Sustainable hydrogen generation substrates, catalysts and methods: an overview

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Abstract— Because of the increasing demand for energy, various alternative sources of energy generation are being examined. Interest in hydrogen generation is on the rise due to its potential as a scalable green energy source, its transportability, and other positive factors. While various studies have been conducted on hydrogen generation, this review explores three major factors in hydrogen generation in relation to sustainability: substrates or hydrogen storage media, catalysts for speeding up the rate of hydrogen reaction, and methods employed.

The media used to store the hydrogen, such as metal hydrides and complex hydrides, is examined in relationship to hydrogen yield, ease of hydrogen generation or treatment, cost and environmental friendliness. A list of popular catalysts - particularly precious/rare earth metals, strong acids and weak acids - is examined and compared in terms of hydrogen yield, environmental friendliness, and cost. The recent trend in hydrogen generation techniques and material treatment innovations such as hydrolysis, and ball milling of nanocomposites is examined. Innovations in hydrogen storage material selection and techniques will go a long way in lowering hydrogen generation cost, increasing hydrogen yield and ameliorating negative environmental impacts.

Keywords- Hydrogen generation, hydrolysis, ball milling, hydrogen storage media, catalyst

1.0 Introduction

Energy plays an important role in the day-to-day activities of man, whether it be for development and sustained growth of an economy, or for industrialization and other sectors of life. As such, there is an enormous pressure to produce enough energy to power the world, oftentimes resulting in an increased energy tariff. Similarly, the demand for energy is expected to skyrocket, owing to myriads of reasons like population growth, industrial growth, etc. [1]. Fossil fuels, hydropower energy, coal and nuclear energy are some energy resources used worldwide. However, some of these sources – particularly fossil fuel, coal and nuclear energy - are non-renewable [2, 3]. Furthermore, they have also been identified as candidates of environmental pollution as a result of the greenhouse gases emitted as by-products of their production and usage [3, 4] . Hydro energy, though renewable, is also affected - by the dwindling availability of water resources in regions stricken by global warming-induced climate change. As such, hydropower's applicability has been limited to nations with suitable geographical and climatic conditions, usually near bodies of water. The realization of these challenges has played a crucial role in the paradigm shift to energy production. Many nations have embraced a multifaceted approach to energy generation. However, the use of the traditional energy generation systems (fossil, nuclear, coal, etc.) cannot be eliminated immediately because of inadequate sustainable green energy substitutes. The time is ripe for an aggressive and systematic approach to investment in renewable energy.

Hydrogen generation for energy use has generated much interest due to its potential as an environmentally benign approach toward energy generation, as well as its ease of transportation [5, 6]. Finding a sustainable approach toward hydrogen generation has long been one of the major challenges. Researchers have been exploring various means of increasing hydrogen yield and reducing production cost in order to ensure a sustainable approach to energy generation. This article reviews the advances in hydrogen generation with regards to the substrates, catalysts and hydrogen generation methods.

This paper is structured as follows: background to hydrogen generation, metal and complex hydrides storage, catalysts in hydrogen generation, advances in material treatment and hydrogen generation techniques, and the write up is rounded up with highlights of recommended future studies.

2. Background on hydrogen generation

The use of hydrogen in the industry for ammonia production dates back to around 1920; however its usage in the energy mix started around 1960 [7]. Hydrogen generation for energy purposes can be attained via various means. The major means of hydrogen production include: steam formation from natural gas, electrolysis, coal gasification, biomass gasification, and photolysis [7, 8]. Other sources include bio-hydrogen generation from microbial electrolysis of wastewater using microbial electrolysis cell (MEC) technology [9] and from chemicals such as metal, complex and chemical hydrides [10-12] . The use of hydrogen to power PEM fuel cells and prototype hydrogen cars is well documented [6, 7] . Major areas of research with regards to hydrogen generation from mobile media focus on the efficient storage and carriage [6, 13, 14] of hydrogen. The focus of this review is on hydrogen generation from light weight metals.

3. Metal and Complex hydrides hydrogen storage

Physisorption and chemisorption approaches to hydrogen storage are attractive options in lightweight materials. The main challenge to physisorption is the low temperature (cryogenic) requirement, which is currently difficult to attain [15]. Similarly, the chemisorption reaction of hydrogen with metals, alloys and other complex compounds results in the formation of hydrides which are good candidates for hydrogen storage [14] . However, the major challenges to this promising method of hydrogen storage include a high temperature requirement, low gravimetric density of the hydrides and prohibitive costs [6]. The rest of this section will review some of the advances in the hydrogen generation from hydrides.

Metal hydrides are the products of the reaction of hydrogen with transition metals and alloys at high temperatures. Most notably, metallic hydrides are binary hydrides formed by the transition block metals due to their metallic nature [15] . Metal hydrides are popular hydrogen storage media. Among the promising metal hydrides often studied as hydrogen storage candidates are the metal borohydrides [16, 17]. Sodium borohydride ($NaBH_4$), for example, contains about 10.6 wt% hydrogen and is one of the attractive hydrogen storage media being studied currently [18, 19]. Li and Wang [20] reported a successful design and incorporation of a 2.5 L cobalt oxide and nickel catalyzed $NaBH_4$ on-demand hydrogen generation reactor with a PEMFC. The reactor was operated under batch mode with the optimum conversion rate and peak energy flow rate performance recorded at 15 wt% substrate concentration at 300 ml batch operation mode. Furthermore, on the $NaBH_4$ studies, Akdim and fellow workers [21] catalyzed hydrogen generation from $NaBH_4$ using acetic acid. The experiment was reportedly conducted using three different substrate-catalyst concentrations (0.5, 1 and 2 M) with 100% conversion rate recorded at 2M acetic acid concentration. The study emphasizes the suitability of $NaBH_4$ as a promising substrate candidate for hydrogen storage in portable applications. The United States Department of Energy (DOE) indicated in the go/no-go article [22] that $NABH_4$ unfortunately is not a suitable hydrogen storage candidate for applications in automobile storage purposes. Similarly, the same report [22], cited corrosiveness as one of the factors that indicted $NaBH_4$ as a non-sustainable substrate for hydrogen generation. Nevertheless, the substrate may still be relevant for small or portable applications.

Complex hydrides are light weight metal hydrides usually formed from the alkali, alkali earth and group three metals [15]. They release hydrogen when reacted with water [23] and usually have two hydrogen atoms attached to each metal atom [15]. Lithium borohydride ($LiBH_4$) is a complex boro-hydride with a huge hydrogen reserve. The gravimetric hydrogen density of $LiBH_4$ is reported to be about 18 wt % [24, 25]. However, the major challenge to effective use of $LiBH_4$, like most metal borohydrides, is managing the high temperature that results from the dehydrogenation enthalpy change [26, 27]. The U.S. Department of Energy (DOE) initiated an interesting thermodynamically enhanced approach called destabilization to improve the kinetics, hydrogen adsorption and desorption rates of metal and complex hydrides for hydrogen storage [28].

According to Klebanoff and fellow workers [29] , destabilization remediation technique entails the addition of another substance to metal or complex metal hydrides with the aim of improving the chemical state when hydrogen is emitted, leading to reduction in enthalpy limitations to hydrogen generation in the light weight metals. The destabilization technology lead to the development of a number of novel destabilized hydrogen storage materials among which $LiBH_4/Mg_2NiH_4$ is regarded as a promising material. The interest in $LiBH_4/Mg_2NiH_4$ is due to its unique attributes which, according to Vajo et al. [30], include reversibility potential, development of a unique ternary boride phase, a low temperature kinetic route, and low enthalpy/entropy [28]. However, practical application of the $LiBH_4/Mg_2NiH_4$ for onboard hydrogen storage use in vehicles is limited by the low hydrogen capacity recorded at low temperature step (2 wt%) which is lower than the recommended value by the DOE [28, 29] . Interestingly, the material has nevertheless opened up various possibilities for other hydrogen generation procedures [29].

3.1 Catalysts in hydrogen generation

The poor thermodynamics – physisorption and chemisorption of most of the light weight hydrogen storage materials is a limitation to hydrogen storage in the mobile storage devices [15]. The development necessitated the use of various substances to improve the reaction kinetics. Among the materials that have been used to improve these reaction thermodynamics include rare earth metal catalysts, strong acids and organic acids. This section reviews some of the materials that have been reported in hydrogen generation studies.

3.2 Noble metals and transition metal catalysts

Noble or rare earth metals are a special group of metals in the periodic table with good catalytic ability. These groups of metals have been employed as catalysts in hydrogen generation experiments to improve the kinetics or thermodynamic properties of the reaction, with remarkable success. Despite their good catalytic ability, these catalysts are expensive, thus increasing the cost of hydrogen generation and posing a sustainability limitation to hydrogen generation.

Liu et al. [31] reported the use of precious metal based catalysts in the hydrolysis reaction of borohydride for hydrogen generation. The performances of Raney nickel (Raney Ni) and Raney cobalt (Raney Co) catalysts and alloys were investigated for reaction kinetics improvement in the study. The authors [31] reported impressive catalytic effects on hydrogen generation and reaction kinetics for Raney Ni and Co catalysts. The study also reports better performance in the alloys compared to that of pure metals (Raney Ni and Raney Co). The author also claims relative low cost for the transition metal catalysts employed in the study. The cost analysis of the experiment was not reported; nevertheless, nickel and cobalt may not be regarded as sustainable catalysts for hydrogen generation because of the high cost of these metals, if the goal of hydrogen generation in a sustainable manner is to be attained.

Ruthenium (Ru) has been reported as catalyst in hydrogen generation experiments [32-34]. Gervaso and fellow workers [34] catalyzed the hydrolytic reaction of sodium borohydride with Ru catalyst for hydrogen generation. The study reported interesting performance in terms of hydrogen yield (hydrogen flow rate) and the safety of the reactor employed for the test. On the contrary, the use of Ru catalyst increased the cost of the experiment. Similarly , as earlier indicated by Chao and Jen [35], notwithstanding the cost limitation owing to the Ru catalyst, the reaction is nonrenewable since the end product of the reaction cannot be reused. Uan et al. [36] also reported the use of platinum (Pt) coated on Titanium (Ti) net as catalyst in the hydrolysis reaction for generation from low grade magnesium scraps in aqueous sodium solution. The experiment was conducted in two formats with: statically loading of the catalyst on the substrate (Mg) and the grinding of the substrate and catalyst. The results from the experiment indicate increased hydrogen yield by displacing the $Mg(OH)_2$ inhibiting the reaction surface and a better hydrogen yield in the grinding mode. Moreover, the study reports another remarkable result in the use of recycled magnesium metal. However, the use of Pt catalyst and Ti net increases hydrogen generation cost, thus posing a sustainability limitation.

3.3 Strong acids

With the challenge of high cost of some of the metal catalysts, researchers have been exploring the use of other cheaper materials to enhance hydrogen generation reactions. The use of strong acids such as hydrochloric acid (HCl) , H_2SO_4, and H_3PO_4 has been reported in hydrogen generation studies to improve the reaction kinetics [21, 37]. Akdim et al. [21], reported the use of HCl as an accelerator to enhance the reaction kinetics of sodium borohydride in an hydrogen generation experiment. The application of HCl enhanced the substrate conversion rate with almost 100% conversion rate 1 and 2 molar ratios HCl-$NaBH_4$. Notwithstanding the alluring potentials of strong acids as strong candidates for accelerating hydrogen generation reactions in small scale applications, their corrosive nature is harmful to the environment. Also, reactions involving strong acids may pose safety issues due to their violent characteristics [38].

3.4 Organic acids

The use of organic acids as liquid accelerators in hydrogen generation studies is gaining momentum. The remarkable qualities of these group materials include environmental friendliness, relative low cost, reduced hazardous potential and good catalytic qualities [21, 35, 37, 38]. In a study by Akdim et al. [39], $CoCl_2/Al_2O_3$ catalysts were treated with five acid accelerators made up of three organic acids (citric, oxalic and acetic acids) and two strong acids (hydrochloric and sulfuric acids) for hydrolysis of $NaBH_4$. The acid accelerators enhanced the catalytic activities of the catalyst and hydrogen yield of the substrate. The results from the study indicated that hydrochloric acid (strong acid) and acetic acid (weak/organic acid) recorded the best performance on addition to the catalysts for hydrogen generation.

In another study, Akdim et al. [21] demonstrated the advantage of acetic acid as an environmental friendly organic acid accelerator in a hydrogen generation experiment over hydrochloric acid, a strong acid. The two accelerators were added to $NaBH_4$ in the hydrolysis reaction for hydrogen generation to measure and compare their reactivities. The two acids exhibited similar kinetics. Accordingly, the hydrochloric acid catalyzed hydrolysis reaction recorded 100% recovery while the acetic acid accelerated reaction recorded over 90% recovery rate. However, the study underscores the advantage of acetic acid as a catalyst for hydrogen generation over HCl in the environmental benign and reduced hazard potential (corrosiveness). Successful application of acetic acid as an acid accelerators in other hydrogen generation experiments have been reported [37, 40].

Citric acid is another weak acid with burgeoning interests in hydrogen generation studies. Uan et.al [41], studied hydrogen generation from low grade magnesium scraps and other magnesium coated metallic wastes in a citric acid catalyzed sea water by hydrolysis. The hydrogen yield during the experiment were about 19 L (5 wt % citric acid) and about 50 L when 20 wt % was used as the accelerator. Another land mark reported in the study was hydrogen purity of approximately 99% after dehumidification. In another study Chao and Jen [35] catalyzed the hydrolytic generation of hydrogen from a magnesium hydride pellet with citric acid. Interestingly, the authors reported high hydrogen yield of hundred 100% under some experimental conditions. Moreover, hydrogen generated from the experiment was estimated to cost about $15/kg. However, the quantity of substrate applied in the reaction was limited due to the violent nature of the experiment, thus limiting real time study of the maximum hydrogen yield obtainable. It is also noteworthy that the use of citric acid has been reported in other hydrogen generation studies [38, 40, 42].

4.0 Advances in material treatment and hydrogen generation techniques

Light weight metals have become a veritable media for hydrogen storage because of its potential for mobile applications. Various innovative techniques have been reported for hydrogen generation and material treatment in light weight metals. This section will discuss methods such as hydrolysis and ball milling.

4.1 Hydrolysis

Hydrogen generation through hydrolysis reactions is one method of hydrogen generation. The application of this technique has recently become popular, especially in solid state hydrogen storage for mobile applications, due to lower temperature requirement and ability to generate delocalized hydrogen [43]. Hydrolysis of various metal and complex metal hydrides has been explored for hydrogen storage [4, 10, 12, 43-47]. For example, hydrolysis of magnesium hydride or various magnesium based metals or complexes has been reported [48] with success. Wang and colleagues [49] reported hydrolysis of aluminium in sodium hydroxide solution using a mini hydrogen reactor. The study recorded hydrogen yield of 38 ml/min with 25 wt% aluminium and 77 % hydrogen utilization ratio. On the contrary, sodium hydroxide is corrosive in nature with a likelihood of safety challenges [35]. Hydrogen generation from hydrolysis reaction is usually hampered by reaction poor kinetics as some reactions are highly explosive or too slow [50]. This development has led to the application of other techniques besides the use of metal catalysts or accelerators, such as ball milling of substrates.

4.2 Ball milling

Ball milling of metal, complex metal hydrides or composites for hydrogen generation entails the reduction of the particle sizes of the constituent materials, usually to nanocrystalline sizes, and usually by grinding. Ball milling increases the reaction surface area, thus improving sorption kinetics of the substrates in the hydrolysis reaction [51]. In one of the early applications of ball milling technique for hydrogen generation, Hout and fellow workers [50] examined the hydrolysis of magnesium hydride and magnesium hydride based nanocomposites. Results from the study indicated that ball milling of the magnesium hydride and composites to nanocrsytalline structure improved the hydrolysis reaction kinetics. Also, longer ball milling time was also reported to enhance the reaction due to production of finer particle sizes. However, the authors did not report the optimum particle size in the reaction below, which reduced crystalline size will not enhance the reaction kinetics. Thereafter many studies have been conducted to examine ball milling [43, 52-62]. Ball milling remains an area to further explore for improved hydrogen generation.

5.0 Future Research Direction

Most of the studies on hydrogen generation from lightweight materials vigorous nature in nature thereby limiting the amount of substrates applied in the experiments for safety reasons. The situation has also limited the understanding of maximum hydrogen yield obtainable form such experiments. In order to lessen the impact of this limitation on the body of knowledge, two approaches should be considered:

1. Modelling of hydrogen yield at high substrates (metal and complex metal hydrides) concentrations
2. Design of reactors capable of withstanding high reaction pressure.

In view of the impressive results from ball milling studies, experiments should be conducted to determine the optimum crystalline size for most of the metal hydrides and complex metal hydrides. Doing this will further develop knowledge base on hydrogen generation, particularly the maximization of the potentials of ball milling technology.

6.0 Conclusion

Hydrogen storage in light weight mobile applications is an important component of the energy niche due to its relatively low environmental pollution characteristics, renewable potentials, applications in PEM fuel cells and automobiles. However, challenges such as poor reaction kinetics have limited hydrogen generation in these media. This review presents innovations in material treatment and catalysts applications aimed at improving the reaction thermodynamics for hydrogen generation from metal and complex metal hydrides.

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