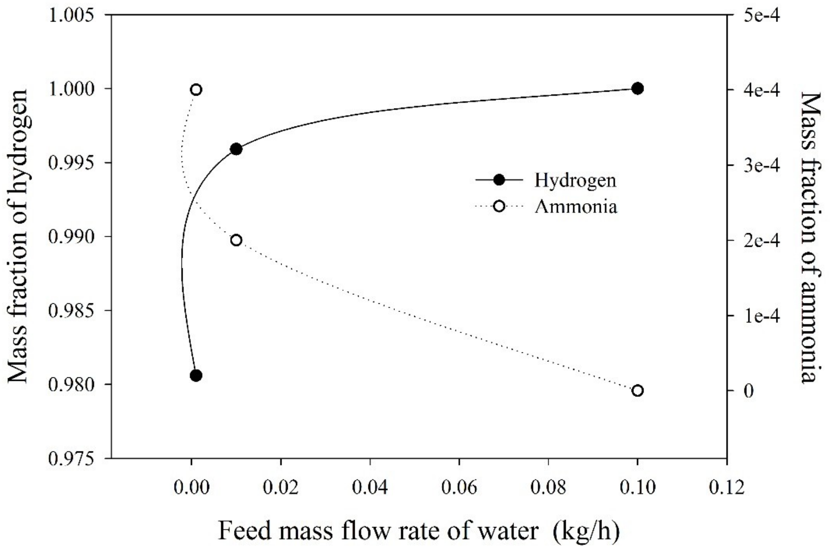

Figure 7: Effect of feed mass flow rate.

CONCLUSION

The hydrogen production from hydrolysis of ammonia borane had been carried out in conversion and Plug flow reactor. The highest hydrogen mass composition was achieved in plug flow reactor. Plug flow reactor calculates the reaction yield according to the reaction mechanism and catalytic properties. Therefore, a plug flow reactor was preferred for hydrogen synthesis. Peng Robinson as the thermodynamic model was selected. Peng Robinson is one of the equations of state model. It can be utilized for multiple phase systems. Then, the general simulation design was investigated. The details of each equipment were explained. After that, the effects of temperature and feed mass flow rate of water were investigated. Firstly, the effect of temperature on the mass fraction of hydrogen was examined. A decrement of hydrogen fraction was detected in high temperature values. This result is related to the exothermic behavior of the reaction. The optimum temperature was found as 20 °C. The feed mass flow rate of water was also investigated. The mass fraction of hydrogen increased with increasing water amount in the feed mixture. As the increment of dilution of the ammonia borane, the formation of ammonia had been decreased. Therefore, the optimum feed mass flow rate was chosen as 0.1 kg/h. Also, the hydrogen was purified with absorption column. At the end of the purification, hydrogen was achieved as 99.15 vol % purity at 1 bar and 30 °C. The study conducted show that ASPEN HYSYS can be used to hydrogen production from hydrolysis of ammonia borane.

CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

REFERENCES

1. Gielen D, Boshell F, Saygin D, Bazilian MD, Wagner N, Gorini R. The role of renewable energy in the global energy transformation. Energy Strategy Rev. 2019; 24:38–50. <URL>.

2. Caruso G, Colantonio E, Gattone SA. Relationships between Renewable Energy Consumption, Social Factors, and Health: A Panel Vector Auto Regression Analysis of a Cluster of 12 EU Countries. Sustainability. 2020; 12(7):2915. <URL>.

3. Parthasarathy P, Narayanan KS, Hydrogen production from steam gasification of biomass: Influence of process parameters on hydrogen yield–A review. Renew Energy. 2014; 66:570–579. <URL>.

4. Koroneos C, Dompros A, Roumbas G. Hydrogen production via biomass gasification-a life cycle assessment approach. Chem Eng Process 2008; 47:1261-1268. <URL>.

5. Yüksel Alpaydın C, Gülbay SK, Colpan OC. A review on the catalysts used for hydrogen production from ammonia borane. Int J Hydrogen Energy 2019; 45(5):3414-3434. <URL>.

6. Dutta S. A review on production, storage of hydrogen and its utilization as an energy resource. J Ind Eng Chem. 2014; 20:1148–1156. <URL>.

7. Ozay O, Inger E, Aktas N, Sahiner N. Hydrogen production from ammonia borane via hydrogel template synthesized Cu, Ni, Co composites. Int J Hydrogen Energy. 2011; 36:8209–8216. <URL>.

8. Kantürk FA. Improved catalytic performance of metal oxide catalysts fabricated with electrospinning

in ammonia borane methanolysis for hydrogen production. Int J Hydrogen Energy. 2019; 44: 8451-28462. <URL>.

9. Ozay H, Ilgin P, Ozay O. Hydrogen production via copper nanocatalysts stabilized by cyclen derivative hydrogel networks from the hydrolysis of ammonia borane and ethylenediamine bisborane. Int J Hydrogen Energy. 2020; 45(35): 17613-17624. <URL>.

10. Staffell I, Scamman D, Velazquez AA, Balcombe P, Dodds PE, Ekins, P, Ward KR. The role of hydrogen and fuel cells in the global energy system. Energy Environ Sci. 2019; 12:463-491. <URL>.

11. Manoharan Y, Hosseini SE, Butler B, Alzhahrani H, Senior BTF, Ashuri T, Krohn J. Hydrogen Fuel Cell Vehicles; Current Status and Future Prospect. Appl Sci. 2019; 9(11):2296. <URL>.

12. Metin Ö, Şahin Ş, Özkar S, Water-soluble poly(4-styrenesulfonic acid-co-maleic acid) stabilized ruthenium(0) and palladium(0) nanoclusters as highly active catalysts in hydrogen generation from the hydrolysis of ammonia–borane. Int J Hydrogen Energy. 2009; 34:6304-6313. <URL>.

13. Rakap M, Özkar S, Hydrogen generation from the hydrolysis of ammonia borane using intrazeolite cobalt (0) nanoclusters catalyst. Int J Hydrogen Energy. 2010; 35:3341-3346. <URL>.

14. Shang N, Zhou X, Feng C, Gao S, Wu Q, Wang C. Synergetic catalysis of Ni Pd nanoparticles supported on biomass-derived carbon spheres for hydrogen production from ammonia borane at room temperature. Int J Hydrogen Energy. 2017; 42:5733–5740. <URL>.

15. Inoue H, Yamazaki T, Kitamura T, Shimada M, Chiku M, Higuchi E. Electrochemical hydrogen production system from ammonia borane in methanol solution. Electrochimica Acta. 2012; 82:392–396. <URL>.

16. Lai SW, Park JW, Yoo SH, Ha JM, Song EH, Cho SO. Surface synergism of Pd/H2Ti3O7 composite nanowires for catalytic and photocatalytic hydrogen production from ammonia borane. Int J Hydrogen Energy. 2016; 41:3428–3435. <URL>.

17. Mohajeri N, T-Raissi A, Adebiyi O. Hydrolytic cleavage of ammonia borane complex for hydrogen production. J. Power Sources. 2007; 167:482-485. <URL>.

18. Liu CH, Wu YC, Chou CC, Chen BH, Hsueh CL, Ku JR, Tsau F. Hydrogen generated from hydrolysis of ammonia borane using cobalt and ruthenium based catalysts. Int J Hydrogen Energy. 2012; 37:2950-2959. <URL>.

19. Gil-San-Millan R, Grau-Atienza A, Johnson DT, Rico-Francés S, Serrano E, Linares N, García-Martínez J. Improving hydrogen production from the hydrolysis of ammonia borane by using multifunctional catalysts. International Journal of Hydrogen Energy. 2018; 43(36):17100-17111. <URL>.

20. Navlani-García M, Mori K, Nozaki A, Kuwahara Y, Yamashita H. Highly efficient Ru/carbon catalysts prepared by pyrolysis of supported Ru complex towards the hydrogen production from ammonia borane. Appl Catal A. 2016; 527:45–52. <URL>.

21. Can H, Metin Ö. A facile synthesis of nearly monodisperse ruthenium nanoparticles and their catalysis in the hydrolytic dehydrogenation of ammonia borane for chemical hydrogen storage. Appl Catal B. 2012; 125:304–310. <URL>.

22. Ma H, Na C. Isokinetic Temperature and Size-Controlled Activation of Ruthenium-Catalyzed Ammonia Borane Hydrolysis. ACS Catalysis. 2015; 5(3):1726–1735. <URL>.

23. Chen G, Desinan S, Rosei R, Rosei F, Ma D. Synthesis of Ni-Ru Alloy Nanoparticles and Their High Catalytic Activity in Dehydrogenation of Ammonia Borane. Chemistry - A European Journal. 2012; 18(25):7925–7930. <URL>.

24. Wright WRH, Berkeley ER, Alden LR, Baker, RT, Sneddon LG. (2011). Transition metal catalysed ammonia-borane dehydrogenation in ionic liquids. Chem Comm. 2011; 47(11):3177-3179. <URL>.

25. Chou CC, Lee DJ, Chen BH. Hydrogen production from hydrolysis of ammonia borane with limited water supply. Int J Hydrogen Energy. 2012; 37:15681–15690. <URL>.

26. Tunç N, Rakap M. Preparation and characterization of Ni-M (M: Ru, Rh, Pd) nanoclusters as efficient catalysts for hydrogen evolution from ammonia borane methanolysis. Renew Energy. 2020; 155:1222–1230. <URL>.

27. Ramachandran PV, Gagare PD. Preparation of ammonia borane in high yield and purity, methanolysis and regeneration. Inorg Chem. 2007; 46:7810-7817. <URL>.