CATALYTIC HYDROGEN PRODUCTION SYSTEMS FOR PORTABLE POWER APPLICATION

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Abstract. *In this short review article summarizes the results of studies of catalytic and photocatalytic systems for the production of hydrogen from metal borohydride and ammonium boranes. Their performance and the main problems for the usage in portable power sources such as polyelectrolyte membrane fuel cells (PEMFC) are discussed.*
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Introduction

Several studies have been conducted to explore the production of H_2 by hydrolysis process from metal hydrides and high H-containing compounds (ammonia borane, hydrazine, etc.) and the research process is still underway. Hydrogen production from hydrogen-rich compounds, at any time, with the desired flow rate and high purity, makes it essential for PEM Fuel Cell-based portable power supplies like a fuel source.

Hydrogen production by means of hydrolysis is possible in solid or solution form of these compounds. In particular, metal hydrides are preferred, since the production of hydrogen from alkaline water solutions of metal hydrides redoubled the amount of hydrogen produced, and the alkaline medium $NaBH_4$, $LiBH_4$, KBH_4 remains stable, can be stored for a long time.

We have systematically presented the hydrolysis of Metal Bor Hydrides such as - NaBH4, $LiBH_4$, KBH_4 and Aminoborane (AB) in subsequent parts of the paper, different description catalysts, photocatalytic systems, and its problems.

A. Hydrolysis with Acids

The reaction of an acid with catalysts increases the yield of hydrogen produced and the efficiency of the hydrogen conversion. Rates of hydrogen production are checked to make hydrogen ions completely consumed in the reaction. The following reaction occurs in acidic hydrolysis of metal borohydrides (1):

$$MeBH_4 + H^+ + 3H_2O \rightarrow 4\,H_2 + H_3BO_3 + Me^+ \qquad (1)$$
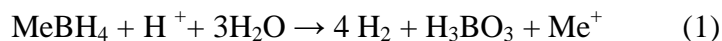
Until the year 2000, acids had been considered as an abortive accelerator for hydrolysis of $NaBH_4$ due to safety problems. However, recent research has shown that some acids can be used as indirect activators for potential direct accelerators or heterogeneous

catalysts **Ошибка! Источник ссылки не найден.**].

Several acids are used as a disposable accelerator for a portable NaBH$_4$ hydrogen generation system. These acids include hydrochloric, sulfuric, nitric, phosphoric, formic and acetic acids. It also found that some acids are capable of delaying the formation of by-products through lowering the pH of the solution to down values. Subramanian et al. reported that H$_2$SO$_4$, H3PO$_4$, HNO$_3$, HCl, and HCOOH were used for the production of hydrogen from NaBH$_4$ in single-use portable systems 1].

Demirci et al. reported that the use of acetic acid in the hydrolysis of NaBH$_4$ is preferable as an environmentally friendly material besides causing high activity in the catalyst. Abdul-Majeed et al. noted that when mixing 30% NaBH$_4$ solution with a flow rate of 1.03 ml/min and the acidic accelerator as a 3M HCl 0.97 ml/min flow rate, hydrogen was produced 98% ratio and hydrogen evaluation rate was 863 ml/min. 2]. Some studies, even despite acid catalysts and metal complex catalysts are perfect catalysts for hydrogen conversion, reported that the rate of hydrogen formation is difficult to control [1, 4, 5].

Using acid catalyst is advantageous at meager hydrogen flow rates. However, when concentrated NaBH4 solution (15-30%) and concentrated acid are used for the production of hydrogen at high flow rates, byproducts are formed due to the exothermic reaction. We proved that these products poison platinum electrocatalyst of PEM fuelcell rate [6]. Abdul-Majeed et al. reported that to purify the produced hydrogen from acid catalysts, additional liquefied nitrogen unit was used [7].

The main disadvantage of using acid catalysts is high impurity rate of hydrogen produced at a high flow rate. Another disadvantage is that long-term use of acid may cause corrosion in some parts of the system.

B. Hydrolysis with Pt metals-based catalysts

It should be added that Pt metals are the most active and long-life catalysts among heterogeneous catalysts in the production of hydrogen by the hydrolysis reaction of metal hydrides, metal borohydrides, and ammonium boranes. The used catalysts are commonly prepared on the surface of different carriers and mostly tested in the H$_2$ production process from alkaline solutions of NaBH$_4$. Production speed (L / min x gram catalyst) was determined at a constant temperature. After determining the speed of the process at different temperatures, the activation energy of the process was calculated under the Arrhenius equation. Note that activation energy values on different carrier surfaces for some catalysts were as follows: Ru-IRA400 (47; 56 kJ / mol H$_2$), Ru / Carbon (66.9 kJ / mol H$_2$),1% Rh / Al$_2$O$_3$ (50.6 kJ / mol H$_2$), 1% Pt / Al$_2$O$_3$ (56.9 kJ / mol H$_2$), Pt / Pd-Si (19 kJ / mol H$_2$)[8]. Amendola et al. produced a hydrogen generator prototype with the help of the Ru catalyst in NaBH$_4$ solution for the first time. In other studies, catalysts were prepared on different carrier surfaces through the use of different platinum metals, and similar studies were conducted [9, 10, 11].

The main problem of catalysts containing platinum metals is that the catalyst price is high.

C. Hydrolysis with Fe, Co, Ni, Cu, base -mono, -bi, -trimetallic catalysts

In the literature survey, it was determined that a large number of different catalysts produced in different compositions revealed that alkali boron hydrides were tested during ammonium borane and hydrazine borane hydrolysis processes. Analysis of these studies is

given in the following studies [12, 13, 14]. Patel et al. were analyzed more than 150 studies on containing Co atoms [15].

New investigations are presently carried out over Co and B containing catalysts due to their high activity and cheaper price than Pt-containing catalysts. Note that Co-B catalyst is produced through the use of carriers as follows: black carbon, activated carbon, functional black carbon, functional MW / CNT structure, open finite carbon nanotube-CNT, closed-finite CNT, SiO_2, SBA-15, MCM-41, FSM-16, porous-Ni, porous Pd-Ni, etc. Depending on the structure of the carrier, the activity of the catalysts has an effect on microstructures of catalysts produced by different methods on the same carrier surface which appears to be different.

As another bimetallic catalyst, Co-P, containing 5% of TiO_2, Al_2O_3, CeO_2, is produced on porous Ni / Cu plate surface by the non-current coating method or by the electrochemical method as well where Co-Ni catalyst acts as a bimetallic catalyst.

Note that addition of M to structures such as Co-B nanoporous, Co-B / CTAB, Co-B / P123, C-Ni-B, Co-Fe-B, Co-Cu-B, Co-Cr-B, Co-Mo-B, Co-W–B prolongs the life of the nanocatalyst by limiting the size of the nanocatalyst. The activity of the catalysts varies depending on the percentage of M added. The catalyst with the highest activity among the triple catalysts tested through deficient concentration (0.025 mol) SBH solution was Co-Mo-B.

Similar studies were performed using Co-B, Co-P-B, C-M-B-P (M = Cr, Mo, W, Cu) powders with 0.025 MNH_3BH_3 solution. Demirci et al. has published a study on the Co-Ni catalyst used as a bimetallic catalyst [16].

The point is aboit criteria that determine the catalyst performance; cheapness, high mol H_2 /m (catalyst) xmin value at low temperatures, long life, suitable for regeneration; conversion of hydrides with a high ratio, maintenance of its activity at high concentrate solution, etc. As catalysts meeting all the criteria have not been produced yet, there is a need in new studies in this field.

D. Hydrolysis with Me^0 (Ru, Pt, Rh, Ni, Co) nanocluster type

The nanocluster type Me^0 catalysts as having large surface areas, exhibit high activity in the hydrolysis reaction. By adding a stabilizer to structures of these catalysts, catalysts run for a long time by blocking the growth of the nanocluster. Generally, it was observed that in the form of a nanocomposite Me^0 catalyst exhibits higher activity than Me catalyst with the same volume due to its dispersion in the hydrolysis medium.

It found that the same nanocatalyst changes its activity in the presence of a different carrier or stabilizer (Özkar et al. 2009, 2011). On the other hand, when the catalysts were produced using two different stabilizers of Co^0 nano composers (HPO_4^{-2} and Poly Acrylic Acid (PAA)), the conversion speed of the HPO_4^{-2} ions tapered nanocatalyst was 5.35 l/min, and when used as a PPA stabilizer, the conversion rate was 3.05 l/ min. However, PAA-stabilized

nanocatalysts were found to be long lasting than HPO_4^{-2} [17-20].

Similar results were also observed when the HPO_4^{2-} and PPA stabilizers were used in Ni (0) nanoclusters. Metin et al. revealed that the total conversion rate of poly ((n-vinyl-2-pyrrolidone) stabilized Ni (0) nanocube catalyst was 8700 mole H_2 and act for 27 hours. Another study was carried on hydrogen phosphate-stabilized Ni (0) nanoclusters and tested under the same conditions. In this case the production rate was 1450 moles of H_2 [20, 21].

Hydrogen production from ammonia boron was carried out using the catalysts Ru (0), and Pd (0) stabilized poly (4-styrene sulfonic acid-co-maleic acid) (PSSA-co-MA) with water. Elik et al. studied hydrolysis of hydro line hydrate of hydrazine borane with Hydroxy appetite carrier-assisted Rh (0) nanoparticles and

Ni (0) particles stabilized with PSSA-co-MA polymer [22, 23].

The hydrolysis reaction is expressed by this equation (2):

$$N_2H_4BH_3 + 2H_2O \rightarrow N_2H_5BO_2 + 3H_2 \qquad (2)$$

The performance of the Rh (0) catalyst is high (TOF) of 6700 h^{-1}. The catalytic systems of nano conversion Me (0) have the following problems. **These studies mainly expore hydrolysis of the non-stabilized water solution when sodium borohydride is used. Since the concentrate of the solution used is very low, it cannot be used to stabilize the solution. However, it may be possible to use PEMFC with deficient power.**

In many studies, hydrolysis studies of the amine borane have been made with the use of methanol, and these reactions are called methanolysis (3):

$$NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2 \qquad (3.1)$$
$$NH_3BH_3 + 4\ MeOH \rightarrow NH_4B(OMe)_4 + 3H_2 \qquad (3.2)$$
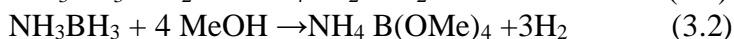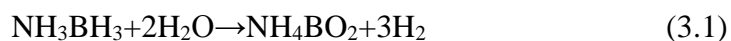
Methanolysis studies have taken place in a series of studies using different catalytic systems [24-29]. Unlike the hydrolysis reaction, the hydrogen capacity is 3.9%. In the hydrolysis process even despite the hydrogen capacity at 8.9%, undesirable NH_3 occurs in the hydrolysis process at high concentrations. Although this byproduct does not form in the methanolic process, the reaction product $NH_4B(OMe)_4$ can be converted back into NH_3BH_3.

The nano-catalytic hydrolysis of AB and Hydrazine borane has been discussed in more than 100 publications published by Zhang-Hi Lu et al. [30]

E. Photo-catalytic hydrolysis

For the first time over five years, the use of photocatalysis was shown to significantly increase the kinetic parameters of NH_3BH_3 hydrolysis [31, 32, 33].

While the hydrolysis of the AB is carried out at room temperature in the presence of photocatalysts under the influence of radiation, hydrogen is not produced when exposed to UV (λ = 10-400 nm) and visible areas (λ = 400-760 nm) but with the use of light on the hydrolysis process; it is possible to control the production of H_2 and reduce the impurities of NH_3. Various catalysts were examined in the process of photocatalytic hydrolysis of the AB in the visible region of the spectrum. In some studies metals and bimetals fixed on Me / TiO_2 (Me = Cu, Au) carriers [34, 35, 36] and in others - studies were carried on Me/Ag/SBA-15 (Me = Co, Ni, Pd, Ru, Pt) [36, 37, 38]

Pd/Me/SBA-15 (Me = Ag, Au) based catalysis examined by [39], Me/g-C3N4 (Me = Co, Fe, Ni, Cu, Ru, CoFe, CoNi, CoCu, AgPd), Pd/$H_2Ti_3O_7$ [40] (Cu/carrier (carrier = Al_2O_3, ZrP, TiO_2, ZrO_2, CeO_2, MIL-101) [41], CuO/TiO_2, cadmium sulfide based - CdS/TiO_2/C [42], CdS/$CdTiO_3$ [43] Oxides of non-stoichiometric transition metals - WO_3-x [31], MoO_3-x [44, 45,46], Mo_xW_1-xO_3-y [47].

Two studies were carried out in the UV spectrum wavelength. One of these studies was carried out by using Ag / Ti-SBA -15 catalyst [48], and another by a complex Ru [49]. It went to show that all catalysts revealed two catalytic (in the dark) and photocatalytic (in the light) activity and catalyst structure made it possible to define properties of the reaction and the ratio between the catalytic and photocatalytic components. However, it is difficult to compare the results of the studies with each other, for most studies provide no information about degree of the radiation. Only in recent studies, radiation values have been reported [50, 51].

Kamegawa et al. reported that AB was hydrolyzed through the use of highly active Pt /

TiO_2 catalyst by photocatalytic decomposition of the by-product ammonia [52]. It argued that such an experimental environment makes it possible to avoid ammonia impurity typical for the gas phase. Note that NH_3 was separated in the gas phase on the Pt / TiO_2 catalyst surface (25°C, UV); this raised H_2 yield from the AB by 3 to 4.5 equivalents due to hydrogen evolved from ammonia.

According to the photocatalytic hydrolysis mechanism of the AB, electron-hole pairs result in forming active OH * and $O_2^- *$ particles that are formed on the surface of catalysts under light and destabilize the hydride structure and accelerate the hydrolysis process of the AB. Therefore, an essential feature of the hydrolysis of aminoborane under the effect of light is rise in purity and yield of the produced H_2, as well as ability to start the photocatalytic decomposition process of ammonia on the photocatalyst surface in a controlled manner. In recent studies, organic ligand metal (MOF) structured photocatalysts were examined in the AB hydrolysis reaction.

Fig. 1. Mechanism of photocatalytic hydrolysis of AB on Cu/MIL-101 catalyst [41]
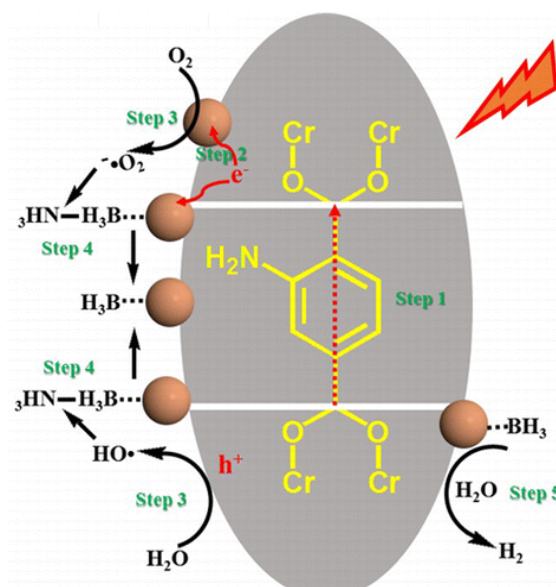
Lin et al. performed controlled photocatalytic hydrolysis for the production of hydrogen from alkali metal borohydrides [53]. It is possible to select the hydrogen production option on the surface of the $P_{25}TiO_2$ catalyst where the activation state at this time reaches 57.8 to 53.86 kJ/mol. This mechanism explains the mechanism of photocatalytic hydrolysis (Fig. 2): holes (H +) react with $BH_4^{(-)}$ ions and H_2 and B $(OH)_4^{(-)}$ electrons (e-) react with H (+) ions H_2 levels TiO_2 (top) Ti $(^{+3})$ crystal structure (spade-shell) are likely to be hydrolysis of the distortion. In the Jo et al. study, hydrogen production by AB photocatalytic transformation was examined by means of plasmonic Au / TiO_2photocatalyst [54]. Au / TiO_2 catalysts prepared on TiO_2 (anatase) containing different amounts of Au (0.5, 1, 2 and 3%) envisaged under both visible and UV light. It found that the TiO_2 catalyst containing Au (1 wt %) had the highest activity in H_2 production. In the meanwhile, activity decreased at higher values of Au. Although LSPR (Localized Surface Plasmon Resonance) raised Au nanoparticle (Au NP) loading, it also facilitated the recombination of LSPR charge pairs.
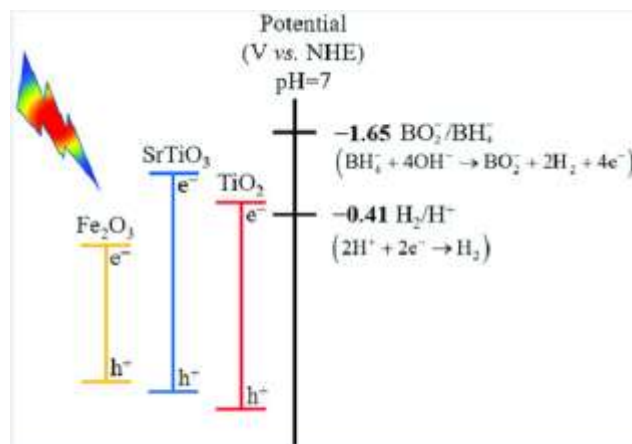
Figure 1. Schematic comparison of the potency of hydrolysis and photocatalytic hydrolysis processes of alkali metal borohydrides [53].

Note that charging pairs are faster at higher Au loading. As a result, the photocatalytic activity of Au / TiO$_2$ was optimized in 1% Au weight to produce 88 mmol of H$_2$ in 4 hours. This study provides a basic understanding of the photocatalytic activity of various photocatalysts based on metal oxide heterocycles. Systematic research shows that catalysts containing photoactive MOFs have higher activity than those containing photo-inactivated MOFs under visible light irradiation; however, photocatalytic activities of all catalysts are increased as compared to activities in the dark [55]. Specifically, the Co catalysts containing photoactive MOFs have total cycle frequency (TOF) values in the range of 81.7-117.7 min^{-1}; this value was much higher than those of noble metal-containing catalysts and comparable to values of the said catalysts. Significantly heightened activity of catalysts backed by photoactive MOFs are illustrated by the invisible-light-driven synergistic electron effect of semiconductor-like MOFs and by plasma-free acyl-metal-free NPs, which raises the Co / MIL-increased photo-current density. The catalyst containing 101 (Cr) -NH$_2$ fragment has a selectivity of 100% H$_2$ after 25 selective catalysts and at high activity.

The literature review in this part to confirmed that, in many studies, there is no ration on the number of quanta (photon yield) falling on the catalyst surface and the magnitude of the release rate of H$_2$ is calculated in various units. Despite the use of photocatalysis in these studies, articles available do not clearly explain the wavelength range that is generally in conformity with the spectrum used. It can be argued that there is no systematic approach at this stage of the studies and that published materials may be a screening feature and organic ligand metal (MOF) of structured photocatalysts may be more active in the hydrolysis reaction.

Conclusion

A future research work will focus on the analysis of bimetallic, FeCo, FeNi, FeCu, CoNi, CoCu nanocatalysts containing cheaper materials on graphitic g-C$_3$N, MoS$_2$, WS$_2$, graphene, TiO$_2$, TiO$_2$-graphene surfaces which are photo-sensitive carriers, on their synthesis and structural description. As a result of performance tests under a suitable light source, the catalytic hydrogen generation system can be produced for portable power systems.

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PORTATİV YANACAQ ELEMENTLƏRİNDƏ HİDROGENİN ALINMASI ÜÇÜN KATALİTİK SİSTEMLƏR

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Bu gısa icmalda katalitik ve fotokatalitik sistemlərdə borhidridlərdən ve ammonium borandan hydrogen alınması reaksiyaları analiz edilmişdir. Bu proseslərin xüsusiyyətləri, portativ yanacaq elementlərində – özəlliklə polielektrolit membranlı yanacaq elementlərində (PEMFC) istifadə edilməsi problemləri araşdırılmışdır.
Açar sözlər: *fotokataliz, borhidridlər, ammonium boran, portativ yanacaq elementləri*

КАТАЛИТИЧЕСКИЕ СИСТЕМЫ ПОЛУЧЕНИЯ ВОДОРОДА ДЛЯ ПОРТАТИВНЫХ ИСТОЧНИКОВ ЭНЕРГИИ

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В краткой обзорной статье обобщены результаты исследования каталитических и фотокаталитических систем для получения водорода из борогидридов металлов и аммин-борана. Обсуждаются их характеристики и основные проблемы использования в портативных источниках энергии, таких как топливные элементы с полиэлектролитной мембраной (PEMFC).
Ключевые слова: *фотокатализ, борогидрид натрия, аммин-боран, топливный элемент.*