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REVIEW ARTICLE

Hydrogen generation from sodium borohydride solutions using different catalysts for the survival of living beings in the long-time space flights

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HIGHLIGHTS

- *This article is an exchange of chemistry knowledge concerning catalysts, state of the art of technology useable in space requirements, such examples include energy, waterproof for long duration space flights.*
- *It provided a review for wide range of catalysts available for this purpose.*
- *Introduction of sodium borohydride as a safe alternative for long duration space flights.*
- *For fuel cells applicable catalyst hydrogen generation rate optimization and also generation rate reduction in critically space flights such as re-entry.*

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ABSTRACT

Hydrogen (H2), an environmentally friendly effective energy carrier with the most advantageous combustion by-products, readily attained from borohydride (NaBH4) with higher hydrogen (H2) generation rates (HGRs) as safer than e other hydrates necessitating the use of various catalysts. The catalysts' performances are major factors in high HGR from NaBH4 regardless of hydrolysis or methanolysis reactions. The HGR is influenced by NaBH4 concentrations, reaction temperature, and the catalyst amounts. Nobel metals e.g., ruthenium (Ru), platinum (Pt), Rhodium (Rh) etc reported as highly effective catalysts for fast H2 production from NaBH4 solutions including ethanol, methanol, and ethylene glycol. Due to shortage and cost considerations of noble metals, transition metal-based catalysts e.g., cobalt (Co), nickel (Ni), and manganese (Mn) have gained great interest for H2 production from NaBH4 hydrolysis/alcoholysis. Metal nanoparticle-based catalysts, and their synthetic and natural polymer composites along with non-metallic catalyst including micro/nanogels, bulk hydrogels, cryogels, and polymeric ionic liquids (PILs) have been employed as catalysts in methanolysis/hydrolysis of NaBH4 to attain lower Ea and high HGR values. Therefore, in this review catalysts whether metal or non-metal used in H2 generation reactions will be surveyed, Moreover, space application of H2 energy systems with their commercial application for future use will be assessed.

Keywords: *Hydrogel; supporting material; Metal Organic Frame (MOF); energy; hydrogen generation*

I. INTRODUCTION

The space vehicle should have a similar environment to Earth for the crew living on board. Air, food, water, and a comfortable temperature are survival requirements of space life including taking away the waste that humans and plants produce such as carbon dioxide, urine, feces. The space vehicle should have an atmosphere similar to Earth and should remove carbon dioxide and contaminated gases and finally should provide to crew and plants a normal humid environment such that;

- Oxygen and nitrogen systems are used to pressurize the space vehicle cabin during the entire flight including launching and landing.
- The circulated air is picking up carbon dioxide and removing carbon dioxide by reacting it with lithium hydroxide. Lithium hydroxide is an attractive choice for space flight because of its high absorption capacity for carbon dioxide and the small amount of heat produced by the reaction.
- Filters and charcoal containers accumulated with odors, dust, and volatile chemicals from leakage, spilling and gas formations must be changed every required period.
- Out of space vehicle is an extremely cold environment and temperatures will vary drastically in different parts of the vehicle. The heating system of the vehicle would be a problem. However, the electronic equipment generates more than enough heat for the ship. The problem is getting rid of the excess heat.
- Cabin heat exchanger cools the air and condenses the moisture which collects in a liquid mixture. The air is recirculated, and the water goes to a wastewater tank using centrifugal force of fan separator to keep apart water from air. Air and water are the most important quantity aboard the space vehicle. Water is made from liquid oxygen and hydrogen in the space shuttle's fuel cells, nearly 11 kg of water per hour. The water tanks are pressurized by nitrogen for the circulation of water that can be used by the crew. Drinkable water is then filtered to remove microbes and can be warmed or cooled through various heat exchangers depending upon the use of food preparation, consumption, and personal hygiene.
- The space vehicle has internal fluorescent floodlights that illuminate the crew compartment. The vehicle has external projectors to illuminate the load compartment. Finally, the control panels are lit internally for easy viewing.
- Necessary electrical interspace shuttle navigation, for the changing direction of the space shuttle and the space communications should be produced during the flight.

The author is highly interested in the space life scenario requirements listed above and the hydrogen and electrical energy production from sodium borohydride solution which will be one of the major sources for space vehicle energy. So that presented article “new catalysts review” would create very important and beneficial alternatives for the rational design alternatives of space fuel cell technology using $NaBH_4$ hydrolysis.

Hydrogen (H_2) is the most abundant compound in the universe. It is present in compounds and 80% by mass of the sun. The mostH_2 in the world is present as compounds and the most common compound is water which composes 11.1% H_2 in its mass. H_2 forms compounds in its compositions more than any other element such as of all natural gases, mineral acids, ammonia, hydrocarbons and organic compounds, alcohols and even in proteins containing hydrogen (Grochala, 2015[40]). Environmentally friendly H_2 should be used as alternative secondary energy and more, as primary energy source required to produce for separating hydrogen from water, since 33% more energy is consumed than what will be gained from H_2 which is traditionally produced from hydrocarbons and water (Retnamma et al., 2011[77]). Limited oil, coal fossil-derived energies and their negative impact of green house, air pollution on the environment, increased use of hydraulic energy and insufficient energy coming from water were strengthened by alternative energy such as solar, wind, biofuel and H_2 sources. Unfortunately, H_2 is secondary energy. The most probable candidates of the energy sources are listed above but nuclear energy can be used as primary energy to produce H_2 and $NaBH_4$. Use of H_2 in any vehicle by using $NaBH_4$ requires less volume, but more energy is highly expensive than the energy of the fossil-derived fuels should we exclude air pollution and human health considerations. The energy content of liquid hydrogen has as 120 MJ/kg whereas 44 MJ/kg for gasoline on mass basis; however, on the volume basis the situation is reversed, the energy content of liquid hydrogen is 8 MJ/L, which is less than gasoline with 32 MJ/L (Giappa et al., 2021[39]; Osman et al., 2022[71]).

Among the H_2 storage systems, the most important high hydrogen containing materials are metal hydrides, and sodium borohydride ($NaBH_4$) is the most remarkable source because it is considered as stable, non-toxic and contains high amounts of hydrogen and easy to process. Turkey has the richest resources in the world in the high-rate capacity of boric acid production which is used for the storage of H_2 in $NaBH_4$. The hydrolysis reaction of $NaBH_4$ forwarded from the well-known Eq. (1);

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad \Delta H = -217\ kJ/mol \qquad \textbf{Eq. (1)}$$

Water handling Eq. (1) is an exothermic and spontaneous reaction, and this kind of reaction can be accelerated by adding different types of catalysts in the reactor system (Santos and Sequeira, 2011[94]). A major issue is the required water volume, but the second major issue is determination of types of catalytic material to be used (Demirci et al., 2010[30]).

In Table 1, the solubility of $NaBH_4$ in different solvents is presented. The stoichiometric chemical reaction of Eq. (1) regarded as at least 2 molar equivalents of water are required for each mole of sodium borohydride in the reaction. The solubility of $NaBH_4$ in water is 550 mg/g (Brack et al., 2015[16]). The gravimetric hydrogen storage capacity of $NaBH_4$ is stated to be quite lower than the theoretical value of 10.8 weight % (wt%), and it is recommended not to be used in automotive engine sector due to its cost as well (Demirci et al., 2009[31]). $NaBH_4$ is cost-effective for small portable equipment such as chargers for mobile phones, tablets, and laptops (Bartkus et al., 2013[13]) where pH can be used as an "on-off" control to reduce E_a and increase HGR in contact with a heterogeneous catalyst.

Table 1. Solubility of $NaBH_4$ in various solvents.

Solvents	Boiling Point (°C)	Reaction Temperature (°C)	Solubility (g/100g solvent)
Water	100	25	55
Methanol	67	20	16.4
Ethanol	78.5	20	4.0
Isopropyl amine	34	28	6.0
Ammoniac	-33.3	25	104.0

H_2 production reactor, lines, and fuel cell with H_2 production unit is shown in Figure 1, and the catalyst made up of fine noble metal powder will be highly explanatory for figuring out the role of catalysts in full aspects of H_2 generation and fuel cell technology. In a $NaBH_4$ used type of fuel cell, H_2 is produced at the anode, and the catalyst platinum powder breaks downs electrons, similarly water or carbon dioxide are eluted, and metal ions are accumulated at the cathode catalyst is zinc, Zn. Typical voltage produced with a loss of energy drops due to voltage drops are caused by component resistance of the fuel cell, ohmic loss of interconnections, and consumption of reactants at catalyst sites in fuel cells.

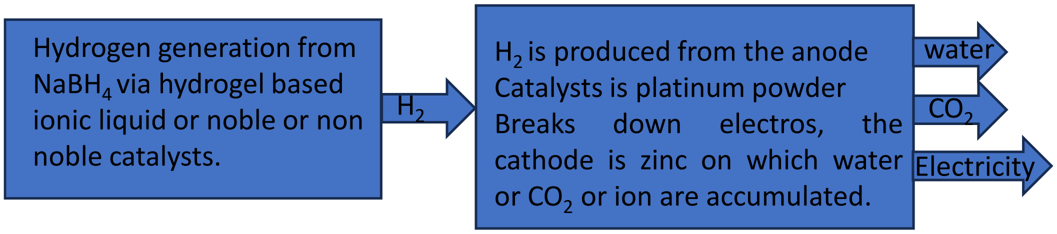

Figure 1. Schematic presentation of fuel cell energy using $NaBH_4$ (Bartkus et al., 2013[13]).

The reaction will progress at the anode with hydrogen reaction energy transfer till the temperatures become very high. In the use of catalysts, catalyst itself, temperature and increase of electrode area are the three main factors of the slowing down of the reaction rates, so that the electrodes are made highly porous. This has the effect of greatly increasing the effective surface area. In fuel cell design the reaction rate is proportional with the area of electrode and the cooperation of catalyst regarding temperature conditions. The fuel is oxidized by the catalyst, and H_2 turns the fuel into a positively charged ion at the anode and it produces negatively charged electrons. The electrolyte is a substance specifically designed so that the ions can pass through it, the ions are reunited with the electrons and the two reacts with a third chemical, usually oxygen, to create water or carbon dioxide. But the electrons cannot pass through it, the freed electron can travel through a wire creating the electric current. In Eq. (1), in the electrolyte, E_a is required for the generation of fuel gas H_2, and (OH^-) ions which should be placed on the surface of the electrode must be removed as the electrons produced. Electrons flow from anode to cathode, but conventional positive current flows from cathode to anode.

II. CATALYSTS USED in H_2 PRODUCTION FROM $NaBH_4$

The developed catalysts used for renewable and environmentally friendly secondary energy source, H_2, obtained $NaBH_4$ hydrolysis are categorized and presented in Figure 2 due to their specific advantages (Abdelhamid, 2021[1]) such as,
-rendering faster reactions kinetics and lowering the activation energy by accurately selecting the catalysts.
-Hydrogen generation rate (HGR) values of $NaBH_4$ hydrolysis reaction generally increases with use of rough and porous catalysts that afford maximum surface area.

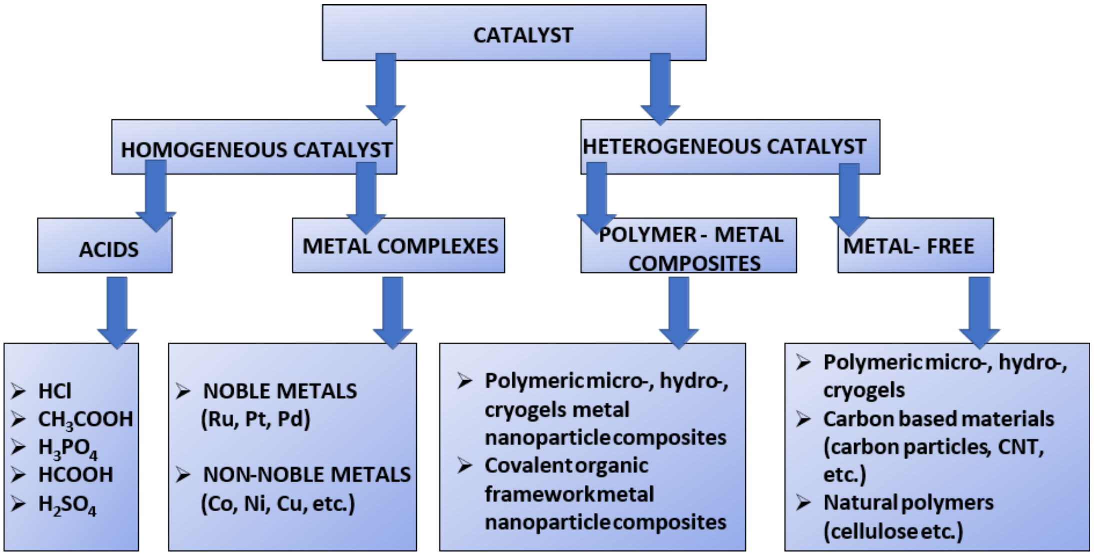

Figure 2. Classification of the catalyst used to obtain hydrogen using $NaBH_4$ (Abdelhamid, 2021[1]).

2.1 Homogeneous Catalysts

As the catalysts and reactants are in the same phase e.g., gas, liquid, and solid, those catalysts are called homogeneous catalysts.

2.1.1 Acids

The mineral acids, hydrochloric acid (HCl), nitric acid (HNO_3), phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), acetic acid (CH_3COOH), or the carboxylic acids (R−COOH) are used as homogenous catalysts in production of H_2 from the hydrolysis or even alcoholysis of $NaBH_4$ reactions.

Homogeneous catalysts made from acids are highly reactive at the optimum conditions; however, these catalysts have no recovery and recycling or minimum side reactions (Abdelhamid, 2021[1]). The most important advantage of these catalysts is their derivation from acids which are considered cheap, easy attainability and usability, and highly controllable nature. As seen in Table 2, the low activation energy of H_2SO_4 and the higher HGR compared to CH_3COOH played an important role in the use of H_2SO_4 in the fuel cell production of the unmanned aerial vehicles (Kwon et al., 2019[57]). Activation energy (E_a) and HGR values of sulfuric acid and acetic acid regarding to ratios at 60°C and 80°C temperature degrees are investigated (Akdim et al., 2009[5]) and summarized in Table 2.

Table 2. Comparison of E_a and HGR values of H_2SO_4 and CH_3COOH used in NaBH4 hydrolysis used at 60°C and 80°C (Akdim et al., 2009[5]).

[H_2SO_4/$NaBH_4$] Ratio	**E_a/HGR of (H_2SO_4) [(kJ/mol)/(ml/min.g)]**		**E_a/HGR of (CH_3COOH) [(kJ/mol)/(ml/min.g)]**	
	Temperatures		**Temperatures**	
	60 °C	**80 °C**	**60 °C**	**80 °C**
0.5	6.2/1800	6.2/1970	7.5/1240	7.5/1240
1.0	5.5/1800	5.5/2040	8.3/1330	8.3/1360
2.0	4.9/2000	4.9/2100	8.8/1350	8.8/1410

CH_3COOH compared to H_2SO_4 is less hazardous, as reactive as H_2SO_4 with similar hydrogen production rates (HGR) and similar total $NaBH_4$ conversions when the experimental conditions are optimized with similar kinetics for hydrolysis, methanolysis or ethanolysis. Also, some E_a and HGR values of different acids are compared in respect to concentration, reaction, condition and illustrated in Table 3 from the catalytic H_2 production from $NaBH_4$.

Table 3. HGR and E_a values for various acids used as catalytic for H_2 generation reaction from $NaBH_4$ (Akdim et al., 2009[5]).

Acid	**Acid Concentration (M)**	**Reaction types**	**HGR (ml/min.g)**	**E_a (kJ/mol)**	**References**
CH_3COOH	0.32	Hydrolysis	920	7.5	(Akdim et al., 2009[5])
HCl	0.32	Hydrolysis	1530	6.2	
CH_3COOH	1	Methanolysis	3960	2.81	(Balbay and Saka, 2018a[11])
HCl	1	Methanolysis	4875	5.84	
H_3PO_4	0.5	Semi-Methanolysis	11684	9.08	(Saka and Balbay, 2019[92])
H_3PO_4	0.5	Semi-Ethanolysis	9981	32.47	
H_3PO_4	1	Semi-Methanolysis	5779	1.45	(Balbay and Saka, 2018b[12])
H_3PO_4	1	Ethanolysis	6423	2.98	(Wang et al., 2017[101])
H_3PO_4	1	Hydrolysis	4296	2.60	
H_3BO_3	50	Hydrolysis	-	18.01	(Balbay and Şahin, 2014[10])

In was also reported that cryogenically cooled liquid hydrogen can be used in a conventional submarine under the sea (Choudhury et al., n.d.[26]). High density, controllable source of H_2 for fuel cells for the oxygen requirement and power generation must rise to the atmospheric surface which makes submarine undefended to adversaries. For that reason, H_2 is produced whenever H_2, demanded in the submarine with an air-independent propulsion (AIP) system. The AIP supply H_2 and fuel cell provides quieter energy for submarines with very high endurance for tactical behaviors. Production designed in the mid-1960s and field-tested since the 1970s, is based on a phosphoric acid (PAFC) fuel cell technology with an onboard sodium borohydride hydrolysis (Choudhury et al., n.d.[26]). Since then, this system has been used successfully with its stable and cost effective performance.

2.1.2 Metal-based homogenous catalysts

Various metal-based catalyst from transition metals or noble metals are commonly used in H_2 production from $NaBH_4$ or other H_2 sources. Some of the reported Ea and HGR values for metal-based homogeneous catalysts such as zinc chloride ($ZnCl_2$), iron (III) chloride ($FeCl_3$), and aluminum oxide (Al_2O_3) catalyzed $NaBH_4$ hydrolysis reactions are summarized in Table 4. Due to very fast dissolution of $ZnCl_2$, the reaction is proceeds very fast with high extent value of heat transfer and very rapid proton production in a short time (Wang et al., 2017[101]). In the $FeCl_3$ catalyzed reaction, the HGR values calculated as 2600 mL/(min.g) with an efficiency of 76% were reported (Boran et al., 2019[15]).

Table 4. Some of the HGR and E_a values of metal halides catalysts used in $NaBH_4$ hydrolysis.

Metal halides	HGR (ml/min.g) (5, 10, 120 min)	E_a (kJ/mol) (0/5/10/15/20 Wt%)	Reference
$ZnCl_2$ (298K)	844, 1039, 1933	79.5/64.3/59.8/54.8/47.7	(Wang et al., 2017[101])
$FeCl_3$	2600	-	(Boran et al., 2019[15])
γ-Al_2O_3 nanoparticles	(0.09 moles/l)	29	(Kaur et al., 2015[52])

Metal complex catalysts have been categorized into two based on metal sources such as noble and non-noble metals. Noble metal is regarded as a metallic chemical element resistant to corrosion. Amongst these mobile metals are gold, platinum, ruthenium, rhodium, palladium, osmium, and iridium are the most common ones whereas silver, copper and mercury are also sometimes included or considered as noble metals. Noble metals because of their catalytic capabilities are also called as active components of three-way catalysts (TWC) as they also play curial role in the mechanism of oxidation of carbon monoxides (CO), hydrocarbons (HC), and in the decomposition of nitrogen oxides (NO_x).

Noble metal-based catalysts are presented in Table 5, with the best catalytic active characteristics towards the hydrolysis of $NaBH_4$ with high HGR. By Ozkar et al.in (Özkar and Zahmakıran, 2005[72]) reports that ruthenium-based catalysts have high HGR of 96,800 ml/(min.g) with water dispersible ruthenium nanoclusters at environmental temperatures. Reaction rate constants at different temperatures are determined from the experimental data and the E_a is found as 66.9 kJ/mol from an Arrhenius plot in (Zhang et al., 2007[108]). The highest HGR of 18,600 ml/(min.g) performance exhibited with ruthenium-based catalyst in powder form generated from a ruthenium salt by reduction with sodium borohydride in (Walter et al., 2008[100]).

Table 5. Some of the E_a and HGR values of noble metal catalyst used in $NaBH_4$ hydrolysis.

Catalyst	HGR (ml/min.g)	$NaBH_4$ (wt%)	NaOH (wt%)	Reference
Ni_3B	1300	5	5	(Walter et al., 2008[100])
Co_3B	6000	5	5	
Ru	18600	5	5	
Pt/Ru-$LiCoO_2$	3000	10	5	

Ru-Pt	15200	10	3	(Demirci and Garin, 2008[32])
Polymer-Ru composite	132	5	1	(Hsueh et al., 2008[42])
Ru Polymer supported	216	1	1	(Chen et al., 2009[20])
Ru on graphite	32300	10	5	(Liang et al., 2010[61])
Ru-RuO_2/C	16800	5	1	(Li et al., 2013[59])
Ultrasmall Ru chitin Nanofibers	55290	-	-	(Zhang et al., 2020[107])

In the recent studies of H_2 production, the range of highest HGR values of 15200 mL/(min. g) was reported (Demirci and Garin, 2008[32]). The used Ru_2Pt_1-TiO_2 catalyst was re-evaluated and almost the same catalytic activities as fresh catalyst was obtained during several cycles, after separation and rinsing with deionized water (Demirci and Garin, 2008[32]). Also, ultrasmall Ru chitin Nanofibers with a HGR value of 55290 mL/(min.g) and Ru particles on graphite with HGR value of 32300 mL/min.g (Li et al., 2013[59]) are very impressive statistics to be considered (Zhang et al., 2020[107]).

Important concentration dependent performance with supported catalysts, $LiCoO_2$ was investigated such that the borohydride concentration was increased beyond 10% in weight, and it is reported that the HGR was decreased. The efficiency of PtRu-$LiCoO_2$ was almost two times higher than the efficiency of Ru-$LiCoO_2$ or Pt-$LiCoO_2$ for $NaBH_4$ concentrations up to 10% in weight in hydrolysis reactions (Liu et al., 2008[63]).

New homogeneous catalysts based on transition metals such as Mn, Fe, Co, Ni, and Cu are desirable due to their economics and environmental advantages compared to noble metals and some of them are summarized in Table 6 for HGR values at certain reaction conditions. As can be seen from the table, Co and Ni have been found to be the most common transition metals with their low cost and similar catalytic performances compared to noble metals.

Table 6. Non-noble metal based, or transition metal-based catalysts used in hydrolysis of $NaBH_4$ for H_2 generation with their HGR and reaction conditions.

Catalyst	HGR (ml/min.g)	$NaBH_4$ (wt%)	NaOH (wt%)	Reference
CoMnPt/Al_2O_3	5600	2	3.75	(Çakanyildirim and Guru, 2021[18])
CoMnPt/TiO_2	6250			
CoB/TiO_2	12503	1	3.75	(Lu et al., 2012[65])
CoB/Al_2O_3	11649			
CoB/CeO_2	10389			
Co–Mo–B	4200/19000	5	5	(Zhuang et al., 2013[112])
CoB/SiO_2	10586	0.5 g	1.875 g	(Yang et al., 2011[105])
Ni/Fe/B	2910	5	4	(Nie et al., 2012[69])

2.2 Heterogeneous catalysts

In general, solid materials added into liquid or gas reaction environments for effective catalytic performance that can reduce E_a and/or increase HGR, called heterogeneous catalysts (Kaur et al., 2015[52]). The heterogeneous catalysts can improve hydrolysis of $NaBH_4$ are cost efficient for hydrogen storage material in portable applications. The pH of water in hydrolysis of $NaBH_4$ can also be influenced based on the nature of catalysts as the catalyst can also be acidic or basic in nature. Recently different heterogeneous noble metals catalyst such as ruthenium, palladium, platinum and rhodium have been used for H_2 production reaction in the hydrolysis of $NaBH_4$ (Chen et al., 2009[20]; Demirci and Garin, 2008[32]; Hsueh et al., 2008[42]; Kaur et al., 2015[52]; Li et al., 2013[59]; Liang et al., 2010[61]; Özkar and Zahmakıran, 2005[72]; Walter et al., 2007[100]; Zhang et al., 2020[107], 2007[108]).

2.2.1. Polymer Metal Based Composites

Transition metals are the most common elements with electron rich clouds in the outermost shells that take part in the formation of chemical bonds with other elements including metallic bounds. Their compounds as heterogeneous and homogeneous catalysts including metals e.g., Yttrium (Y), Zirconium (Zr), Niobium (Nb), Molybdenum (Mo), Technetium (Tc), Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Silver (Ag), and Cadmium (Cd), with their sulfides and metallic salts, and other formulations with other materials can be used as heterogenous catalysts. Also, hydroperoxides and ion exchangers are also heterogeneous catalysts in a different phase from the reactants. For the catalysts various supporting materials including polymer, silicate and alumina are widely used. Since the surface area of the catalyst plays a significant role in the catalytic performance, to prepare catalysts with high surface area is of significant importance. One of the well-known methods to increase the surface area the catalyst covers is their distribution over the support material. Support material may or may participate in the catalytic reactions. Some of the inert or active supports material are presented in Table 7.

Table 7. Most commonly used support materials with some of their specifications employed in the preparation of catalysts.

Supporting Material	Symbol	M_w (g/mol)	Surface area (m^2/g)
Active Carbon Vulcan XC72	C	12.01	240
Active Carbon,5303	C	12.01	253
Active Carbon Ensaco	C	12.01	65
Zirconia Oxide	ZrO_2	123.22	<10
Aluminum Oxide	Al_2O_3	101.945	255
Carbon Nanotube (multiwall)	C	12.01	>>100
Silicon Carbur Powder, 30 nm	SiC, β	40.10	109

Some of the values of HGR and E_a Co based catalyst prepared in different support materials are given in Table 8. In the references (Baydaroglu et al., 2014[14]) and (Zhu et al., 2012[111]), a quite high HGR values are obtained as 8034 ml/min.g and 10400 ml/min.g, respectively. In the alumina supported amorphous alloy Ni–Co–P/γ-Al2O3 catalysts were prepared by using electroless plating for H_2 production from catalytic hydrolysis of $NaBH_4$ (Li et al., 2014[60]). Various parameters such as deposition time, pH, $NaBH_4$ concentration and the Co/Ni atomic ratio are the parameters that are affective on the HGR, and the optimum values of HGR of 6600 mL/min.g and Ea = 52.05 kJ/mol were reported (Li et al., 2014[60]).

Table 8. HGR and E_a values of some Co based catalyst prepared on some C and on γ-Al_2O_3 supports used in $NaBH_4$ hydrolysis.

Catalysts	HGR (ml/min.g)	E_a (kJ/mol)	Reference
Co-B, supported C	8034	56.7	(Baydaroglu et al., 2014[14])
Coll. Carbon Supported CCS Cobalt	10400	24.04	(Zhu et al., 2012[111])
Alumina supported catalysts (Ni–Co–P/γ-Al_2O_3)	6600	52.05	(Li et al., 2014[60])

2.2.2 Electrocatalysts

An electrocatalyst is a catalyst that participates in electrochemical reactions. Electrocatalysts are the catalyst that contain functional groups on the electrode surface itself. An electrocatalyst can be heterogeneous such as a platinized electrode or homogeneous electrocatalysts, which are soluble assist in transferring electrons between the electrode and reactants and facilitate an intermediate chemical transformation for an overall half reaction. The rate of chemical reactions of the materials in the process of functioning at electrode where the surfaces are modified and increased without being consumed is also named as electrocatalyst. Electrochemical sensing applications of 3D porous nanomaterials which are derived from noble metal-based alloys can be prepared readily using different reaction tools for different electrocatalytic applications (Demir et al., 2018[27]; Dursun and Solmaz, 2024[35]; Kutyła et al., 2020[56]; Lu, 2019[64]; Solmaz and Yüksel, 2019[97]). Fuel cells with electrocatalysts can also afford advantages for electrochemical sensors, and the by implementing nanoporous noble metal-based alloys in electrocatalysis in fuel cells using methanol, ethanol, formic acid and oxygen can also be used as electrochemical sensors for small biomolecules such as glucose, hydrogen peroxide, dopamine, ascorbic acid, uric acid, nitrite, drugs, etc.

2.2.3 Carbon based materials

Various forms of carbon materials have been utilized including sheets made of a single layered carbon atoms, graphene, and carbon nanotubes (CNT), carbon particles and carbon black and so on. CNTs are long, hollow tubes made of carbon atoms in a lattice just thickness of one atom. Dimensional and structural advantages of various forms CNTs are leading to intriguing applications including nanotechnology, electronics, water treatment because of their attractive physicochemical properties e.g., electrical conductivity, mechanical strength, chemical resistant, optical properties, and thermal stability, large surface areas and so on. Some of the carbon-based macromolecules, used for different purposes including catalytic application is demonstrated in Figure 3.

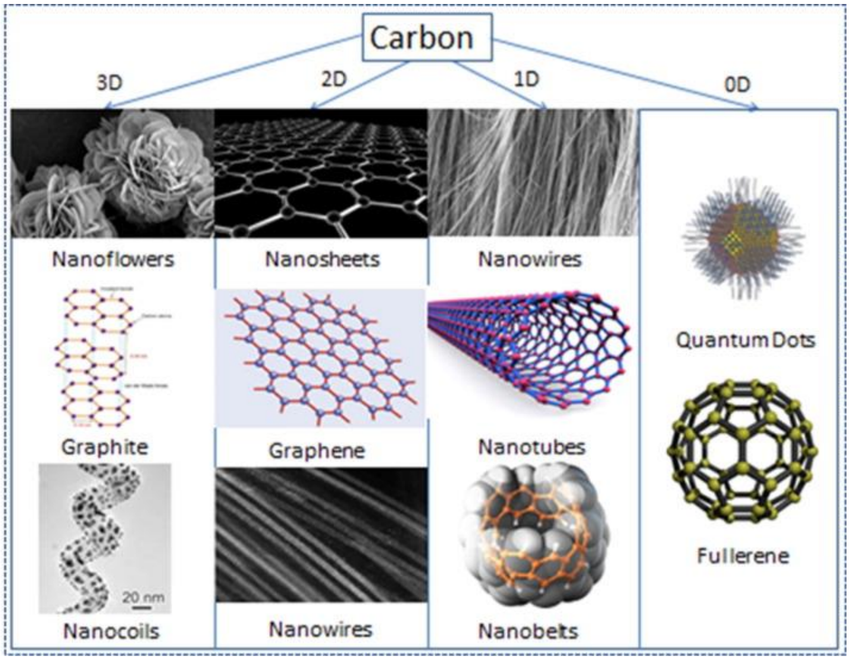

Figure 3. Some examples of carbon-based materials (Karamveer Sheoran et al., 2022[51]).

Multi wall carbon nanotubes (MWCNTs), carbon fibers, mica and most types of carbon black, are widely used as additives to improve the material properties of the starting even with 0.01% by total weight. As shown in Figure 4, MWCNT differs from single walled carbon nanotubes (SWCNT) based on their multi-walled telescopic tube structure and rigidity, and from carbon nanofibers based on their different wall structure such as smaller outer diameter, and hollow interior.

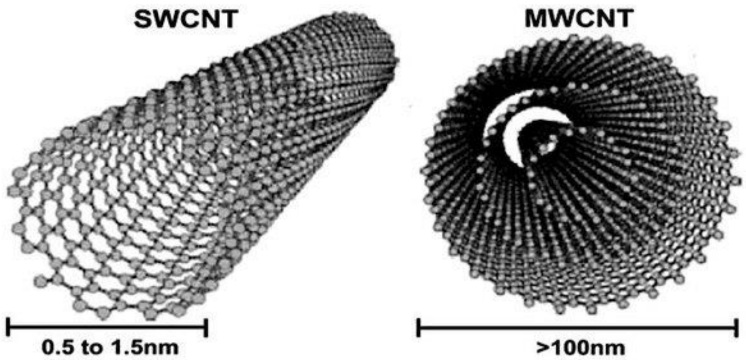

Figure 4. Comparison of the lumen size of single walled (SWCNT) and multi walled (MWCNT) nanotubes (Meyyappan and Srivastava, 2002[68]).

Catalysts that are used in H_2 production from $NaBH_4$ hydrolysis utilizing various formulation of CNT are presented in Table 9 with relevant HGR and Ea values.

Table 9. Various forms of CNT coating catalyst used in $NaBH_4$ hydrolysis and/or methanolysis with relevant HGR and E_a values.

Carbon nano tubes	Temperature (°C)	E_a (kJ/mol)	HGR (ml/min.g)	Reference
CoPt nanoparticle PEDOT:PSS/MWCNT	25	47.3	6900	(Wang et al., 2015[102])
(Co–B/MWCNT)	25	40.40	3100	(Huang et al., 2008[43])
(Pt/MWCNT) - (Pt/C)	27–67	27-36	-	(Uzundurukan and Devrim, 2019[99])

It was reported that CoPt-PEDOT:PSS/MWCNT catalyst performs excellent catalytic performances in $NaBH_4$ hydrolysis reaction with an E_a value of 47.3 kJ/mol and HGR value of 6900 mL/(min.g) at 298 K (Wang et al., 2015[102]). The mesoporous catalyst, Co–B/MWCNT was found to have a lower E_a, 40.40 kJ/mol, and HGR value of 3100 mL/(min.g) which is lower than the average HGR of 5100 mL/(min. g) of Co–B/C catalyst and quite stable for the continuous hydrolysis under the same conditions for the hydrolysis of $NaBH_4$ (Huang et al., 2008[43]).

On the other hand, a natural clay, halloysite nanotubes (HNTs) which similar to CNT in shapes were reacted with (3-aminopropyl)triethoxysilane (APTES) and then protonated upon HCl treatment to obtain modified HNT, mod-HNTs ($HNTs\text{-}NH_2.HCl$) and used as catalyst in H_2 generation from methanolysis $NaBH_4$ (Sahiner and Sengel, 2017[84]) also demonstrated comparable catalytic performances with CNT base materials used for the same purposes..

The activation energies values for Pt/MWCNT and Pt/C catalysts were found to be 27 kJ/mol and 36 kJ/mol, respectively however, it was reported that Pt/MWCNT is more efficient than Pt/C catalyst, and the efficiency% were approximately 98% and 95%, respectively (Uzundurukan and Devrim, 2019[99]). The hydrolysis system based on $NaBH_4$ in the presence of Pt/MWCNT catalyst was suggested to be an alternative source as HGR are concerned in mobile proton exchange membrane fuel cell (PEMFC) applications. On the other hand, MWCNT-COOHs are found to be very efficient catalysts compared to the metal-based nanoparticle catalyzed for H_2 production reactions from the methanolysis of $NaBH_4$ (Sahiner, 2017[78]). HGR of H_2 is found as 8766 ml/(min. g) and the activation energy E_a is calculated as 20.1 kJ/mol, for the methanolysis of $NaBH_4$ with MWCNT-COOHs and assumed highly preferable among the metal based nanoparticle catalyst in the literature.

2.2.4 Three Dimensional (3D) Structures

For larger catalyst e.g., 3D structured catalysts, the distribution of specific atoms on the surface of catalyst particles are generally investigated by atomic resolution atom probe tomography, electron microscopy and spectroscopy equipment. For example, 3D structures of 10 nm sized Co_2FeO_4 and $CoFe_2O_4$ nanoparticles during Oxygen Evolution Reaction, OER, are investigated by using atom probe tomography and the performance of electrocatalysts has been optimized

(Xiang et al., 2022[103]) for effective catalytic performances. In Ni-Co@3DG nanostructure, simply 3D graphene with nickel and cobalt, Ni-Co@3DG used as the catalyst in the $NaBH_4$ hydrolysis reaction for H_2 production (Karaman, 2022[50]) using the artificial neural network, ANN, and the structure, and performance were evaluated. The active surface area such as 885 m^2/g was established by the physicochemical characterizations with homogeneous Ni-Co bimetallic alloy distributions. The results were shown as an excellent catalytic performance for Ni-Co@ 3DG with HGR of 82650 mmol/min.g. Also, it was found that Ni-Co@ 3DG catalyst can maintain 95.96% reusability of its initial performance after five successive uses in the same catalytic H_2 production reaction of $NaBH_4$ hydrolysis.

2.2.5 Metallic Nanoparticles within Polymeric Hydrogel Network

Hydrogels are chemically stable material with high amounts of water imbibing ability within their polymeric network. The hydrogel matrices can embed various metal particles are found to be cost efficient and superior usable catalyst for various aquatic and non-aquatic catalytic reactions. As the metal particles are protected from the outside environments within hydrogel matrices, they have shield from the oxidation and interact with the functional groups of hydrogel network e.g., these functional groups act as chelating and capping agents for metal nanoparticles. Additionally, the metal ions such as Fe(II/III), Co(II), Ni(II), Cu(II), Ru(II), Au(III) metal ions can be precipitated to their corresponding metallic particle forms with the different size within hydrogels network using preferably green chemicals or non-toxic reduction agents such as $NaBH_4$, or H_2 (Sahiner, 2013[79]). Metal composites of hydrogels have been reported using natural and synthetic hydrogels for the in-situ preparation various metal nanoparticles or nanoclusters as flexible and tunable systems (Sahiner, 2013[79]). Various techniques in the use of hydrogel-metal composite with excellent size, composition, and topography and interfaces can be readily designed and used in not just in H_2 production reactions but also in the catalytic degradation of toxic chemicals such as dyes and nitro compounds. Therefore, the use of soft and flexible hydrogel reactors of polymeric network at various dimensions provides many advantages over bare or other support materials for a continuously and environmentally benign workable capabilities. In addition to categorizing hydrogels based on sources such as natural and synthetic in origin, they can also be categorized depending on the nature of functional groups such as neutral or charged (anionic or cationic) (Sahiner, 2013[79]).

Some of the hydrogel templated metal nanoparticles used as catalyst in $NaBH_4$ hydrolysis and hydrolysis reaction along with reaction temperature and Ea values are given in Table 10.

Table 10. Comparison Ea values of hydrogel-metal nanoparticle composite catalyst used in $NaBH_4$ hydrolysis and/or methanolysis.

Hydrogels	Temperature (°C)	E_a (kJ/mol)	Reference
p(EP-g-AA) Cu & Ni	30	42.61&39.10	(Zhao et al., 2017[109])
P(AMPS)-Ag	25	29.95	(Ghorbanloo and Nazari, 2020[38])
GH-CoCu	30	63.16	(Zaier and Metin, 2021[106])
P(AAm)-Pd-NiB	30	31.10	(Liu et al., 2013[62])
WSC based hydrogel-Ni	30	32.66	(Ding et al., 2018[33])
Starch hydrogel-Co	30	52.18	(Chairam et al., 2019[19])

In the preparation of hydrogel from diverse sources such as monomer and polymer different polymerization and crosslinking techniques were utilized (Elsayed, 2019[36]). An efficient hydrogen generator for portable fuel cell applications was designed using nickel–cobalt–boride (Ni–Co–B) catalysts and their catalytic hydrolysis reaction with alkaline $NaBH_4$ solution elaborated (Ingersoll et al., 2007[47]). The activation energy for hydrogen generation is found to be 62 kJ mol^{-1} which may be considered as very close and reasonable result with that of hydrogen generation catalyst such as ruthenium. These kinds of catalyst systems can also be prepared within a super porous hydrogel network called cryogels. Cryogels present better catalytic performance than conventional hydrogels due to their highly porous network and some of the cryogels used as template for metal nanoparticle preparation and as catalyst in the hydrolysis $NaBH_4$ reaction are given in Table 11.

Table 11. Metal nanoparticle embedded super porous cryogels composites used as catalyst in H_2 production from $NaBH_4$ hydrolysis.

Cryogels	Temperature (°C)	E_a (kJ/mol)	HGR (ml/min.g)	Reference
p(HEMA)M:Co	18	-	26641	(Seven and Sahiner, 2014[95])
Q-P(VI)-M cryogel	70	-	14566.9	(Sahiner et al., 2015[86])
P(4-VP)-M (M:Co, Ni, Cu)	25	28.78		(Sahiner and Yildiz, 2014[87])

The micro/nano structures are an artificial structure with special functionality, dimensions, , and physical properties at micro-nano scale such as nanoparticles, graphene, CNT, nanocomposites, titanium dioxide, core-shell, etc. Recent advances in nanoparticle–hydrogel composites have been focused on the specific material design, synthesis, potential applications, and their inherent accompanying feature utilization (Thoniyot et al., 2015[98]). For example, polymeric particles can also be directly used as catalyst in H_2 production reactions with or without containing metal nanoparticles for hydrolysis or methonolysis reactions of $NaBH_4$, respectively.

Some of the values of E_a and HGR for the polymeric microparticle hydrogel catalyzed $NaBH_4$ reactions are presented in Table 12. Various cross-linking techniques using different monomer/comonomer ratios, and some structures materials such as graphene can used to prepare hydrogels with suitable pore and functional groups.

Table 12. Microgels, microgels-metal nanoparticle composites used as catalyst in H_2 generation reactions in $NaBH_4$.

Microgels	Temperature (°C)	E_a (kJ/mol)	HGR (ml/min.g)	Reference
(p(AMPS-TDA-1)	25	14.3	854	(Demirci et al., 2019[29])
p(MTMA)	(-15)-(45)	24.1	-	(Ozturk et al., 2018[73])
Poly(styrene)-Ru	25	-	215.9	(Sahiner and Sengel, 2016[85])
P(NIPAM)-Ni	40-60	48.28	-	(Cai et al., 2016[17])
PVDF-NiB capsules	30-50	-	-	(Chen et al., 2011[22])
Co@AHs	30-60	55.6	-	(Ai et al., 2014[2])

Upon synthesizing the cationic microgel from (3-Acrylamidopropyl)-trimethyl ammonium chloride (p(APTMACl)) by inverse suspension polymerization technique, these polymeric microparticles were mixed with $CoCl_2$, $NiCl_2$, $CuCl_2$, $FeCl_2$ and $FeCl_3$ metal salts solutions in ethanol (Sahiner et al., 2014[80]). As shown in Figure 5, the digital camera images of bare metal salts are loaded, and *in situ* metal nanoparticle prepared microgel composite have different colors. Using this Co metal nanoparticle containing microgels composite as catalyst, H_2 is produced by as magnetic ionic liquid colloid catalyst (Sahiner et al., 2014[80]).

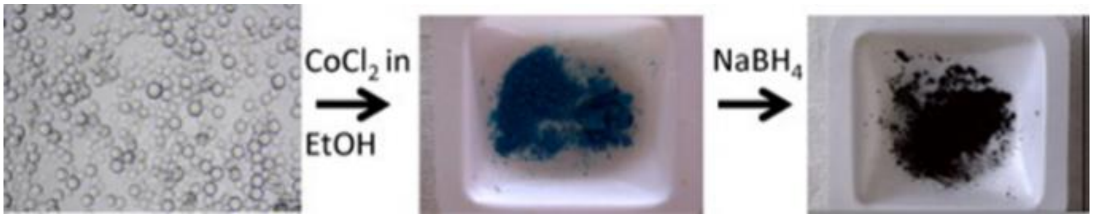

Figure 5. The digital camera images of bare microgels, $CoCl_2$ loaded microgels, and microgel-metal nanoparticle composites (Sahiner et al., 2014[80]).

The microgel system based on p(APTMACl)-M composite IL are used as catalyst systems in H_2 generation from the hydrolysis of $NaBH_4$ or ammonia borane. The activation energy values for the hydrolysis reaction were calculated for two of the catalyst systems and were found to be 53.43 and 26.74 kJ/mol for p(APTMACl)–[$CoCl_4$] and p(APTMACl)–[$NiCl_4$], respectively (Sahiner et al., 2014[80]). Some of the HGR and Ea values of PIL catalysts used in H_2 production reaction frm $NaBH_4$ are given in Table 13.

Table 13. The HGR and Ea values of polymeric ionic liquid as catalyst used in H_2 production from $NaBH_4$.

Catalyst	Reaction	Temperature (°C)	E_a (kJ/mol)	HGR (ml/min.g)	Reference
Hypercross-linked microporous polystyrene (PS) ionic liquid (IL) membranes	Hydrolysis	30-50	52.50	3621	(Chinnappan et al., 2015a[23])
graphene oxide-ionic liquid grafted chitosan composites	Hydrolysis	20-50	38.0	-	(Jia et al., 2018[48])
PVDF/PEG/EGDMA/IL chemically cross-linked nanofibers	Hydrolysis	25-55	37.86	-	(Chinnappan et al., 2015b[24])
Co-doped Co_xO_y nanofilms water/ionic liquid	Hydrolysis	30-45	43.19	8055	(Guan et al., 2022[41])
MWCNTs/IL/Mn nanohybrids	Hydrolysis	30-50	40.80	350	(Chinnappan et al., 2015c[25])
RuNP@NH_2-PIILS	Hydrolysis	21-40	38.9	-	(Paterson et al., 2022[76])

Polymeric ionic liquids (PILs) have been stated as a rising class of ion-conducting polymers based on the familiar chemistries of ionic liquids and these PILs have afford many advantageous such as high conductivities, strong thermal and chemical stability (Lebedeva et al., 2024[58]). The preparation of magnetic (Fe_3O_4) nanoparticles (NPs) by coating them with amino-functionalized silica (SiO_2@NH_2) as Fe_3O_4@SiO_2@NH_2 particles were turned into ionic liquid (IL) colloids with the treatment of hydrochloric acid (HCl), nitric acid (HNO_3) and sulfuric acid (H_2SO_4), respectively. The maximum HGR value of 13188 mL/(min.g) was attained at 500mM $NaBH_4$ by Fe_3O_4@SiO_2@$NH_3^+Cl^-$ as catalyst at 25 °C. Moreover, the activation energy E_a values for the methanolysis of $NaBH_4$ was found as 32.5 kJ/mol.
Protonation is the addition of a proton to a chemical species such as an atom, molecule, or ion making the structure more acidic and ionic (Martínez et al., 2023[67]). Protonation is different from hydrogenation, as during protonation, a change in charge of the protonated species occurs, while the charge is unaffected during hydrogenation. Examples can be given as the formation of the ammonium group where NH_4^+ is formed by protonation of ammonia NH_3 or water may be protonated by sulfuric acid:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-. \qquad \textbf{Eq. (2)}$$

As protonation occurs in many catalytic reactions, both protonation and deprotonation occur in most acid-base reactions. As a species is either protonated or deprotonated, its mass and charge change, as well as its chemical properties are altered. For example, protonation may change the optical properties, hydrophobicity/hydrophilicity, or reactivity of a substance. Protonation can be described as a fundamental chemical reaction, and it is an important step in many stoichiometric and catalytic processes. For example, polyethyleneimine (PEI) is a cationic polyelectrolyte and investigated for various purposes including as catalysts. PEI modification and protonation, the reuse and regeneration as catalysts in $NaBH_4$ dehydrogenation in methanol was reported (Sahiner and Demirci, 2016[82]).

Nonmetal green catalysts attracted many researchers greatly because a green nonmetal catalyst has many advantages such as high activity, low cost, and environmental friendliness. A nonmetal catalyst for $NaBH_4$ hydrolysis produced through the covalent modification of sand samples with PEI and then protonated (Inger et al., 2020[46]). The successful formation of the catalyst was verified by transmission electron microscopy, thermogravimetric analysis, and Fourier transform infrared spectroscopy. The hydrolysis of 15 mg $NaBH_4$ catalyzed by 50 mg catalyst could provide a hydrogen generation rate as high as 117.53 mL min^{-1} at 20 °C (Inger et al., 2020[46]). Although the catalytic activity decreased after several uses, it could be restored easily by regenerating in hydrochloric acid treatment of used catalysts (Inger et al., 2020[46]).

The HGR and turnover frequency (TOF) values were calculated and compared for PEI hydrogels with different sizes and morphologies (Sahiner and Demirci, 2016[82]). The specific HGR and TOF are formulated by Eq. 3&4 below.

$$HGR = \frac{V_{H_2O}(mL)}{t(\min).m(g)} \qquad \textbf{Eq. (3)}$$

Turnover frequency (TOF), which quantifies how many catalytic reaction cycles proceed per site and per unit of time can be formulated as:

$$TOF = \frac{n_{H_2}(mol)}{t(\min).n_{cat}(mol)} \qquad \textbf{Eq. (4)}$$

The natural minerals such as sulfide rich ore of pyrite was modified with PEI used as a catalyst in H_2 generation from $NaBH_4$ methanolysis (Inger, 2019[45]). The effect of solvent at various ratios of methanol/water, and the amount of catalyst, concentrations of $NaBH_4$, and temperature on H_2 production from $NaBH_4$ in methanol in the presence of PEI modified pyrite as catalyst were investigated. The catalytic performances of pyrite, pyrite-PEI, and protonated pyrite-PEI (pyrite-PEI^+) were determined as HGR values of 795, 2883, and 4320 mL H_2/(g of catalyst.min), respectively for H_2 production from $NaBH_4$ methanolysis. The E_a values were calculated for pyrite-PEI, and pyrite-PEI^+ catalyzed in H_2 production as 47.2 and 36.8 kJ/mol, respectively. It is important that the amount for the pyrite-PEI^+ catalyst is decreased to 76.2% after five consecutive uses with 100% conversion for each re-use study. Therefore, pyrite was reported to be to be a useful re-generable and economic green catalyst for H_2 production in many important applications (Inger, 2019[45]).

2.2.6 Metal Organic Frameworks (MOF)

Metal-organic frameworks (MOFs) as depicted in Figure 6 is an organic-inorganic hybrid crystalline porous materials consisting of an array of positively charged metal ions or clusters surrounded by organic linkers together to form a repeating cage-like structure of organic linkers.

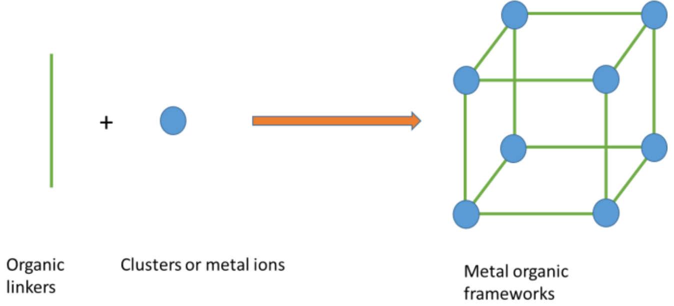

Figure 6. Schematic demonstration of Metal-organic frameworks (MOFs) prepared from a organic linker and metal ions (Singh et al., 2021[96]).

MOFs are constructed from organic linkers and metal ion nodal points coordinated in 1D, 2D and 3D forms of frameworks. 3D MOF structures are porous and can be filled with guest molecules like sponges absorbing water. The pore sizes of most reported MOFs have pore diameter smaller than 2 nm, which makes them suitable for the adsorption and separation of small guest molecules, such as gas, small organic molecules and coordination complexes where an ion or molecule attached to a metal atom by coordinated bonding. Due to this hollow structure, in some cases an extraordinary amount of large internal surface area, 7800 m^2/g for certain MOFs have been synthesized reported (Xu et al., 2021[104]). Uniform pore structures, atomic-level structural uniformity, tunable porosity, extensive varieties, and flexibility in network topology, geometry, dimension, and chemical functionality are the options of various metal ions containing porous MOF structure. Moreover, MOFs are capable of storing hydrogen even at high gravimetric and volumetric density requirements, as a clean alternative to hydrocarbon fuels in cars and other mobile applications. With exceptionally high surface areas and chemically-tunable structures, microporous metal–organic frameworks have recently emerged as some of the most promising candidate in many energy-related applications.

Moreover, magnetic MOFs, containing cobalt ion with two identical monomers linked by strong and/or weak covalent or intermolecular bonds, various magnetic exchange interactions which can also be strong or weak, covalent or intermolecular interaction has been studied (Kurmoo, 2009[55]). The different forms of short-range magnetic ordering, rising to single-molecule-magnets and single-chain-magnets, to long-range ordering of two- and three-dimensional networks were constantly investigated for certain applications**.** The H_2 production reaction from $NaBH_4$ hydrolysis in the presence of MOF structures as catalyst were also studied (Jung et al., 2018[49]; Luo et al., 2019[66]; Onat et al., 2021[70]) Some of these MOF based catalysts used in H2 generation from NaBH4 are given in Table 14. As can be seen because of the high specific surface area and metal content, the determined HGR values are higher in comparison to the common metal nanoparticles.

Table 14. Some of the E_a and HGR values of metal-organic frameworks (MOF) used as catalyst in H_2 production from $NaBH_4$.

Catalyst	**Temperature (°C)**	**E_a (kJ/mol)**	**HGR (ml/mol.g)**	**Reference**
CoNPs@ZIF-8	30	-	14000	(Luo et al., 2019[66])
Co-Ru@ MOF	30	41.41	15144	(Onat et al., 2021[70])

Various platforms of MOF have been successively investigated and significantly low E_a and high HGR are reported (Jung et al., 2018[49]). For unmanned aerial vehicles (UAVs) hydrogen is produced by a $NaBH_4$ hydrogen generation system and electrical energy was produced 95.96 W maximum power and 185.2 Wh energy density by using a PEMFC system (Jung et al., 2018[49]).

2.2.7 Thin Film Coating

The deactivation of Co catalyst prepared as thin film by magnetron sputtering technique was reported (Paladini et al., 2017[75]). Magnetron sputtering is a high-rate vacuum coating technique and can be utilized for various materials e.g., for metals and ceramics are deposited onto as many types of substrate materials by the use of a magnetic field applied to a diode sputtering target. Study of the catalyst surface and solid reaction precipitations were investigated by using X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM) and scanning transmission electron microscope (STEM). Similarly, magnetron sputtering thin film coating method was reported form different support for diverse application (Arzac et al., 2018[9]; Arzac and Fernández, 2020[8]; Kutyła et al., 2020[56]; Paladini et al., 2014[74]). For example, electrodeposition of cobalt supported catalyst supported on nickel foam was reported as catalyst in hydrolysis of $NaBH_4$ (Akdim et al., 2011b[4]). Similarly, for cobalt electrodeposition over nickel polycarbonate membrane (PCM) foam is used as stable supported catalyst thin films for H_2 production (Akdim et al., 2011a[3]). Furthermore, thin-film CoB alloy catalysts were prepared on Ni-foam substrates using electroless as well as electroplating techniques (Krishnan et al., 2009[54]).

Many catalyst systems are developed for the recycling of byproducts obtained from aqueous $NaBH_4$ hydrolysis, $NaBO_2 \cdot 4H_2O$. For example, this by product can be reacted with Mg_2Si to regenerate $NaBH_4$ via ball milling at room temperature under an argon atmosphere (Zhong et al., 2018[110]). The regenerated $NaBH_4$, with a maximum yield of 74%, has the same physicochemical properties as a commercial sample. Also, the regeneration of $NaBH_4$ by ball milling for the by-product, $NaBO_2 \cdot 2H_2O$ or $NaBO_2 \cdot 4H_2O$, with MgH_2 at room temperature and atmospheric pressure has been reported (Chen et al., 2017[21]). Results show that $NaBH_4$ at 90.0% for $NaBO_2 \cdot 2H_2O$ and 88.3% for $NaBO_2 \cdot 4H_2O$ are achievable.

It was reported that $NaBH_4$ reacted slowly with water to liberate H_2 at room temperature and was accelerated by applying metal–metal oxide catalysts such as $Pt–TiO_2$, Pt–CoO and $Pt–LiCoO_2$ (Kojima, 2005[53]). The gravimetric Hydrogen densities of some of the H_2 storage material are given in Table 15.

Table 15. Gravimetric hydrogen densities of several H_2 storage materials (Kojima, 2005[53]).

Materials	**Temperature (K)**	**Density (wt%) of Grav.H_2**
$NaBH_4+2H_2O+PtLiCoO_2$, high pressure	296	9.2
LiH + H_2O (H_2 yield:34%)	ordinary	2.6
NaH+1.5 H_2O	ordinary	4.0
MgH_2	573	7.6
$NaAlH_4$	373	3.4
Ti-xV-Cr-MnX=45-55, Ti-Cr-Mn=24-31-10, H_2, 7-0.01MPa	313	2.5
Super activated carbon, (AX21,5MPa)	298	0.9
Super activated carbon, (AX21,3MPa)	77	5.1

The chemical hydrides such as $NaBH_4$, LiH, and NaH are high amounts of H_2 containing materials (Dragan, 2022[34]; "Hydrogen Storage and Transport by Organic Hydrides and Application of Ammonia," 2019[44]). $Pt-LiCoO_2$ is a favorable catalyst for the production of H_2 by the hydrolysis of $NaBH_4$ solution where water to $NaBH_4$ mole to mole ratio is 2 at high pressure (0.6 MPa) ratio of H_2. In the 10kW capacity hydrogen generator is equipped with $NaBH_4$ storage solution pump vessel, storage tank of $NaBO_2$ solution separator, hydride reactor, is monolith coated with the $Pt-LiCoO_2$ catalysis. $NaBH_4$ is synthesized by annealing $NaBO_2$ with MgH_2 at high pressure as shown in Figure 7.

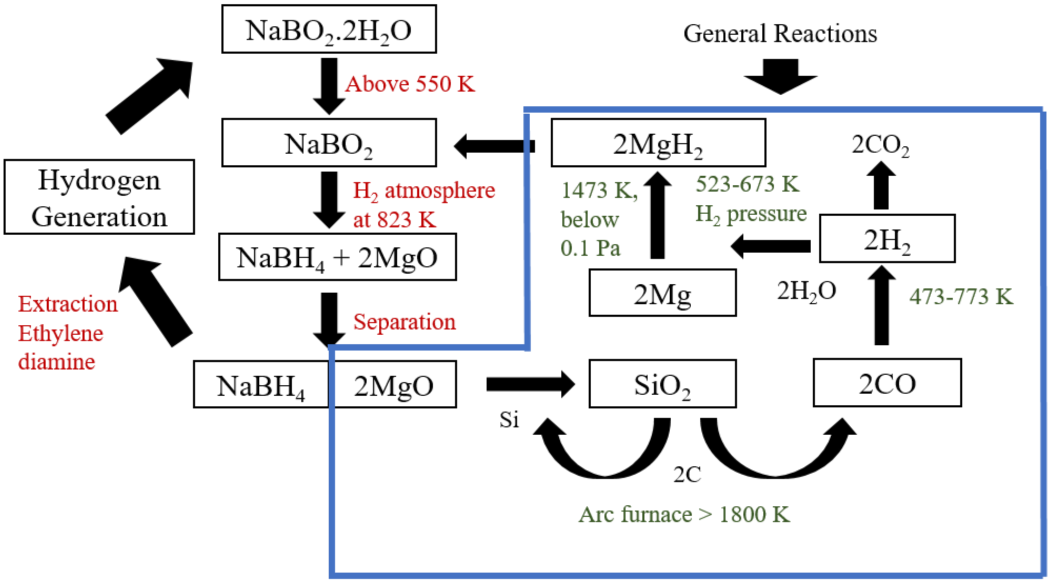

Figure 7. Recycling process of the $NaBH_4$ (Kojima, 2005[53]).

The authors stated that "energy efficiency of the recycling process is low with very high gravimetric densities in the chemical hydride systems, the system can be highly effective for a fuel cell uninterrupted power supply (FCUPS) for the use of emergency power supply" (Kojima, 2005[53]).

2.2.8 Non-Metal Based Complex as catalyst for H_2 production

Non-metal catalysts have been utilized as an alternative to metal-based catalysts in H_2 production from $NaBH_4$ or other hydrides due to their non-metallic nature. They are considered effective but environmentally friendly and economical. In this section, non-metal-based materials such that carbon-based nanomaterials, cellulose based nanomaterials, silica-based nanomaterials as well as their PIL forms are considered as metal-free catalysts.

2.2.8.1 Carbon Based Catalyst

Catalysts based on carbonaceous material with adjustable porosity, uniform geometry, surface functionality, controllable particle size distribution, and chemical inertness and thermally stable are the important fabrication specifications of carbon particles or carbon spheres (CSs). Natural and synthetic forms of carbon, metals, metal oxides others such as clays are used as catalyst with nano sized or high surface area are of catalyst afford high catalytic activity, with absorptive characteristics in H_2 production. Carbon, carbon blacks, carbon nano tubes, inorganic tungsten and boron nitride nanotubes, graphite, diamonds, buckyballs (which is 1 nanometer in diameter, a hollow spherical molecule composed of many carbon atoms in active layer of materials), fullerene and finally graphene are considered as nano size catalysts (Saka, 2021a[90], 2021b[91]; Samatya Ölmez et al., 2022[93]). For example, porous carbon (PC) particles were modified with PEI to obtain amine functionalized PC-PEI particles (Demirci et al., 2020[28]). PC-PEI was treated with HCl, PC-PEI$^+$ and used as catalyst for H_2 production studies in the methanolysis of $NaBH_4$. In the methanolysis reaction of $NaBH_4$ catalyzed by PC-PEI$^+$ catalyst, high HGR value, 4040 mL/(min.g) and low E_a value of 23.9kJ/mol were obtained.

As a carbon source, carbon black (CB) obtained from car tires rubber was used as catalys (Ari et al., 2019[7]). Firstly, CB was oxidized by treatment with H_2SO_4 and HNO_3 and then the oxidized CB was modified with PEI and treated with HCl for protonation. Protonated CB-PEI as CB-PEI-HCl was used as a catalyst in the methanolysis of $NaBH_4$. The Ea was calculated as 34.7 kJ/mol in the temperature range of -20 °C to +30 °C. The HGR value was calculated as 3089 mL/min.g for the conditions reactions conditions of 50 mg catalyst, 125 mM $NaBH_4$, 20 mL methanol, at 25 °C under 1000 rpm mixing rate).

Another biobased waste as green catalyst used is apricot kernel shell utilized as a free-metal catalyst with 15% H_3PO_4 for $NaBH_4$ hydrolysis reaction and a HGR value of 20,199 mL min^{-1} gcat^{-1} and the activation energy was equal to 30.23 kJ mol^{-1} was reported.

2.2.8.2 Natural materials as catalysts

A natural clay, halloysite nanotubes (HNTs) shown in Figure 8 have been experimented as catalyst in H_2 production from methanolysis of $NaBH_4$ and the natural HNTs upon modification with (3-aminopropyl) triethoxysilane (APTES) and then treated with HCl to obtain mod-HNTs (HNTs-$NH_2 \cdot HCl$) (Sahiner and Sengel, 2017[85]). The activation energy was calculated as 30.41 kJ/mol, the catalytic activity of mod-HNTs. The mod-HNT catalysts showed greater reusability with catalytic activity (91%) after 10th use having 100% conversion at each time with comparable HGR of about 220.5 ml/(min.g) as well. There is also montmorillonite-based catalyst were also reported in literature (Saka, 2024[88], 2023[89]).

The schematic presentation of amine modified Halloysite Nanotubes as catalyst for H_2 production from $NaBH_4$ methanolysis reaction is shown in Figure 8.

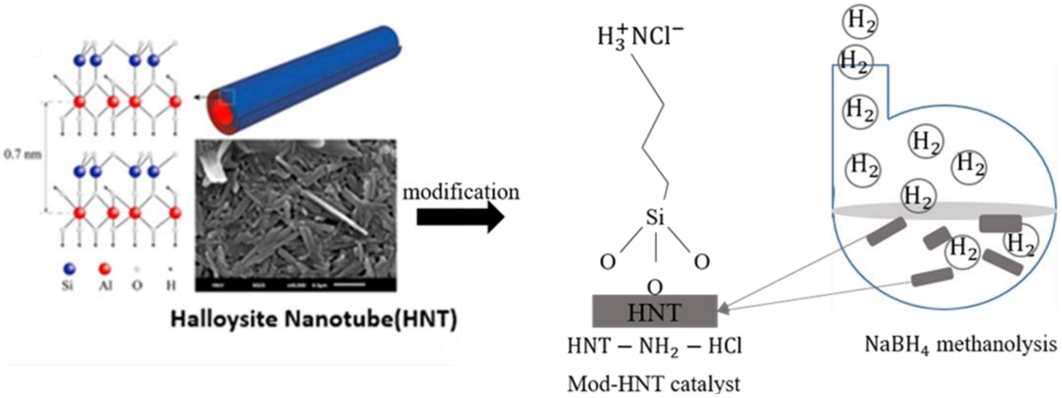

Figure 8. The schematic demonstration of amine modified Halloysite Nanotubes (HNT) as their use catalyst for H_2 production from $NaBH_4$ methanolysis (Sahiner and Sengel, 2017[84]).

Microgranular cellulose were modified with epichlorohydrin and followed by the modification with diethylenetriamine (Cell-EPC-DETA) and then protonation by hydrochloric acid as Cell-EPC-DETA-HCl and was used as metal free catalyst directly in methanolysis reaction of $NaBH_4$ for hydrogen (H_2) production (Sahiner and Demirci, 2017[84]). The (HGR) values for bare Cell catalyzed $NaBH_4$ methanolysis reaction were calculated as 408 mL H_2/(g of catalyst.min), and increased to 2015 mL H_2/g of catalyst.min for Cell-EPC-DETA. Remarkably, HGR value has almost increased 160% to 3215 mL H_2/(g of catalyst.min) for Cell-EPC-DETA-HCl catalyzed $NaBH_4$ methanolysis reaction. Likewise, the activation energies of Cell-EPC-DETA and Cell-EPC-DETA-HCl were determined as 38.2 and 34.4 kJ/mol.

A low activation energy (E_a), almost 14.41 ± 0.46 kJ mol^{-1} is calculated for $NaBH_4$ methanolysis reaction using Cellulose cotton fibers (CF) coated chitosan (CH), CF-A-CH as catalyst at temperature range 0 °C - 45 °C (Ali et al., 2019[6]). Moreover, the catalyst reusability is also analyzed and no decline in conversion % is reported, whereas a little reduction in performance % is detected after every cycle and only 18% lost is observed in its percent activity after completion of five successive cycles.

2.2.8.3 Silica Based catalysts

Silica (SiO_2) particles are classified as an alternative catalyst for the production of green energy carriers such as H_2. Nanosilica shells, nano structured silica, silica-carbon composites, silica hybrid, organic, inorganic, and mesoporous silicas are the silica-based material which can be used as natural minerals as catalysts. For example, the hydrolysis of $NaBH_4$ offers substantial applications in the production of H_2 but requires an inexpensive catalyst. Consequently, phosphorylated silica (SP-PA) was reported to be used as catalyst in $NaBH_4$ hydrolysis to generate H_2 as shown in Figure 9. The HGR values of 762.4 mL min^{-1} g^{-1} for SP-PA particles is higher than that of bare silica particles, 133 mL min^{-1} g^{-1} of catalyst. The calculated activation energy for $NaBH_4$ hydrolysis for SP-PA catalyst is 29.92 kJ.mol^{-1} indicating the high catalytic activity of SP-PA particles.

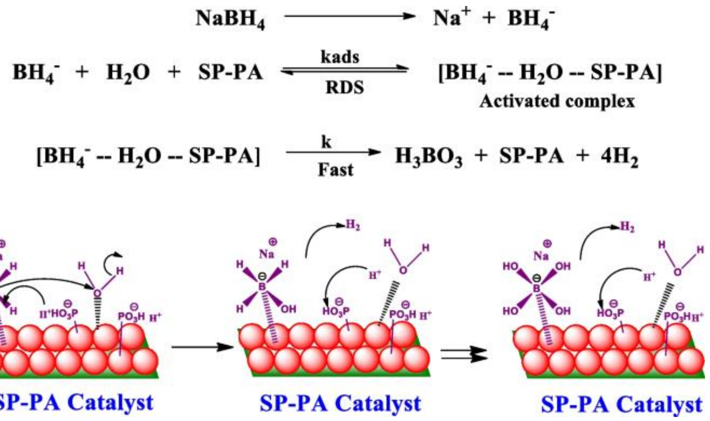

Figure 9. Catalytic hydrolysis of $NaBH_4$ for H_2 production catalyzed by phosphorylated silica particles (SP-PA) (Ganesan et al., 2022[37]).

The H_2 production from dehydrogenation of $NaBH_4$ in methanol was carried out in the presence of PEI modified two different sand samples (T and P) as catalysts (Inger et al., 2020[46]). Similar HGR values of these PEI modified sand samples have been found, 1344 and 1190 mL H_2/(g of catalyst.min). It was also reported that the activation energy of sand catalyst was found to be lower than the several metal catalysts which were 24.6 and 25.9 kJ/mol and increased higher values upon, protonation e.g., 36.1, and 36.6 kJ/mol for T-PEI^+ and P-PEI^+ samples, respectively.

III. CONCLUSION AND OUTLOOK

In this review article, homogenous and heterogeneous catalysts are examined for H_2 production from $NaBH_4$ hydrolysis reactions. As H_2 is the most important energy carrier, energy production system using H_2 is of paramount significance for the future of humanity. For example, during the long trip of the spacecraft flight in space, long term accommodation in space stations, stays in the planets and habitats, H_2, O_2, water, electric energy profoundly be needed by the travelling crew members, plants and animals for their survival. The weight and volume data for sodium borohydride ($NaBH_4$) hydrolysis or methanolysis and the catalyst requirements for the production of H_2, O_2, water, and electric energy including space agriculture will be important input data for designing spacecraft. Here, all types of catalyst including homogeneous to heterogenous catalysts that can be used in H_2 production from hydrides hydrolysis or methanolysis were evaluated. HGR and E_a are two important performance parameters that depend on the choice of catalyst. Although high HGR would be preferable, it is desirable to control HGR as desired for specific applications.

On January 28, 1986, the Space Shuttle Challenger crashed 73 seconds just after takeoff. Several hundred-ton liquid cryogenic fuel elements stored in external tank units stored liquid hydrogen at -253 °C and liquid oxygen at -183 °C. The storage and handling of these cryogenic liquids requires high performance insulation technology. The seven astronauts of the Colombian vehicle were lost during the takeoff, because of the very small damage occurred in the insulation of the external fuel storage system, caused few degrees °C increase of the fuel temperature. The function of catalysts that provide sodium borohydride and H_2 production rate plays crucial role in the return of spacecraft to the atmosphere (REENTRY), especially when the vehicle reaches about 23 times the speed of sound and turns the space shuttle into a fireball at a temperature of about 2000°C-2500°C, the system should be able to slow down or even to stop the H_2 production if necessary. H_2 should only be produced supply for on demand basis without being stored can reduce the risk of explosion.

A manned spacecraft is a clustered volume that flies in a vacuum, close to external environments. In addition to the CO_2 emission of the living beings in the spacecraft, if there is a CO_2 release from the catalyst used from the sodium borohydride hydrolysis, this is an undesirable result. It is preferred that the catalyst be environmentally friendly and green in nature. Otherwise, CO_2 emissions accumulated in the spacecraft must be cleared by converting to energy.

Although, even HCl can be used as a homogeneous catalyst in $NaBH_4$ hydrolysis in Unmanned Aerial Vehicle. Then, phosphoric acid (PAFC) was used as a catalyst in $NaBH_4$ hydrolysis for Submarines. Finally, H_2, O_2, H_2O and electricity were produced by three sets of fuel cells located in the vehicle's Service Module and transmitted to the Apollo Command Module, using sodium borohydride hydrolysis and catalysts ranging from 300 W to 5 kW in the Apollo spacecraft. Apollo 11, the first to land on the Moon, had three hydrogen fuel cells in its modules. Apollo 11's hydrogen fuel cell, capable of producing up to 2,300 W per unit, produced electricity to power countless devices on spaceships, and the electricity generation met most of the astronauts' needs. Finally, it is concluded that discussions for current perspectives and future outlook of $NaBH_4$ as an efficient energy/hydrogen carrier of space vehicle requirements.

Catalytic decomposition of hydrogen peroxide was used to generate O_2, and H_2O. Pure O_2, was provided to a fuel cell and the H_2O was stored separately. $NaBH_4$ in the solid state was used as a H_2 source in the present study. Pure H_2 can be generated by a catalytic hydrolysis reaction in which the H_2O source can be obtained from the H_2O_2 decomposition. Two catalytic reactors were prepared; one is for decomposition reaction of H_2O_2 and the other is for hydrolysis reaction of $NaBH_4$. For that reason, acids, metal hydrides, noble metals and then non-noble metals and their powders as homogeneous/heterogenous catalysts have been examined. In the further research of hydrolysis and fuel cell concepts hydrogel, Polymeric Ionic Liquid (PIL), polyethyleneimine (PEI), magnetic hydrogel-M composites, Metal Organic Frames (MOF) and Thin Film Coating type of catalysts will play important roles in space technology requirements.

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CRediT authorship contribution statement

Erk Inger: Conceptualization, Funding acquisition, Formal analysis, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

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