Hydrogen Production using Aluminum and Nano Modifiers

A Thesis Submitted to the Department of Chemical Engineering, School of Chemical and Materials Engineering (SCME), NUST, Islamabad, in the partial fulfillment of of the requirements for the degree of

Masters of Science (MS)

In

Energetic Materials Engineering

Submitted by

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ABSTRACT

The present research is focused on enhancement of hydrogen generation rate in well-known Al-H_2O reaction by removing passive oxide layer (Al_2O_3) under ultrasonic field and varying temperature (40°C, 50°C , 60°C) various hydroxides (lithium hydroxide, calcium hydroxide) and nano modifiers (nickel oxide, manganese oxide, cobalt oxide). Lithium chloride was also tested but without milling it has no profound effect. These modifiers were tested in various ratios for better yield/production rate (aluminum to weight ratios, 1:1, 1:2, 1:3 and 1:4). The results revealed that aluminum powder easily reacted with degassed water in the presence of modifiers and hydrogen generation took place. The aluminum-water reaction was greatly influenced by initial water temperature, particle size and the kind of modifier used. Ultra sonic field also played an important role and increased hydrogen yield as well as generation rate.

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Thesis Supervisor	**HoD**	**Dean**

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ (١:١)

IN THE NAME OF ALLAH THE MOST MERCIFUL THE MOST BENEFICIENT

Certificate

It is certified that the entire work in the thesis i.e. "**Hydrogen production using Al & nano modifiers**" by Imran Yousaf, for award of MS degree in Energetic Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan; is an original work completed in the presence of my guidance and supervision. Research work is authentic and fulfills the required criteria of MS.

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Dedication

I dedicate my work to

My parents and all teachers whom ultimate guidance and sincere efforts able me to be a noble part of society

“And make yourself submissively gentle to them (parents) with compassion, and say: O my Lord! Have compassion on them, as they brought me up (when I was) little”. [Al-Isra 17:24).

ABSTRACT

The present research is focused on enhancement of hydrogen generation rate in well-known Al-H_2O reaction removing passive oxide layer (Al_2O_3) under ultrasonic field and varying temperature (40^oC, 50^oC, 60^oC) various hydroxide (lithium hydroxide, calcium hydroxide) and nano modifiers (nickel oxide, manganese oxide, cobalt oxide). Lithium chloride was also tested but without milling it has no profound effect. These modifiers were tested in various ratios for better yield/production rate (aluminum to weight ratios, 1:1, 1:2, 1:3 and 1:4). The results revealed that aluminum powder easily reacted with degassed water in the presence of modifiers and hydrogen generation took place. That aluminum-water reaction was greatly influenced by initial water temperature, particle size and the kind of modifier used. Ultrasonic field also played an important role and increased hydrogen yield as well as generation rate. Larger particle size aluminum including raw aluminum was also introduced in experiments to make efforts cost effective and better results were achieved with hydroxides. Temperature played a crucial role in enhancement of hydrogen yield and ultrasonic field enhances oxidation process many fold.

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First and foremost acknowledgments goes to Allah Almighty whose countless blessing we can never pay off. He provided me the strength, wisdom and determination to overcome all the hurdles and difficulties occurred during the entire course.

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I have no words to mention the support of my family who stood beside me every step of life and their prayers turned my hard work into meaningful product.

(Imran Yousaf)

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List of Abbreviations

EDS - Energy Dispersive Spectroscopy

PSA - Particle Size Analyzer

SEM - Scanning Electron Microscope

TG/DTA - Thermal Gravimetric / Differential Thermal Analyzer

XRD - X-Ray Diffraction

Chapter 1: Introduction

1. *This chapter initially unfolds present energy related problems and the role of renewables in helping to reduce the impact of those problems. Later Properties of aluminum and hydrogen are discussed in depth to highlight the importance of this study.*

1.1. Motivation of Study

Environmental constraints and existing resources have forced the world to think that recent fossil fuel based economy is generally categorized as unsustainable. One of the options which attract the world is the development of a hydrogen-based economy, due to its large quantity and environmentally friendly fuel character. Free hydrogen required to be produced by various means and does not occur naturally therefore it is not considered as primary energy source like petrol rather it is an energy carrier. The main obstruction in the large scale utilization of hydrogen as a fuel is high pressure storage systems. The prevailing trend of on demand production of hydrogen helping to reduce the storage system requirement. One of the producing on-demand hydrogen for fuel cells is utilizing Al-water reaction under certain conditions for production of hydrogen. This method has practical implementation in many sectors as large as a hydrogen refueling center and as small as portable handheld devices or onboard generation for vehicles. However, certain parameter plays a crucial role in case of aluminum – water reaction of generating on-demand hydrogen. The edge it gives over other methods of hydrogen production is its simplicity, environment friendly and safe method [1].

1.2. Energy Demands

Continuous and rapid increase of energy demand is an open secret and seeking attention of the whole world. In 2014 the total energy consumption of world has reached nearly 500 quadrillion (btu). The alarming increase of environmental problems adds on and further aggravates the present situation as this figure is expected to increase further in the coming time. Many factors are significant in estimating the future requirement of the energy production and consumption like, fuel prices, population growth and technological developments. The high increases of energy consumption worldwide would continue to increase and it is believed that such high rates cannot continue further. This is because even an increase of 2% per year of primary energy demand would be doubled in 2037 and tripled by 2057 as compared to 2002. Such demanding energy expected in coming 50 years fuelled by world population forced to look into at all available strategies to gratify the future demand, especially for electricity and transportation.

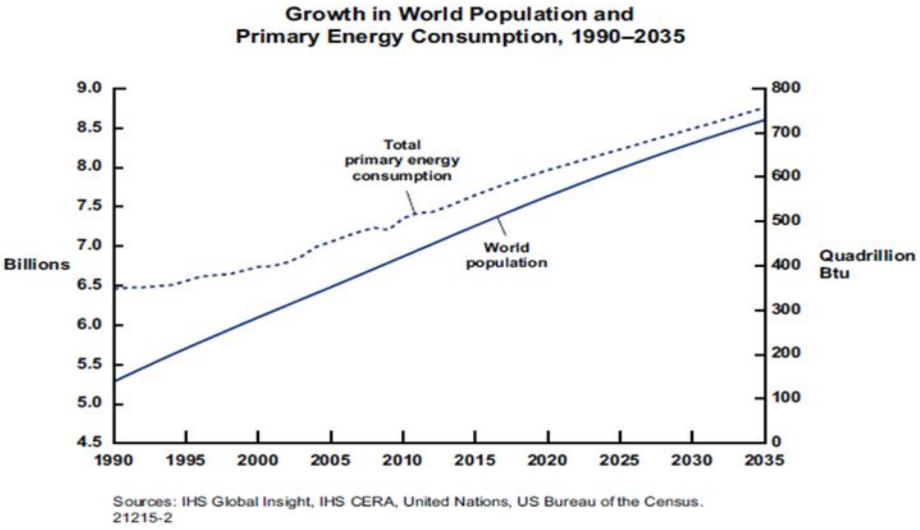


Figure 1.1: Showing primary energy consumption

1.3. Present Energy Scenarios

In the last century the great revolution in energy sector took place when shift from steam engine to bullet trains and from bicycle to supersonic jets, along with industrial revolution enriched the energy requirements more than ever and this goes on and on. The primary categorization of fuel is oil, gas, and coal which forms the basis of all modern day machinery. Keeping available energy resources, technology and their consumption rate in mind we will be unable to survive on them in future a head as shown in Fig 1.2. Moreover gases produced by fossil fuel such as CO_2, CH_4, CFCs, N_2O also cause greenhouse effect which contributes in rising the earth's temperature. These parameters forced the world to convert on renewable source of energy due to their availability, cheap and harmless effect on environment.

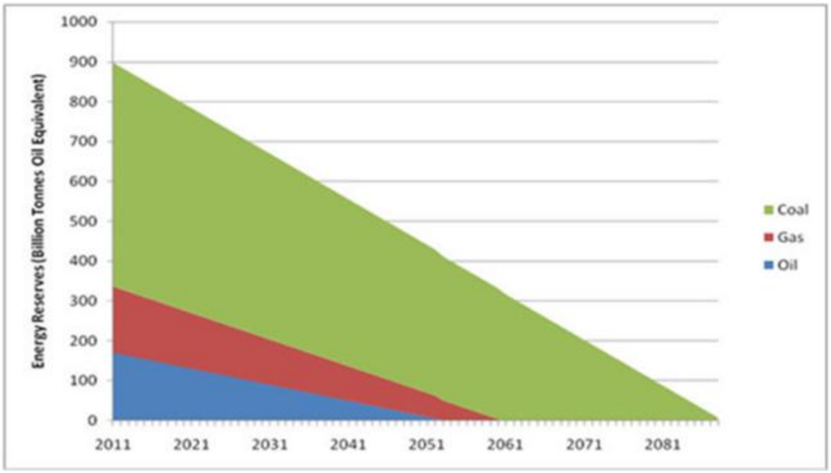


Figure 1.2: Exhaustion rate of fossil fuels

1.4. History of hydrogen

Credit of its discovery goes to Robert Boyle by carrying out his work on between iron filings and dilute acids in 1671 while in 1766, hydrogen gas as a discrete substance was introduced by Henry Cavendish later experiments performed by French and British scientists lead to the first flight of hydrogen balloon it was discovered that applying electricity to water can produce hydrogen and oxygen. 19th century's discoveries included the fuel cell effect in which the combination of oxygen and hydrogen produced water and electricity. Soon after German engineers used hydrogen and hydrogen-mixed fuel cells to power trucks as well as submarines [2].

The explosion of the German dirigible Hindenburg of Lakewood (New Jersey) in 1937 steered widespread public attention about the safety of hydrogen. Investigators of U.S and German brought out the fact that static electricity which ignited a hydrogen leak was the main reason of the accident.

1.4.1. Properties

It is tasteless, odorless colorless, and non-toxic. Above 20 K it is a gas and is highly diffusible with a density almost 14 times less as compared to air. As it is diffusive and buoyant, therefore it dissipates quickly in open areas and can move through small spaces making it challenging to store. it is flammable over a wide range of gas concentration (from 4 to 74 %), while its lower flammability limit that is, the lowest temperature and pressure at which it will combust is greater than some of common fuels such as gasoline, propane or diesel [3].

1.4.2. Occurrence

Hydrogen in atomic form as ‘’H’’ is the most plentiful chemical element of universe, forming up 75 percent of normal matter by mass and over 92 percent by number of atoms [4] it is found in great abundance in stars and gas giant planets and plays an important role in powering them [5]. On earth it exists in combination with other elements such as nitrogen (ammonia), oxygen (water) and carbon (hydrocarbons). Even though it may sometimes be used as a fuel but most often used as an energy carrier like electricity and not an energy source. To make hydrogen a usable, stand-alone fuel, it must be separated from these other elements by chemical, thermal or electrochemical processes.

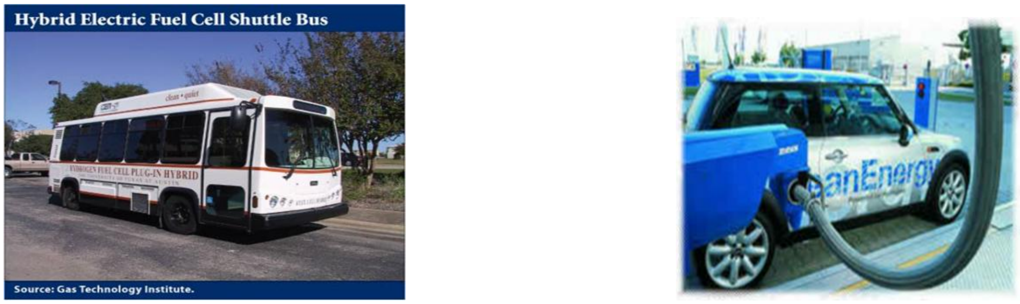
1.4.3. Current applications of hydrogen

The most common modern uses of hydrogen do not involve in power production. Presently it is widely used in the fertilizer industries and refining which are important industrial sectors. In fertilization sector it is utilized in the manufacture of ammonia-based nitrogen fertilizer where as in refining processes for removal of sulfur in petroleum that produce gasoline. Today, NASA is a leading user of hydrogen outside of the petrochemical industry. NASA uses it to generate spaceship power, heat and water. Space shuttles use fuel cells to power such things as computers, life-support systems and lighting. In addition, the cells perform double duty by also providing heat and synthesizing pure water for astronauts to drink and use.

1.4.4. Consumption in developed countries

Today, the shift of hydrogen to be used as fuel has already been in practice in developed countries like USA (Texas) possesses few stationary hydrogen power facilities and one hydrogen fueling station in Austin where a fuel cell bus of the University is already on roads. National Hydrogen Association quote that entire nation has 66 hydrogen fueling stations [6]. The U.S. Department of Energy (DOE) reports that there are hundreds of hydrogen fuel cell vehicles on the road in the U.S.

The National Renewable Energy Laboratory claim approximately 250 fuel cells are in utility to power in office, hospitals and various buildings in nineteen countries [7]. Similarly State Energy Conservation Office (SECO) of Texas in study of 2002 illustrated the emergent state of hydrogen development by estimating more than 300 fuel cells being used in the both public and private sectors in the world generating 50 megawatts of electricity which was sufficient enough to lighten up 20,000 homes [8].



Source: Gas Technology Institute.

Figure 1.3: Showing fuel cell shuttle bus Texas University and hydrogen fuel pump

1.5. Production of hydrogen (Sources)

Presently, sources of hydrogen production can be represented as 48% from natural gas, 30% from oil, 18% from coal water electrolysis accounts for only 4% global [9].

1.5.1. Methods (In practice)

- **Steam Methane Reforming**. In this, methane is combined with high temperature steam in presence of a catalyst to form hydrogen production. It is least expensive and most common method of production in use today.

- **Electrolysis**. An electric current "splits" water into hydrogen and oxygen.

- **Gasification**. Heat is applied to coal or biomass in a controlled oxygen environment to produce a gas that is further separated using steam to produce hydrogen.

1.5.2. Methods (In the research / development stage)

- **Renewable Liquid Reforming.** Biodiesel/ Ethanol resulting from biomass in the presence of steam produces hydrogen.

- **Nuclear high-temperature electrolysis.** Water is split to form hydrogen using heat from a nuclear reactor.

- **High-temperature thermochemical water-splitting.** Solar concentrators are used to split water.

- **Photo biological microbes**. Some microbes yield hydrogen during their metabolic processes. Artificial arrangements are made to improve their natural metabolic processes.

- **Photo electrochemical systems**. Sunlight and semiconductors are used to make hydrogen from water [10].

1.6. Future scope

The leading/developed countries have considered and realized hydrogen as "future energy" Japan and USA are considered the leading countries that always come up with new ideas and technology. These countries have set up very high values in the field of research and development. Just considering these two countries will high light how desperately they want breakthrough in this field.

1.6.1. Hydrogen and fuel cell “a vision of future”

The applications of hydrogen and fuel cells are openly accepted by worldwide, but only their widespread use will dictate their fully apparent potential. Usage of H_2 in fuel-cell systems results in low emissions of dangerous ambient as carbon, carbon monoxide or sulphur dioxide. Fuel cell systems their high power quality and low noise are considered best in hospital/IT sectors along with mobile applications. Their high efficiency is independent of size. Fuel cell electric drive train provides reduction in regulated emissions and energy consumption. Cells when used as Auxiliary Power Units (APU) in stationary back-up systems or combination with internal combustion engines, saves energy and reduce air pollution. Some of its applications can be clearly depicted from fig 1.4.

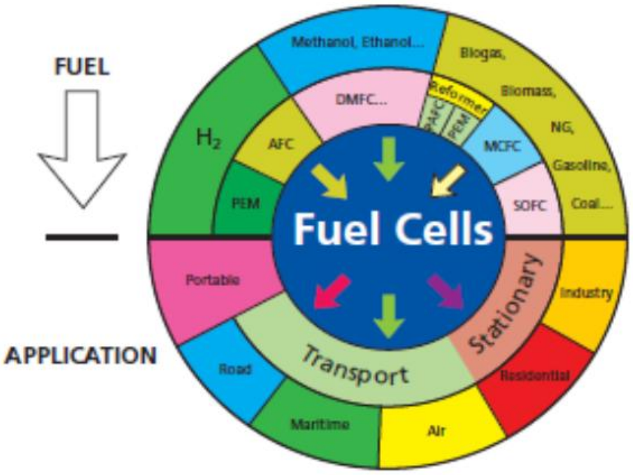


Figure 1.4: Showing sources of hydrogen production and applications of fuel cells

1.7. A strong drive in the world for hydrogen

USA fuel cell stakeholders and its coalition entitled 10 years USA Federal Government programed to be implement and set up hydrogen and fuel cell technologies. They have devoted $5.5bn of public funding and US Administration responded by total of $1.7 billion for the next 5 years to develop infrastructure of hydrogen fuel cells including advanced automotive technologies. This will result in 750 000 new jobs till 2030. Japan is not far behind in this field spending $240m merely on the research and demonstration in 2002. The Japan Fuel Cell Commercialization Conference had commissioned six hydrogen fuelling stations in major cities like Tokyo and Yokohama in 2002-3. Initial commercialization targets was of 50, 000 fuel cell vehicles till 2010 and 5m by 2020 and enhancing stationary fuel cell capacity of 2,100 MW till 2010 and 10,000 MW by 2020.

Electrolyzer-storage-fuel cell units in case of local emergency power are valuable due to low maintenance requirement and ease of location as associated to internal combustion driven generators. Iceland has steadfast to be the world's first hydrogen economy till 2050. It produced 2,000 tons of hydrogen gas by electrolysis in year 2002. Iceland is also developing an aluminum-smelting industry. The UK has also realized the significance of this technology and developed a fuel cell pilot program in 2004, according to which two fuel cell buses were on route till 2007. The Hydrogen Expedition is also on its way for creating a hydrogen fuel cell ship and demonstrating it to circumnavigate the world as a way to demonstrate the capability of hydrogen fuel cells. The United Nations Industrial Development Organization (UNIDO) signed $40M contract with Turkish Ministry of Energy and Natural Resources for Istanbul of the International Centre for Hydrogen Energy Technologies (UNIDO-ICHET) which started operation in 2004. A hydrogen cart/ forklift, and a mobile house powered by renewable energies were demonstrated at that platform. The headquarters of Istanbul Sea Buses Company also enjoying the power supply system since 2009 [11].

1.8. Why hydrogen

Hydrogen has been already categorized as the fuel of future as it is fully conversant with some of the parameters set for future energy systems must meet the following societal needs at affordable prices:

- Mitigate the effects of climate change

- Lessen toxic pollutants
- Cater for fading reserves of oil.

Failure to meet above mentioned needs will have substantial impacts on economy, environment and health.

1.8.1. Energy security and supply

Present society crucially depends on the constant availability of affordable fossil fuels which will be concentrated in a lesser number of countries thus making the probable for geopolitical and price instability. Hydrogen opens access to an extensive range of primary energy sources like fossil fuels and renewable energy sources (e.g. wind, solar, ocean, and biomass), as they are broadly available, as a result price and availability of hydrogen as a carrier have to be more stable than any single energy source. Hydrogen and electricity also allows options for centralized and decentralized power depending on managed, intelligent grids, and power for remote locations like mountain and island sites. Decentralized power is striking in both ways to ensure power quality as per specific customer needs along with reducing exposure to terrorist attack. The capability of hydrogen to store it more easily than electricity gives it an additional edge in load leveling / balancing the intermittent nature of renewable energy sources.

1.8.2. Economic competitiveness

Since the first oil crisis in the 1970s, economic growth has not been directly linked with growth in energy demand in the industrial sector, whereas in the transport sector increased mobility still leads to a proportionate increase in energy consumption. The amount of energy needed per unit growth must be reduced, while the development of energy carriers and technologies to ensure low-cost energy supply is of great importance. Development and sales of energy systems are also major components of wealth creation, from automobiles to complete power stations, creating substantial employment and export opportunities, especially to the industrializing nations.US and Japan considered hydrogen and fuel cells to be fundamental technologies in 21st century and vital for economic prosperity. There is strong speculation and industrial activity in the hydrogen and fuel cell arena in these countries, driving the transition to hydrogen – independently of Europe.

1.8.3. Air quality and health improvements

Upgraded technology and post combustion cures for orthodox technologies are constantly dropping pollutant emissions. Nonetheless, oxides of nitrogen, carbon and particulates remain a problem in certain areas whereas the overall trend towards urbanization stresses the essential for clean energy solutions and improved public transport. Automobiles and stationary power generation powered by hydrogen are zero emission devices with consequential local air quality advantage.

1.8.4. Greenhouse gas reduction

Hydrogen can be generated from carbon neutral energy sources and carbon free or from fossil fuels with carbon dioxide capture and storage (sequestration). Accordingly, its use could abolish greenhouse gas emissions from the energy sector. Fuel cells offer both clean and efficient electricity generation from a range of fuels moreover allowing exploitation of the heat generated in the process if sited near to the point of end-use.

1.8.5. Fuel cells

Developments in fuel cells enhances the importance of hydrogen many fold as it has wide applications in many sectors. Fuel cell converts fuel and air directly into electricity producing heat plus water in an electrochemical process contrasting to conventional engines. Fuel cells do not burn the fuel, run pistons/ shafts so have less efficiency losses, and no moving parts means mechanical simplicity, zero emissions with hydrogen and very low emissions when other fuels, high ratio of electricity to heat paralleled to conventional combined heat and power plants. In vehicles efficiency ratio of fuel cells to Internal combustion engines remained 60:20 due to very negligible side losses [11].

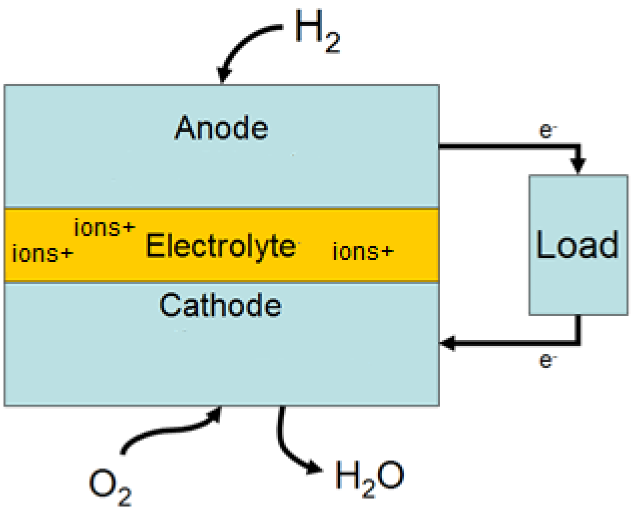


Figure 1.5: Showing working of fuel cell [12]

1.9. Challenges

Despite so many breakthroughs in field of research and technology still certain areas imposes a considerable problems in its implication as wide spread market identity.

1.9.1. Storage issues

As a gas it is about 14 times gravimetrically lighter than air. Transport of compressed gaseous hydrogen is an uphill task as it is only probable in heavy/ expensive containers that can bear pressures up to 10,000 psi and in case of pipelines that must either be constructed from the bottom up or retrofitted from existing natural gas pipelines. Cryogenic hydrogen poses less problems than gaseous but the conversion from gaseous to liquid hydrogen is energy intensive/ inefficient and considerably expensive. A phenomenon known as hydrogen embrittlement causes storage containers and pipelines to crack and fail over time.

Storage research at present is largely dedicated on compressed gas, metal hydrides, and cryogenic hydrogen. Most mature storage technology is compressed gas but it complements inefficiencies to the hydrogen life cycle and requires stronger, expensive materials for container construction. Recent efforts for storage brought carbon-fiber wrapped tanks as they are lighter and safer than customary steel tanks. Solid storage in metal hydrides is in preliminary research and proposes that metal hydrides will be prominent in the future hydrogen economy.

1.9.2. Cost effects

Today, steam reformation/electrolysis production of unit of hydrogen fuel is almost 3 - 6 times more costly than equivalent unit of fuel from natural gas[13]. The energy content of fuels is not a product of human effort so no cost assigned to it, merely the extraction/refining, transportation and production costs are measured. The hurdle in lowering the price of hydrogen is a cost of 35 kWh of electricity for each kilogram of hydrogen gas. Hydrogen produced through steam reformation is three times the cost of natural gas per unit of energy produced. This shows if costs of natural gas are $6/million BTU then it will be $18/million BTU for hydrogen. Also, producing hydrogen from electrolysis with electricity at 5 cents/kWh will cost $28/million BTU slightly less than two times the cost of hydrogen from natural gas. Note that the cost of hydrogen production from electricity is a linear function of electricity costs, so electricity at 10 cents/kWh means that hydrogen will cost $56/million BTU. Demonstrated advances in electrolyzer and fuel cell technology by ITM Power are claimed to have made significant in-roads into addressing the cost of electrolyzing water to make hydrogen. Cost reduction would make hydrogen as one of the major fuel source for refueling vehicles [14].

1.9.3. Challenges for fuel cells:

Some of the challenges for fuel cell which are proving barrier for its wide range applications are as under:

- **Cost**: Fuel cells are expensive for commercial introduction excluding major applications such as backup power generation for premium financial institutions.

- **Lifetime**: Majority of the fuel cells still be to be proven in this context, however successful demonstration of many systems for thousands of hours have been on record.

- **Reliability**: Auxiliary apparatus like fuel processors must be proven.

- **Novelty**: conservative markets demand significant support and public understanding in order to compete.

- Technological breakthroughs are required for successful fuel cell performance, reliability and cost.

- **Infrastructure**: Its infrastructure has not been matured in term of refueling, commercial scale manufacturing processes and things associated with it like trained personnel/people awareness etc.

1.9.4. Other Risks

Safety of hydrogen as an energy carrier or fuel is also a point of concern. It is highly flammable and demands proper attention while other fuel sources (e.g. gasoline or compressed natural gas) are subject to safety codes and standard industrial safety practices. Hydrogen has unique properties such as small molecular size and buoyancy demands different techniques to store, transport, and its usage. Department of energy (DOE) perceives development of codes and standards as essential for bringing hydrogen energy systems to market.

Some codes and standards do exist as developed by the U.S. department of transportation, Environmental Protection Agency in cooperation with industry groups, National Highway Traffic Safety Administration. The aim is to have the essential codes and standards in place to support the early commercialization of hydrogen energy technology [15].

1.10. Aluminum through the ages

In 19th century aluminum was considered as semi-precious metal having a price similar to silver because of its very high cost of production. It was mainly used to make ornaments, metal ware and religious objects. In 1893 the Angel of Christian charity, universally stated as Eros is one of the first statues to be cast in aluminum positions on top of Shaftesbury Monument memorial fountain in Piccadilly Circus (London) as shown in figure 1.6:

Figure 1.6: showing angel of Christian charity at Piccadilly Circus (London) [16]

Hall-Héroult electrolysis process made its production economical and made possible its use to diverse sectors. In 1910 aluminum as an alloy expand its range of applications it played a decisive role in the development of the aeronautical industry in the World War I. In the architectural sector aluminum also catches the attraction of world Atomium model was built in 1956 for the 1958 World Exhibition in Brussels as shown in figure 1.6: In World War II the undeveloped aluminum industry made exceptional advances. Alcan supported Canada utilized aluminum in military aviation. In 1947 aluminum made its first appearance in the automotive industry[17]. The first mass production cars use this metal on the Dyna Panhard production chain as shown in figure 1.7:

Dyna Panhard **Atomium model**

Figure 1.7: showing Dyna Panhard and Atomium model at Brussels

1.11. Uses of aluminum

Aluminum has wide range applications in every day of life starting from utensils till flying plane some of the sectors/areas where aluminum is being utilized is shown in figure 1.8:

Figure 1.8: Uses of aluminum in different sectors of life [18]

1.11.1. Aluminum as Reactive Metal

Metals with high combustion enthalpies remain area of interest as high energy density materials. Aluminum is also considered as metal with high combustion enthalpies. Since the beginning of twentieth century various formulations such as Hexal, Tritonal, Ammonal explosives etc. used aluminum in their composition. Despite that many researchers still believe that properties of aluminum as an additives has more to offer in coming future [19].

1.11.2. Aluminum as fuel

Aluminum is currently utilized one another way as potential source of future fuel in many sectors. Some of the areas where its applications are immensely recognized are discussed below.

1.11.3. Aluminum as Energetic Material for Rocket Propellants

In year 2007, Meda et al. evaluated the performance of aluminum powders in composite rocket propellants. The formulation contained Ammonium perchlorate (68%) as oxidizer, Hydroxyl Terminated Poly Butadiene (17%) as binder and aluminum of various particle sizes was added as 15% mass fraction. Chemical investigation was related to physical and ballistic performance in a multidisciplinary manner. Ignition temperatures, ignition times and burning rate were compared and results showed substantial impact of particle size of aluminum on these kinetic parameters [20].

1.11.4. Aluminum–air batteries

These batteries produce electricity by the reaction of aluminum with oxygen in the air having highest energy densities of all batteries, on the other hand limitation in term of high anode cost and removal of byproduct while using traditional electrolytes restricted their use to military applications and not on commercial scale. Their efficiency is more than eight times the range of a lithium-ion battery with a considerably lower total weight [21].

1.11.5. Alydro technology (Aluminum-Hydro)

Aluminum and water reaction generates enormous heat, aluminum oxide, and hydrogen that can then be used in fuel cells to produce electricity for powering a car. Alchemy Research on vehicles effectively utilized the above stated reaction for the future electric vehicles according to it such vehicles can go along 2,400 km on standard fuel tank as compared to 700- 800 km.

1.11.5.1. Benefits

Presently, there are two main problems associated with electric cars one low energy density of batteries compared to gasoline thus demanding big/heavy batteries for a relatively modest range. Fuel-cell vehicles being more energy efficient as per Alydro technology theoretically explains both of these issues. Aluminum being energy dense once combined with a turbo generator produces 6.5 kWh of power from one liter. Alchemy Research recommends 60 liter tank can store 390 kWh of energy. Where an electric car yardstick suggests 100 km/62 miles against 15 kWh so Alydro car range 2,400 km/ 1,491 miles in 60 liter. Alchemy Research lists many advantages along with range as it does not pollute, aluminum-oxide can be recycled into aluminum.

1.12. Occurrence

The third most abundant element is aluminum (after oxygen and silicon) and the most plentiful metal in the Earth's crust. By weight it makes up approximately 7 percent of the earth’s solid surface. It is very reactive chemically to occur naturally as the free metal. That’s why it is found combined with more than 270 different minerals. Its discovery took place in 1821 from reddish brown rock (bauxite) in Les Baux (France). The chief ore of aluminum is bauxite which is a blend of hydrated iron oxide and hydrated aluminum oxide.

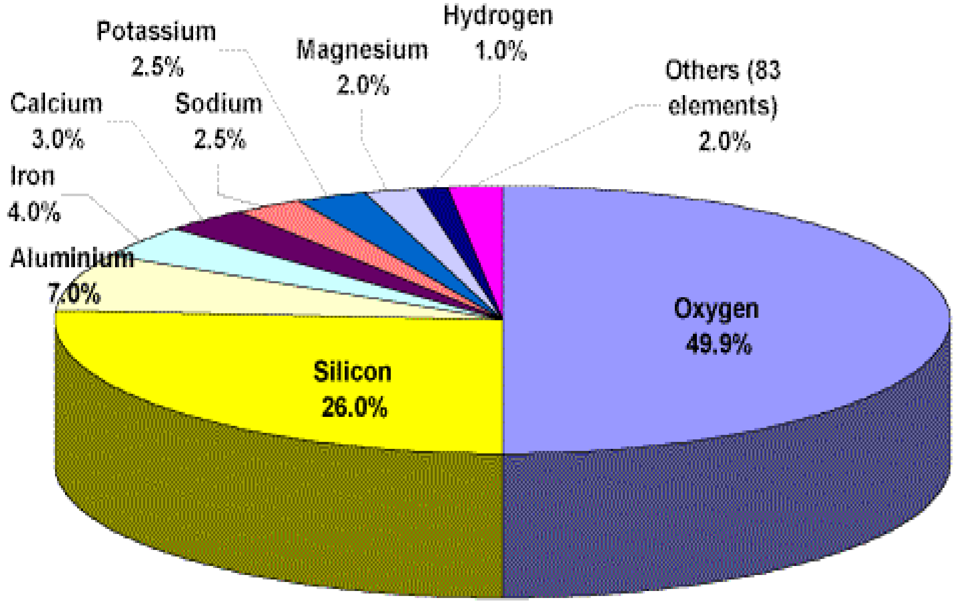


Figure 1.9: Showing distribution of elements in earth [16]

1.12.1. Properties

It is a metal silvery-white in color, light in weight (density 2.70 g/cm3), and nontoxic and can be easily cast or machined with an electrical conductivity 60 percent as compared to copper and extensively used as electrical transmission lines. Unalloyed aluminum is soft and brittle but alloying with small amounts of silicon, magnesium and copper can strengthened it. It is very light three, times less dense compared to iron however possesses high tensile strength. It is an excellent conductor of heat / electricity and a good reducing agent having oxides nontoxic and non-corrosive in nature.

Figure 1.10 Showing physical outlook of aluminum[16]

1.12.2. Strength to Weight Ratio

Its high strength to weight ratio makes it vital to transportation sector allowing increased payloads and fuel savings. Tensile strength of aluminum is not high but the mechanical properties may be manipulated by making good alloys of aluminum as per the requirement. Distinctive alloying elements are manganese, silicon, copper and magnesium.

1.12.3. High Density Fuel

Aluminum is regarded as the concentrator of energy and if we compare it with other known fuels its high energy density makes it prominent. Figure 1.11: shows specific energy and energy density of various common fuels.

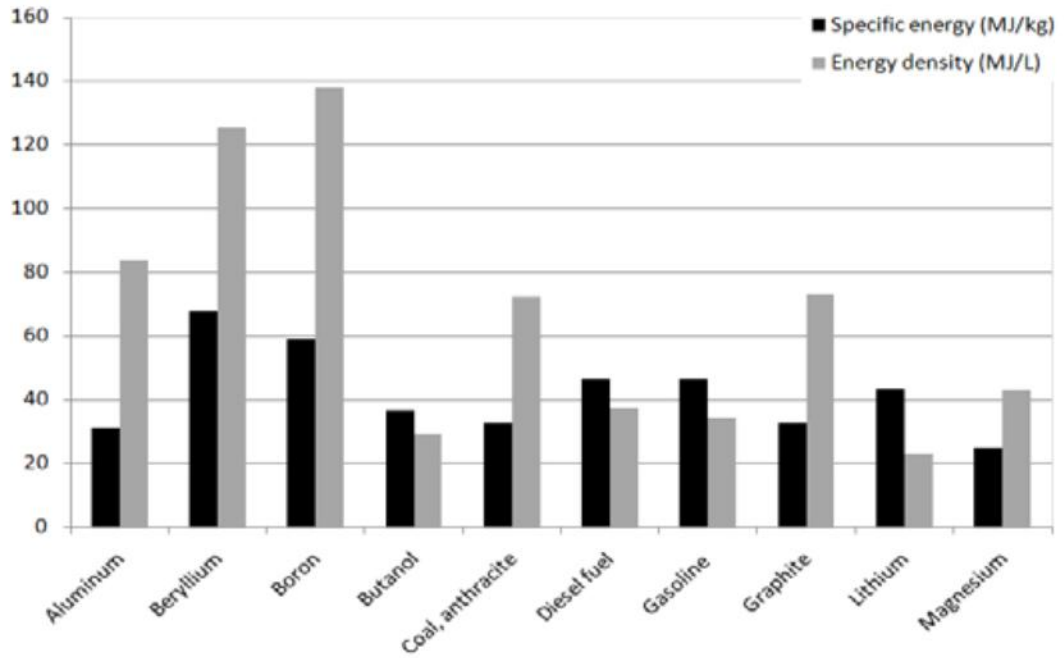


Figure 1.11: Specific Energy and Energy Density of Various Common Fuels

1.13. Aluminum Water Reaction

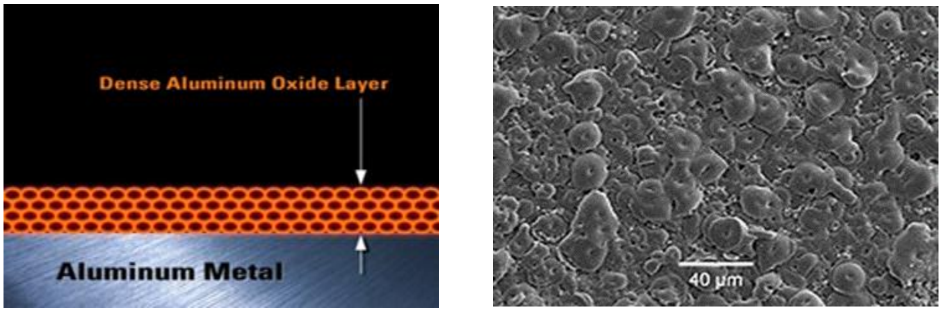
The idea of generating hydrogen using reaction of certain metals with water has fascinated researchers from a long time. In 1972 a paper by Smith [22] defined a methodology using an amalgamated aluminum surface based on even earlier work. USA scientist Gutbier and Hohne Patent indicated hydrogen can produced in the reaction of magnesium/aluminum mixtures with sea water in 1976 [23]. In recent times much of patents and publications are focused at the production of hydrogen through reactions between aluminum and water. These papers proposed to circumvent the passive layer of aluminum oxide permitting the reaction with water to react.

1.13.1. Reaction equation

At STP aluminum and water react to form aluminum hydroxide and hydrogen as per following equation:

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2$$

The volumetric and gravimetric capacity of hydrogen is 46 g H_2/L and is 3.7 wt % from this reaction respectively. Despite being thermodynamically favorable this reaction does not proceed because of adherent and coherent layer of aluminum oxide also known as alumina (Al_2O_3) preventing water to come into direct contact with the aluminum. The basic rule to maintain this reaction at near room temperature is the continual removal / disruption of this coherent/adherent aluminum oxide layer shown in figure 1.12:



PRESENTATIONAL VIEW **SEM IMAGE**

Figure 1.12: Showing images of protective layer of alumina

The following are possible reactions of aluminum with water under different conditions:

- $2Al + 6H_2O = 2Al\,(OH)_3 + 3H_2$ (1)
- $2Al + 4H_2O = 2AlO\,(OH) + 3H_2$ (2)
- $2Al + 3H_2O = Al_2O_3 + 3H_2$ (3)

The end products form as per equation 1, 2 and 3 are the ($Al\,(OH)_3$/ aluminum hydroxide known as (bayerite), ($AlO\,(OH)$) /aluminum hydroxide (boehmite) and Al_2O_3 aluminum oxide along with hydrogen respectively. All of these reactions are thermodynamically possible from room temperature past the melting point (660^oC) of aluminum and also highly exothermic. $Al\,(OH)_3$ is the stable product from room temperature to 280^oC, while $AlO(OH)$ is from 280 to 480^oC and Al_2O_3 above 480^oC.

1.13.2. Reaction-Promoting Approaches

- Hydroxide Promoters
- Oxide Promoters
- Salt Promoters
- Combined Oxide and Salt Promoters
- Aluminum Pretreatment

1.13.3. Recycling advantage

In aluminum production process ore-mining is the first step after that bauxite is refined into alumina which is electrolytically reduced into metallic aluminum as final step. Alumina emerges is an intermediate product from bauxite to pure aluminum. In fact 1.98 kg of alumina (Al_2O_3) is required to get 1 kg of aluminum. Average technologies consume about 7.59kWh for generating 1.98 kg of Al_2O_3 emitting 1.7kg of carbon dioxide/kg aluminum during these processes. Therefore energy and emissions due to the ore-mining and refining process can be considerably reduced when recycling back the aluminum oxide as it is accounted only one time when the recycled aluminum has to be integrated with a further amount [24].

Chapter 2: Literature Study

2. *This chapter deals with detailed study carried out on the subject by analyzing different published papers so that a well and comprehensive literature review can be collected. Aluminum water reaction to produce hydrogen has been source of inspiration for many researchers and many believe it alternate of future energy. The presence of passive coherent oxide layer on Aluminum prevent oxidation reaction to be proceed at reasonable rate .Many methods /modifiers has been utilized to curb this behavior few of them are briefed in this chapter.*

2.1. Use of Aluminum for On-Board Vehicular Hydrogen Storage

According to a study released by "United States Department of Energy (US-DOE) in 2008 on the Al-water reaction for hydrogen generation [25]. The aim of this paper was to gauge the potential of Al-water reactions for on-board H_2 powered vehicle applications.

The 2010 DOE targets for gravimetric and volumetric hydrogen capacity of H_2 generation systems are 6 wt. % hydrogen and 45 grams of hydrogen per liter respectively. The corresponding parameters for the aluminum-water hydrogen generation system with a hydroxide promoter are 2.5 wt. % of hydrogen and 35 grams of hydrogen per liter respectively. This paper also contains a detailed section on "System Considerations" which outlines various factors that need to be considered for any engineering work based on this reaction. Investigations need to be made in the issues of storing fresh reactants as well as the separation, storage, loading and unloading of reagents and byproducts. Moreover, they make mention of the need for developing mechanisms for generating hydrogen in response to variable demand profiles, as well as employing thermal management systems. The authors also remark that the most straightforward way to control the reaction would be to control the rate of liquid flow to the metal reactant, while still retaining a buffer storage system for highly variable loads".

2.2. Effect of structural evolution of aluminum powder during ball milling

In November 2012, S.S Razavi et al. investigated enhancement of hydrogen generation rate by studying effect of milling time on structure of pure Al powder. Milling caused changes in grain orientation and lattice imperfections, size and morphology. High energy ball milling was done in planetary ball mill having stainless steel cups (dia.28 of 16 mm) in argon atm at 200 RPM for 0.25, 0.5 , 1, 2, 4, 7 , 11 , and 19 hours[26]. The results supported with characterization of samples that surface area of 4 and 7 hours are higher than 19 hours milled Al powder which was smaller in particle size. The same two samples having more surface area produced more hydrogen when reacted with 200 ml water at 80 Celsius.

Milling up to 7 hours caused decreased in particle size, increased in lattice imperfections. The inter layer spaces in microstructure increased the surface area that was in contact with water however these parameters cannot be used as universal rule as it varied from sample to sample.it was also revealed that milling along with decrease in particle size it also introduced new surfaces in samples which resulted in increased surface area and consequently higher yield and generation rate of hydrogen.

2.3. Reaction of Al-water under ambient conditions

In 2012, Wei Zhuo et al. "Examined six different sized Al powdered (98.38nm, 2.25, 7.29, 15.08 24.94 micrometer respectively) their effect under different temperature conditions were studied it was found that as particle sized decreases the induction time also decreased. The aluminum powder of 98.38 nm can react with water and produced hydrogen at 20 celcius however the induction time was too much nearly 13 hours and sample was not fully consumed even after 82 hours.

In case of higher particles more than 40 Celsius was required to initiate the reaction. According to the paper induction time was related to H diffusion in bulk Al and critical gas pressure in hydrogen bubbles on interface of aluminum and alumina. Moreover reaction of Al-water is controlled initially by chemical surface reaction after that diffusion of H_2O through the layer of byproduct. End products depending upon the temperature are bayerite, boehmite, or mixture of them".

2.4. Reaction of Al with NaOH

In 1970 Belitskus conducted experiments on the Aluminum and aqueous sodium hydroxide [27]. "This paper provide qualitative and quantitative information regarding the factors which can affect the rate of reaction. He used large "Ingots" of aluminum powder, along with compacted pelletized powder for his study, 0.2 grams of Al and 200 ml of sodium hydroxide were kept as standards. According to him 0.2 grams of high surface area powder in 1M of sodium hydroxide proceeded to completion (275 ml) in 10 minutes. The rate of H_2 generation was proportional to size of sample used, and the delay in evolution increased with the reduction in surface area of the powders. When aluminum along with solid NaOH were added to water without mixing, H_2 generation was as rapid as compared to sodium hydroxide was pre-dissolved. He also reports that gas evolution rates are inversely proportional to density of the pellets and that pellet density was more important than surface area in determining the rate of reaction. These experiments were also conducted with low solution volume for identification of effect of reaction heat. Increased concentration reduced reaction delay time".

2.5. Use of metal oxides as Modifiers

In year 2011, Hong Wen Wang et al [28] "Used metal oxides nanocrystals such as TiO_2,Co_3O_4,Cr_2O_3,Fe_2O_3, Mn_2O_3, NiO, CuO and ZnO as modifiers on the metallic aluminum (Al) powders for the production of hydrogen in deionized water or tap water at room temperature. In particular, the influences of TiO2 nanocrystals with various crystal sizes on the production of hydrogen from the reaction in tap water under ambient condition were investigated in details. It was found that hydrogen was barely generated from metal Aluminum powders in tap water at 25-45^{o}C but significantly produced in deionized water above 35^{o}C without any modifiers. TiO_2, Co_3O_4, and Cr_2O_3 nanocrystals were very effective to promote hydrogen generation from the reaction of Al and deionized water at 25^{o}C. In addition, while other oxide nanocrystals were ineffective to promote hydrogen generation in tap water, TiO_2 nanocrystals (P90, 14 nm in diameter) were found to be highly effective in facilitating the production of hydrogen from the reaction of Al with tap water".

2.6. Hydrogen generation by mean of activated Al

In year 2012, A.V ilukhina et al "Selected a method in aluminum wire along with gallam alloy were crushed in porcelain morter and then it was subjected to high energy ball milling at 550 rpm for 15 minute .gallam alloy samples were prepared in following manner Ga-In (70:30), Ga –In –Sn (62:25:13), Ga –In –Sn-Zn (50:30:10:10).different particle sizes were used and was found that aluminum wire required less mechanochemical treatment and produced good results as far as results are concerned.

Effect of particle size was measured and found that being larger specific area they produced better results. Similarly different composition of gallam alloy was observed and it was observed that Ga has profound effect on hydrogen generation rate as well as yield however it was not cost effective but due to addition other metals Ga quantity can be reduced and better results can be achieved as well".

2.7. Enhancement of hydrogen generation rate using NaCl

In year 2010 Korosh Mahmoodi et al used aluminum particles of less than 75 μm and NaCl of 100 - 200 μm particle size milled together for 15 hours in argon atmosphere. The samples were treated with water for hydrogen generation on 70 to 90 Celsius. The effect of amount of water was considered varying different ratios it was found that increasing the amount of water slow down the reaction. Similarly when salt ratio is increased it also resulted in better yield and generation rate. Moreover the milling of salt formed a protective layer around the aluminum and able it to be stored it for longer time. Addition of silicon and bismuth also improved the results [29, 30].

2.8. Summary of literature survey

Literature survey reveals that aluminum water reaction for hydrogen production catches the attention of many researchers because of its countless advantages but presence of passive oxide layer is the main hurdle in oxidation process. There are many ways to remove it and most promising among them is Alloying, using alkaline solution, milling of chlorides and metal oxides to remove the layer. The parameters like temperature, particle size, concentration of modifiers, purity of water plays a crucial role.

Chapter 3: Resources and Approaches

3. *This chapter deals with all the resources available for characterization of samples and end products their working techniques/principles. Moreover under which conditions samples were prepared to obtain the desired results are discussed in detail.*

3.1. Particle Size Analyzer (PSA)

Particle Size analyzer is an experimental technique to characterize the various kind of powders according to their particle size as well as their state of distribution at various sizes. Horriba LA-920 can measure particles that range from 0.02 to 2000 microns.

3.1.1. Working Principle of PSA

Particle size analyzer works on principle of light scattering / Laser scattering technique. These techniques are based on physics principles that can be used to find out the size distribution profile of small particles in suspension.

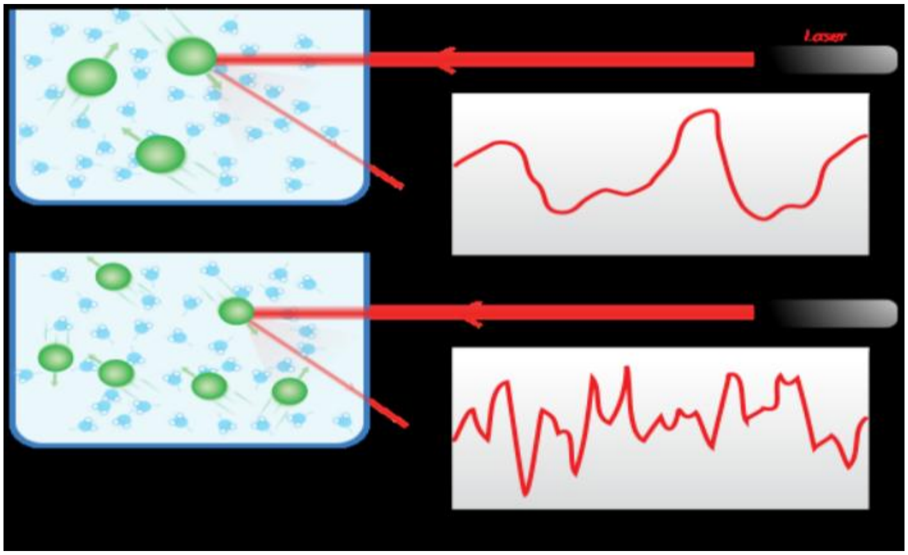


Figure 3.1: Working Principle of PSA

3.1.2. Sample Preparation

1 mg of aluminum powder was added to 500ml ethanol and sonicated for half an hour. When the sample completely suspended in ethanol, 200 ml of suspension was poured into analysis chamber for particle size analysis.

3.2. Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that uses electron beam to generate images of a sample by scanning. The electron gun generates electron beam which when interact with the sample surface produces various signals about the sample surface, topography and composition. These signals are detected and interpreted automatically and microscopic image of the sample is generated

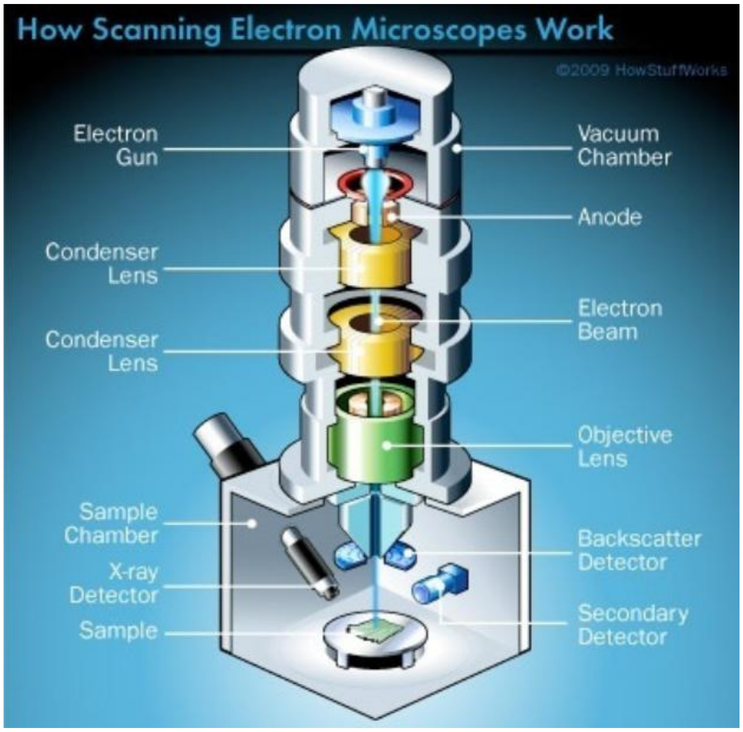


Figure 3.2: Schematic diagram of SEM

3.2.1. Working Principle of SEM

SEM produces various kinds of signals which includes secondary electrons, back scattered electrons, characteristics X-Rays and transmitted electrons. SEM is equipped with secondary electron detectors which detects such signals. Back scattered electron signals gives information related to sample composition and elemental distribution.

3.2.2. Sample Preparation

Sample for SEM analysis was prepared like a disk having 13mm dia and 2mm thickness according to sample holder which further was attached to copper disk with adhesive carbon tape. The sample must be conductive at the surface and for this reason the sample was coated with gold before it was analyzed in SEM.

3.3. X-Rays Diffraction (XRD)

X-rays are electromagnetic radiation having wave length 10-10 m or 1 Å, occurred in the region between Gamma-rays and Ultra violet waves. XRD (X-ray diffraction) is non-destructive technique of characterization used for analysis of all kinds of matter including fluids, solid, powders and crystals. This technique is used in various fields including mineralogy, metallurgy, archeology, forensic science, biological, pharmaceutical sciences and archeology science. Generally XRD is widely used to examine crystals, giving information's about the crystal structure, distribution of elements in the crystals, chemical bonds, strains, etc.

3.3.1. Working Principle of XRD

XRD is used to identify unit cell parameters using x-rays. These x-rays when interact with material at various planes of atoms are diffracted at an angle which is measured, analyzed and XRD peaks are generated. Analysis of peaks using Bragg's Law tells us the location of a peak with Miller indices [hkl]. Miller indices are related to inter planar spacing, d, as follows:

$\lambda = 2dhkl \sin \theta hkl$

$1/d = 2 \sin \theta / \lambda$

$1/d^2 = 4 \sin2 \theta / \lambda^2$……………………………. (1)

We know that for a cubic phase the d-values can be calculated from the Miller indices (hkl):

$1/d^2 = (h^2 + k^2 + l^2)/a^2$……………………………. (2).

Combining these two equations

$$(h^2 + k^2 + l^2)/a^2 = 4 \sin^2 \theta / \lambda^2$$

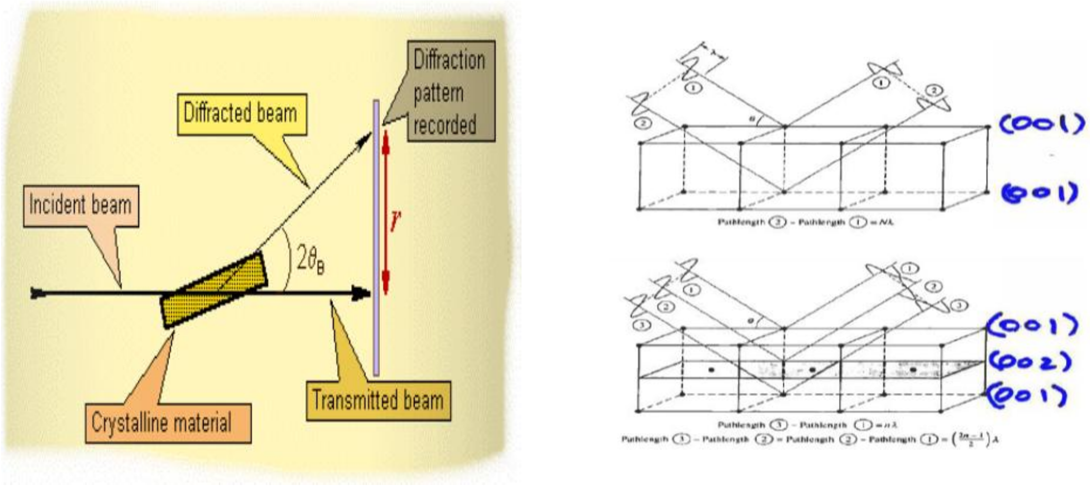
Or

$$\sin^2 \theta = (\lambda^2/4a^2)(h^2 + k^2 + l^2)$$

Where λ and ‘a’ are constants, hence $\lambda^2 / 4a^2$ is constant. λ is wavelength in angstrom (1.54 Å for copper) ,θ is diffraction angle in degree and ‘a’ is lattice parameter.

Sin2θ is proportional to $(h^2 + k^2 + l^2)$ i.e., planes with higher Miller indices will diffract at higher values of θ. In cubic systems, the first XRD peak in the diffraction pattern will be due to diffraction from planes with the lowest Miller indices

– Simple cubic, (100), $(h^2 + k^2 + l^2) =$ 1
– Body-centered cubic, (110), $(h^2 + k^2 + l^2) =$ 2
– Face-centered, (111), $(h^2 + k^2 + l^2) =$ 3



(a) **(b)**

Figure 3.3 :(a) XRD Working Principle. (b) X-Ray Diffraction Pattern at Planes

Chapter 4: Experimental Work

4. *This chapter will depict in detail study of preparation of catalysts, characterization of aluminum, nickel oxide, magnesium oxide. Experimental setup will be explained along with modifiers. Results obtained will be represented in succeeding chapter.*

4.1. Characterization of Aluminum Powder

4.1.1. Particle Size Analysis

Four types of aluminum powders were obtained, complete details regarding their specifications is given in table 4.4. However, raw aluminum was collected from lathe machines materialized in doors/ windows are manufacturing. Aluminum samples were characterized by Laser Scattering Particle Size Analyzer (Horiba LA-920). The mean particle sizes were found 10, 20 and 30 μm except later mentioned particle. Following Figures 4.1, 4.2 and 4.3 shows the graph obtained from Particle Size Analyzer for each samples respectively.

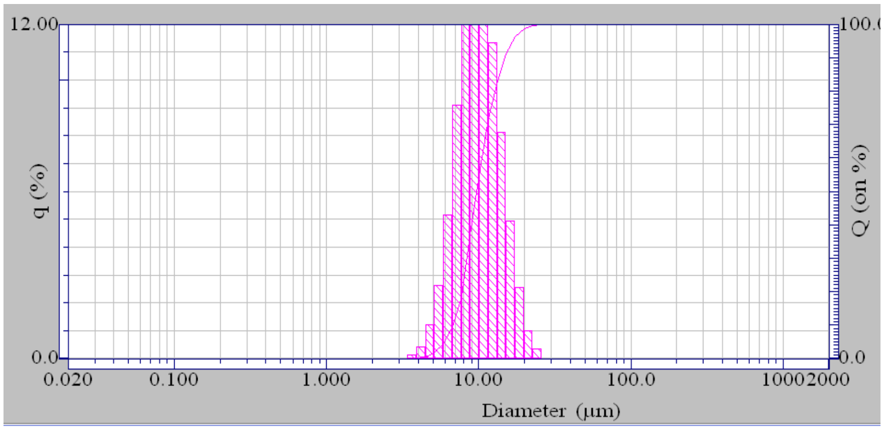


Figure 4.1: Particle Size Analysis Result (10 μm)

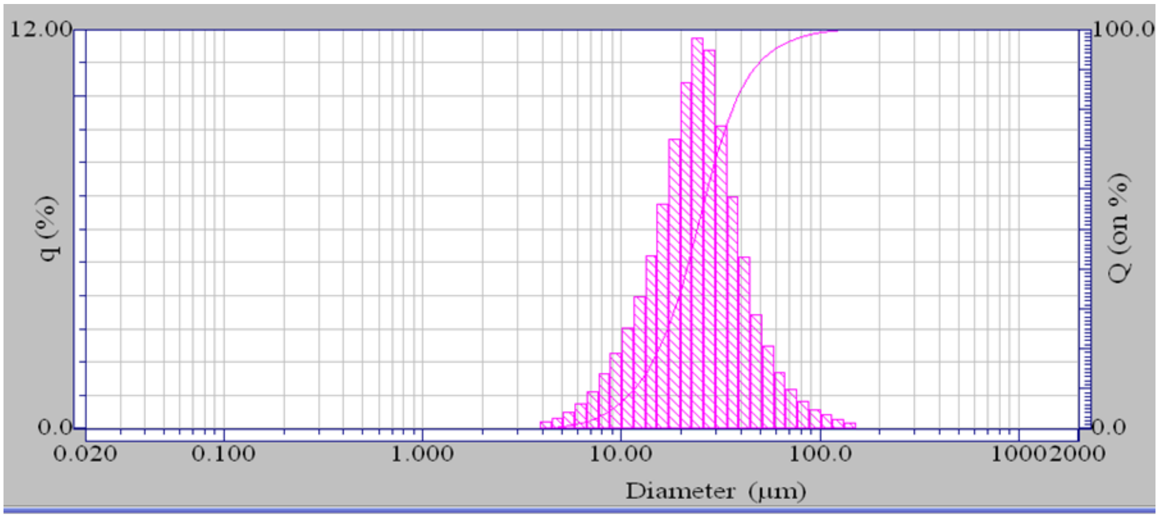


Figure 4.2: Particle Size Analysis Result (20 μm)

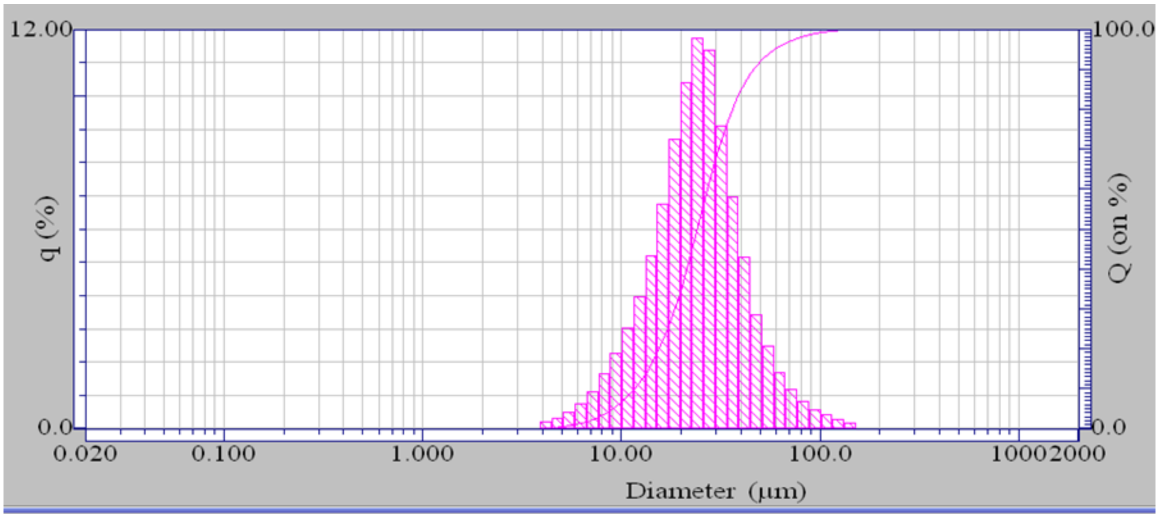


Figure 4.3: Particle Size Analysis Result (30 μm)

4.2. SEM and EDS Analysis

SEM and EDS analysis were carried to characterize the aluminum powders and it was found that the Aluminum powder with average particle size of 10μm, 20μm, 30μm are is spherical in shape where as raw aluminum powder were small strips in mm. Average particle size of these particles of was also confirmed on SEM image as shown in Figure 4.4, 4.5, 4.6 and 4.7 respectively

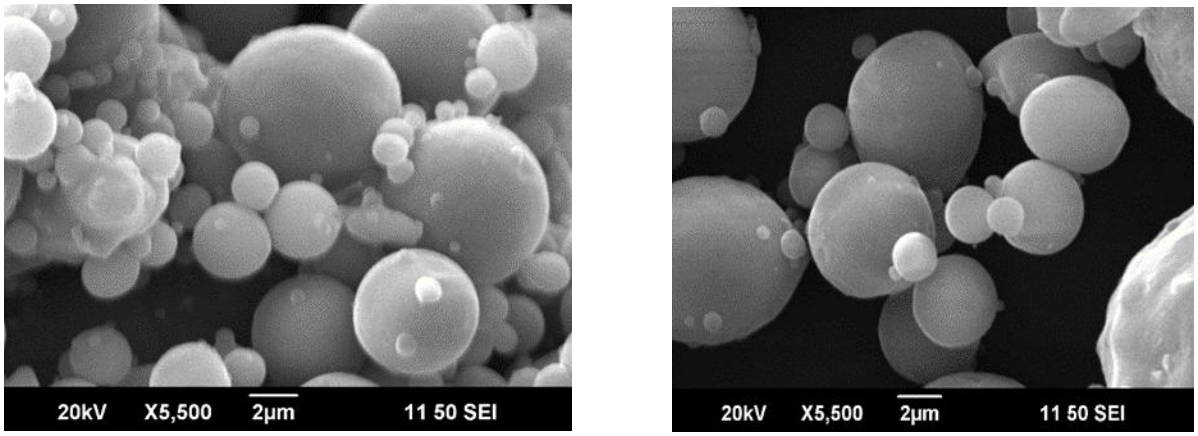


Figure 4.4: SEM Images of Aluminum Powder 10 µm

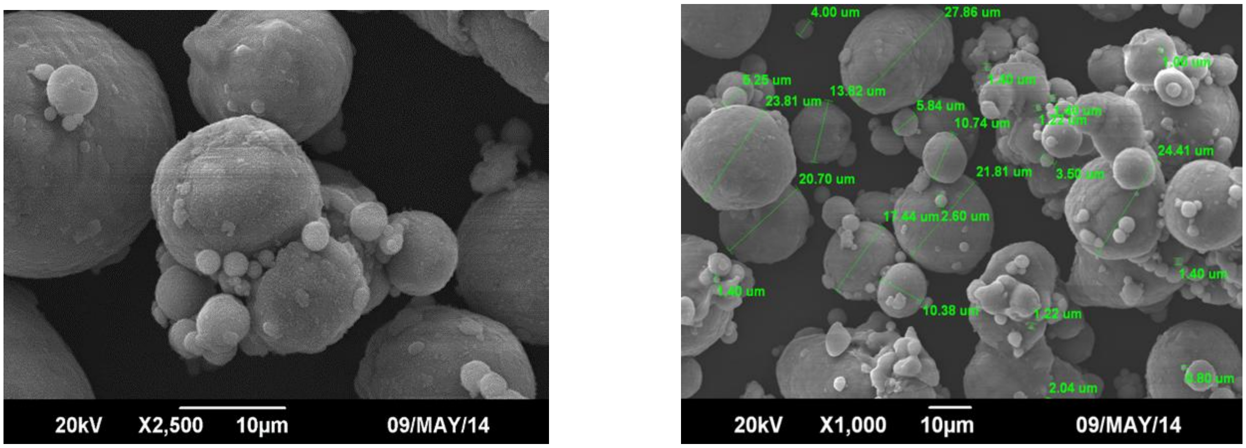


Figure 4.5: SEM Images of Aluminum Powder 20 µm

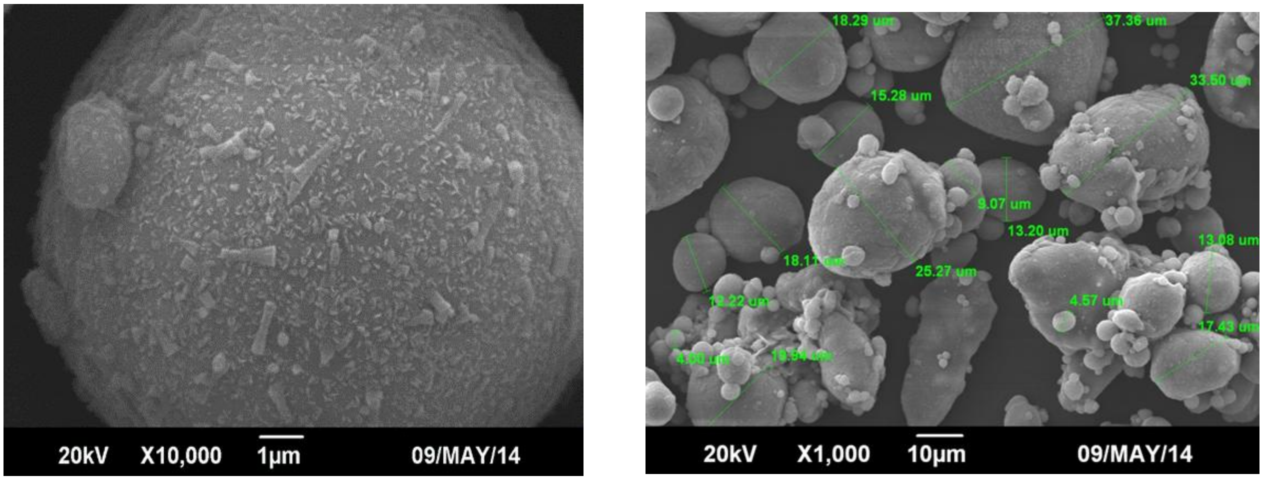
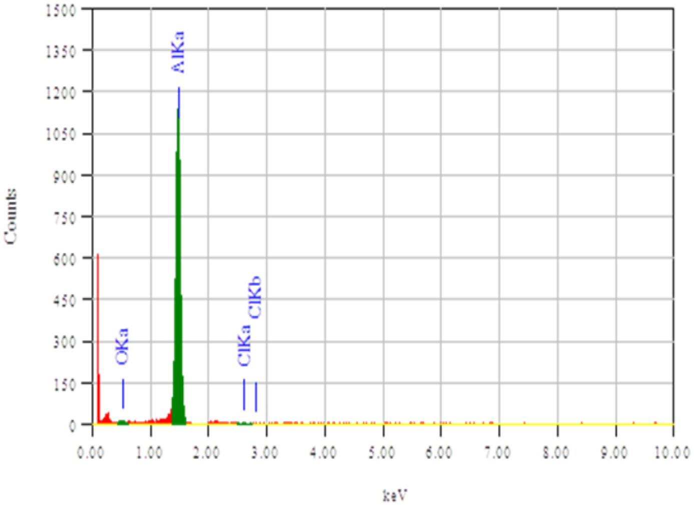
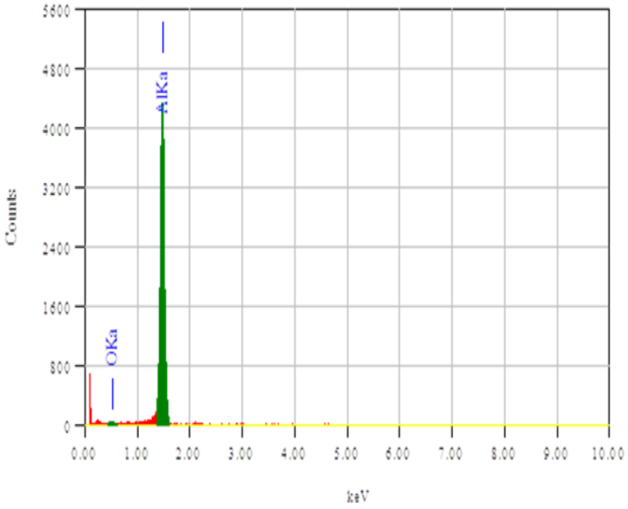


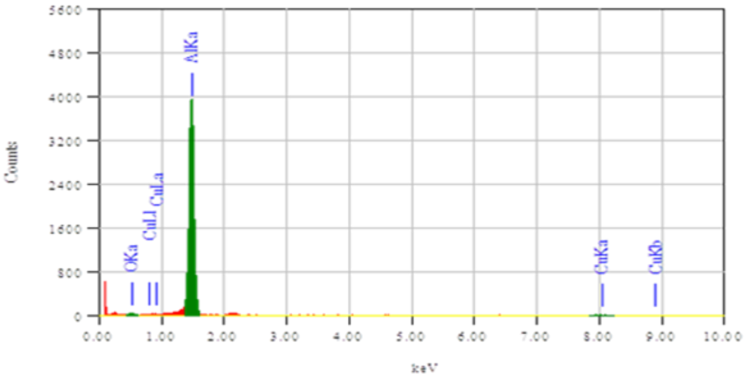
Figure 4.6: SEM Images of Aluminum Powder 30 µm



(a)



(b)



(c)

Figure 4.7: (a) (b) (c) showing EDS Spectrum of Aluminum Powder 10, 20 and 30 µm respectively

Table 4.1: EDS result of Aluminum Powder 10 µm

Element	(keV)	Mass%	Error%	Atom%	K
O K	0.525	2.94	4.32	4.86	2.0079
Al K	1.486	96.30	1.42	94.57	97.4359
Cl	2.621	0.76	2.60	0.57	0.5562
Total		100.00			100.00

Table 4.2: EDS result of Aluminum Powder 20 µm

Element	(keV)	Mass%	Error%	Atom%	K
O K	0.525	3.46	3.18	5.70	2.4027
Al K	1.486	96.54	1.06	94.30	97.5973
Total		100.00			100.00

Table 4.3: EDS result of Aluminum Powder 30 µm

Element	(keV)	Mass%	Error%	Atom%	K
O K	0.525	3.34	2.64	5.62	2.5262
Al K	1.486	93.09	0.96	92.87	94.2168
Cu K	8.040	3.57	8.59	1.51	3.2570
Total		100.00			100.00

4.3. XRD Analysis of Aluminum Powders

The aluminum powders were also analyzed on XRD and peaks (Figure 4.10) matched to the stick pattern 01-089-2837 (Figure 4.11) of pure aluminum. The peaks emerged at 2θ values 38.377, 44.609, 64.923 and 78.008 corresponding to (111), (200), (220), and (311) family of planes. The crystal structure found as Face Centered Cubic and density 2.68 g/cm3 which also confirms to pure aluminum.

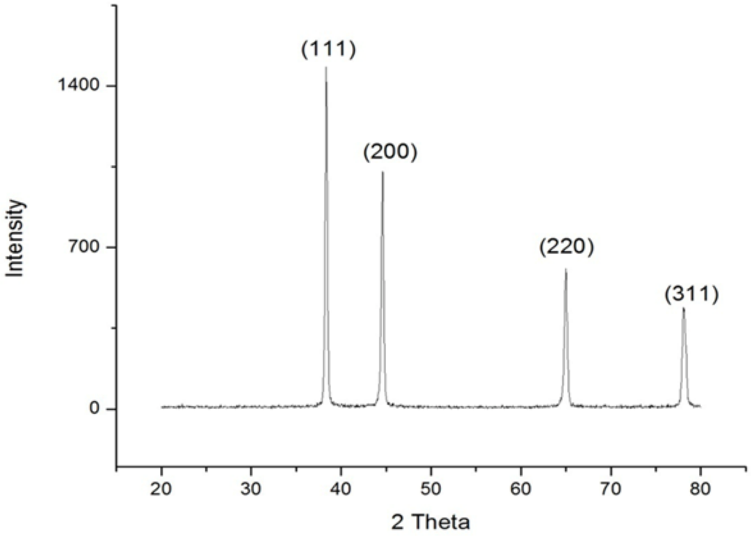


Figure 4.8: XRD analysis of aluminum powder showing hkl values

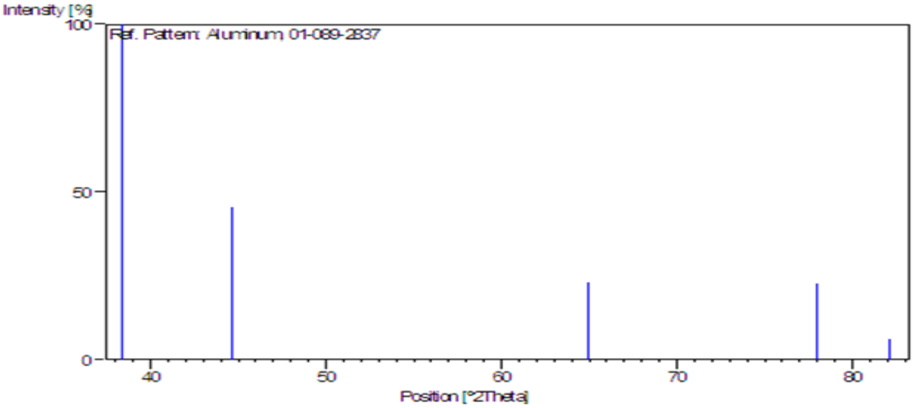


Figure 4.9: showing stick pattern 01-089-2837

4.4. Thermal and Gravimetric Analysis of Aluminum

The aluminum powders (10, 20 and 30 µm) were used for thermal and gravimetric analysis. In order to investigate oxidation process of aluminum, the experiments were carried out on TGA. In temperature range up to 1000°C having atmosphere of Oxygen with heating rate 10°C/ min and sample mass 24mg gradual increase in mass is observed till 550°C but then sharp curve showing increase in mass is observed at 660°C which is the melting point of pure aluminum . The intense increase in mass beyond 800-1000°C is due to high oxidation process which under take because high temperature.

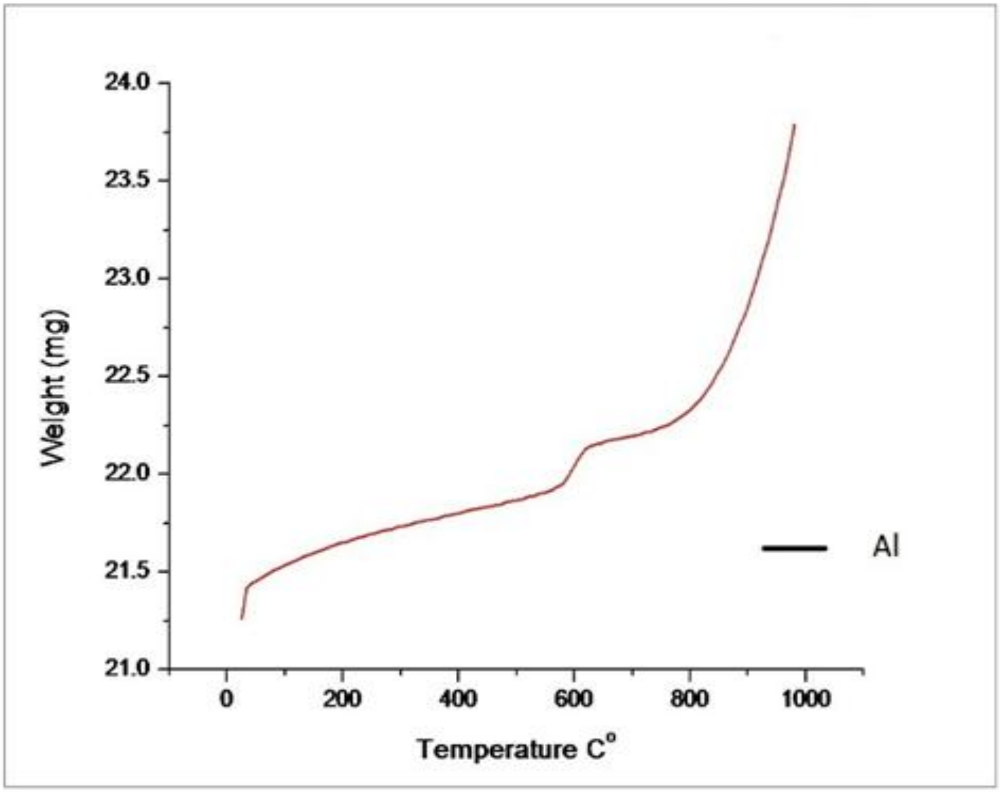


Figure 4.10: TGA Analysis of Aluminum powder

4.5. Materials and Modifiers used

The materials and modifiers used in experiments are enlisted below in table:

Table 4.4: Precursors used in study

Precursors	**Purity (%)**	**Mean Particle Size**	**Remarks**
Al (10 um)	**97**	**10 µm**	**Carl Roth**
Al (20 um)	**97**	**20 µm**	**BDH**
Al (30 um)	**94**	**30 µm**	**Local Vander**
Al (raw)	**92**	**1-2 mm**	**Collected from lathe machines**
LiOH	**99**	**Bulk**	**Sigma Aldrich**
$Ca(OH)_2$	**97**	**Bulk**	**BDH**
NiO	**98**	**30-35 nm**	**Synthesized at NCP**
MnO_2	**97**	**40-45 nm**	**Synthesized at NCP**
Co_3O_4	**99**	**Bulk**	**Deajung**
CoO	**99**	**Bulk**	**Deajung**
LiCl	**98**	**Bulk**	**Deajung**

4.6. Experimental Steps for Hydrogen Production

4.6.1. Step 1- Degassing of Distilled Water

At this step, the soluble gasses present in distilled water were removed by degassing in ultra-sonic water bath for half an hour.

4.6.2. Step 2 - Preparation of Solution

At this step, the modifier (if required) was added to the degassed water and flask was placed in ultra-sonic water bath for half an hour.

4.6.3. Step 3 - Reaction

At this stage, Aluminum powder was precisely weighed and added to the solution. The reaction was allowed to take place either at certain temperature which was pre-maintained in Water Bath or in ultra-sonic water bath at room temperature. Temperature in ultra-sonic water bath continuously increased under the influence of ultra-sonic waves. However it was maintained by continuous observation at 45^oC.

4.6.4. Step 4 - End Products

Hydrogen so produced was collected in measuring cylinder. After the reaction was completed, the solution was filtered through the filter paper to split water and end products of reaction. Analysis of solid end products on SEM and XRD was carried out.

4.7. Experimental Setup

The apparatus for hydrogen production was setup using lab glassware as shown in figure 4.13 below. Digital water bath used to record and maintain temperature. Measuring cylinder, filled with water, was placed upside down in water tub to collect the hydrogen gas. Rubber corks were used to secure the flask mouth and gas leakage.

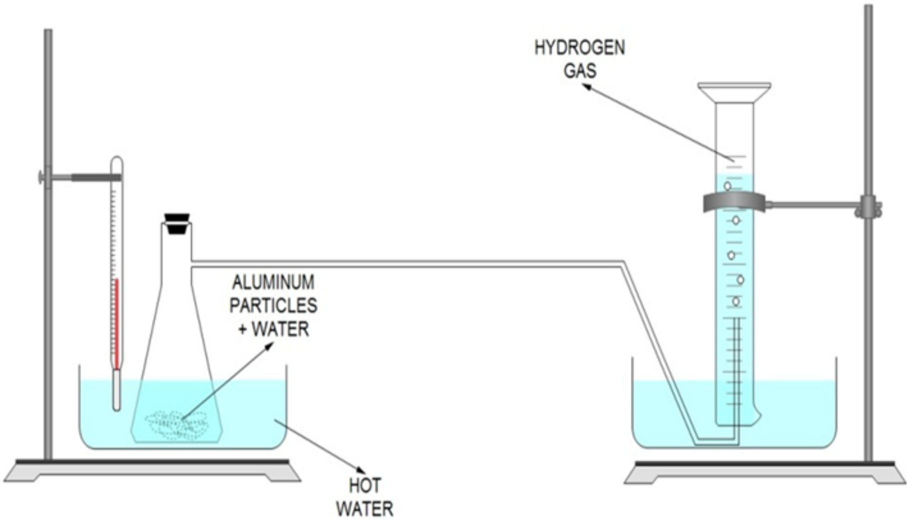


Figure 4.11: Schematic Diagram of Experimental Setup

Table 4.5: List of Glassware/Equipment Used in Experimental Setup

Glassware	**Volume**	**Quantity**	**Remarks**
Flask	250 ml	1	
Measuring cylinder	250 ml	1	
Thermometer	-	1	
Glass tube/ Pipe	-	1	2-3 ft
Water Bath	4 Gal	1	
Ultra Sonic Water Bath	2.5 Gal	1	Make: Cole Parmer
Flask Cork	-	1	

4.8. Experimental Work

4.8.1. Aluminum – Water Reaction (without modifier)

The experiments were conducted in following conditions as described in table 4.5. The reaction was allowed to take place at temperatures mentioned against each for 72 hours in water bath and for 6 hours in ultra-sonic water bath. Aluminum and water quantity was kept constant for better comparison.

Table 4.6: Experiment Conditions (Al raw + Without Modifier)

Temp	Aluminum (Raw)	Water (Degassed for ½ Hour)	Modifier	Reaction Time	H_2 Yield %
40 °C	150mg	150 ml	No	72 Hours	4 %
50 °C	150mg	150 ml	No	72 Hours	6%
60 °C	150mg	150 ml	No	72 Hours	9%
Ultra Sonic Field (45 °C)	150mg	150 ml	No	6 Hours	11%

The results confirmed that hydrogen production takes place at low temperatures but the rate of production was too low. The increase in temperature had a positive effect on hydrogen yield. Ultra sonic field had significant effect not in terms of yield 11% yield is achieved in 6 hours as compared to 4% yield in 72 hours.

Table 4.7: Experiment Conditions (Al 30 µm + Without Modifier)

Temp	Aluminum (30 um)	Water (Degassed for ½ Hour)	Modifier	Reaction Time	H_2 Yield %
40 °C	150mg	150 ml	No	72 Hours	17%
50 °C	150mg	150 ml	No	72 Hours	24%
60 °C	150mg	150 ml	No	72 Hours	29%
Ultra Sonic Field (45 °C)	150mg	150 ml	No	6 Hours	34%

Table 4.8: Experiment Conditions (Al 20 µm + Without Modifier)

Temp	Aluminum (20 um)	Water (Degassed for ½ Hour)	Modifier	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	No	72 Hours	35%
50 ^{o}C	150mg	150 ml	No	72 Hours	40%
60 ^{o}C	150mg	150 ml	No	72 Hours	47%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	No	6 Hours	60%

Table 4.9: Experiment Conditions (Al 10 µm + Without Modifier)

Temp	Aluminum (10 um)	Water (Degassed for ½ Hour)	Modifier	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	No	72 Hours	50%
50 ^{o}C	150mg	150 ml	No	72 Hours	63%
60 ^{o}C	150mg	150 ml	No	72 Hours	80%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	No	6 Hours	85%

4.9. Aluminum – Water Reaction (using metal oxide)

Metal oxides were utilized with each sample under varying conditions and ratios. Two out of four metal oxide were synthesized at laboratory while rest were purchased as mentioned in table 4.4.

4.9.1. Synthesis of NiO

The precursors used in sonochemical process for the synthesis of NiO nanoparticles were nickel acetate hexa hydrate $Ni(CH_3COO)_2.6H_2O$, (Deajung), NH_4OH (E.Merck) was used as a precipitant as well as for homogeneity and pH value of the solution, All of the experiments were performed under atmosphere conditions. First, 50 mL nickel acetate solution (0.14M) sonicated for 30 min and then, enough volume of NH_4OH solution (0.34 M) was slowly added. In this step, nano-structured nickel hydroxide was formed during the following reaction:

$$Ni(CH_3COO)_2(aq) + 2NH_4OH(aq) \longrightarrow Ni(OH)_2(s) + 2CH_3COONH_4\ (aq)$$

At the end of the process of adding NH_4OH solution, the mixture was additionally sonicated for 30 min. The precipitated nickel hydroxide was filtered and washed with distilled water and ethanol for three times. 50 mL ethanol was added to the obtained precipitate and the mixture was sonicated for 30 min and then, the sonicated mixture was filtered. The final obtained precipitate was dehydrated at 550 ºC for 4 h. The following reaction took place during the dehydration phase:

$$Ni(OH)_2(s) \longrightarrow NiO(s) + H_2O_{(g)}$$

The NiO nanoparticles were sonicated in ethanol for 30 min to eliminate agglomeration. In final step, the mixture was filtered and dried at 110 ºC. The final product was obtained in nano-powder form. The nanostructured nickeloxide powder was characterized by SEM and its particle size was also determined from Laser Scattering Particle Size Analyzer (Horiba LA-920).

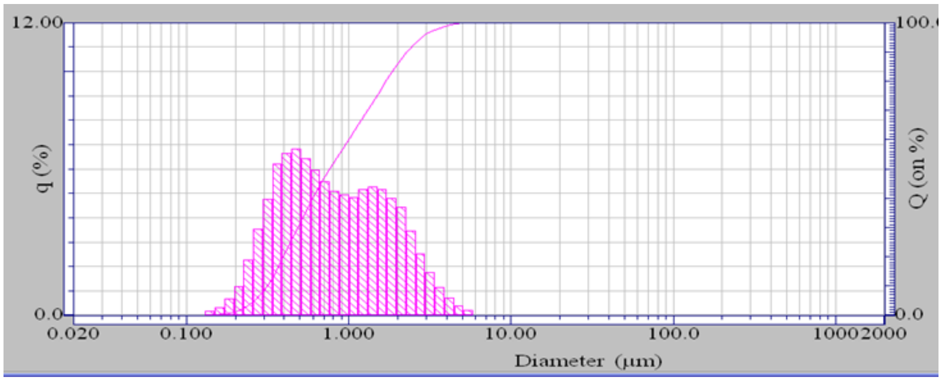


Figure 4.12: Particle Size Analysis of NiO

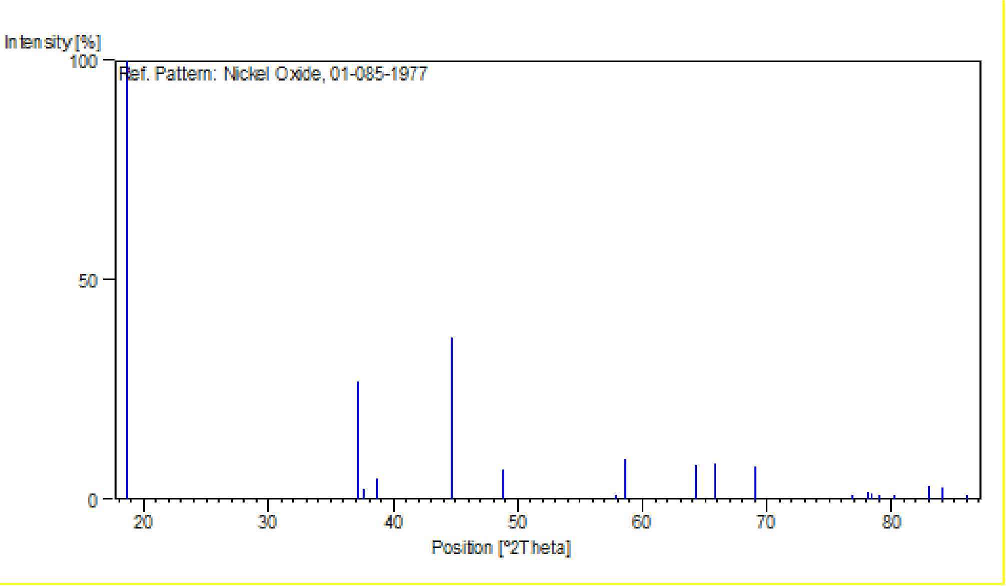


Figure 4.13: XRD/STICK PATTERN OF NiO

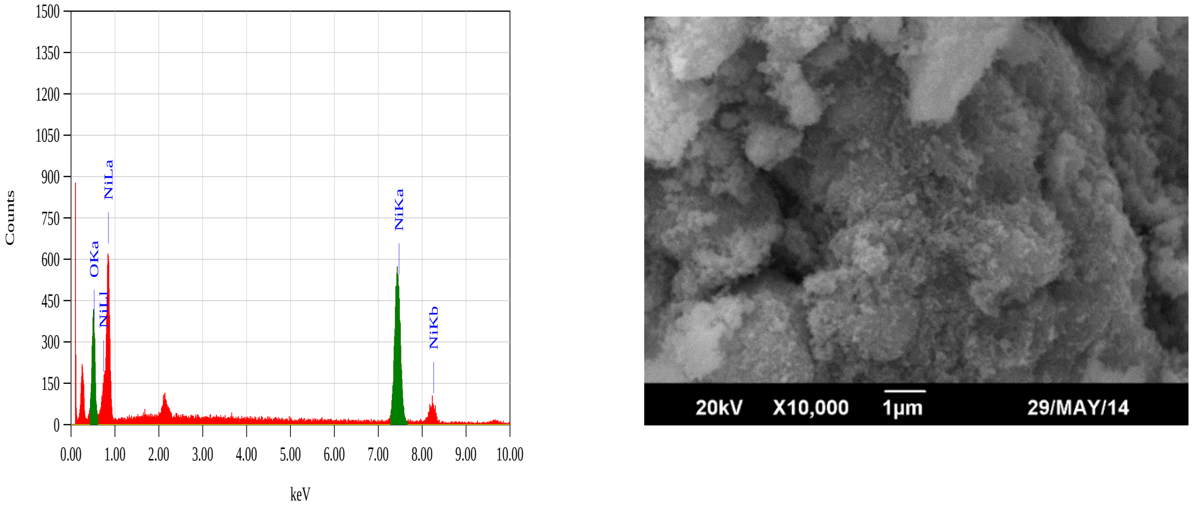


Figure 4.14: SEM / EDS of NiO

4.9.2. Synthesis of MnO

The precursors used in sonochemical process for the synthesis of MnO nanoparticles were magnesium acetate hexa hydrate $Mn(CH_3COO)_2.6H_2O$, (Deajung), NH_4OH (E.Merck) was used as a precipitant as well as for homogeneity and pH value of the solution, All of the experiments were performed under atmosphere conditions. First, 50 mL magnesium acetate solution (0.14M) sonicated for 30 min and then, enough volume of NH_4OH solution (0.34 M) was slowly added. In this step, nano-structured nickel hydroxide was formed during the following reaction:

$$Mn(CH_3COO)_2(aq) + 2NH_4OH(aq) \longrightarrow Mn(OH)_2(s) + 2CH_3COONH_4\ (aq)$$

At the end of the process of adding NH_4OH solution, the mixture was additionally sonicated for 30 min. The precipitated nickel hydroxide was filtered and washed with distilled water and ethanol for three times. 50 mL ethanol was added to the obtained precipitate and the mixture was sonicated for 30 min and then, the sonicated mixture was filtered. The final obtained precipitate was dehydrated at 550ºC for 4 h. The following reaction took place during the dehydration phase:

$$Mn(OH)_2(s) \longrightarrow MnO(s) + H_2O_{(g)}$$

The MnO nanoparticles were sonicated in ethanol for 30 min to eliminate agglomeration. in final step, the mixture was filtered and dried at 110 ºC. The final product was obtained in nano-powder form. The nanostructured magnesium oxide powder was characterized by SEM and XRD.

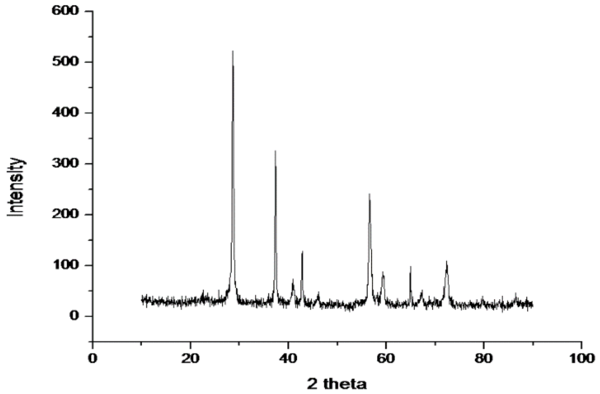


Figure 4.15: XRD Analysis of MnO

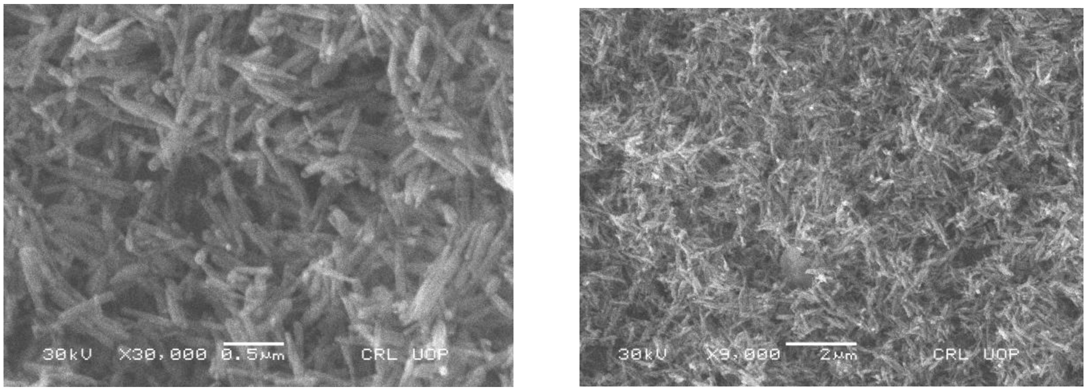


Figure 4.16: SEM images of MnO

4.9.3. Aluminum- Water Reaction in Presence of NiO

In the following experiments, NiO was added at various ratios and the 1:4 was found as best ratio to support hydrogen production. Table 4.10 till 4.13: shows conditions and results of experiment so conducted with NiO. If we compare the results with tables 4.6 to 4.9 (Al + No modifier), the results depicts no significant effect of NiO on hydrogen yield even in presence of ultra-sonic field. Yield at various temperatures has a minor increase, which is almost negligible. The results are not comparable to literature because no prior processing was carried out on both nano-modifiers and aluminum powder. Nano-modifiers have no profound effect on the hydrogen yield in aluminum-water reaction in absence of prior processing such as ball milling and alloying.

Table 4.10: Experiment Conditions (Al raw + NiO)

Temp	Aluminum (Raw)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 °C	150mg	150 ml	NiO	72 Hours	6%
50 °C	150mg	150 ml	NiO	72 Hours	9%
60 °C	150mg	150 ml	NiO	72 Hours	12%

Ultra Sonic Field (45 °C)	150mg	150 ml	NiO	6 Hours	15%

Table 4.11: Experiment Conditions (Al 30µm+ NiO)

Temp	Aluminum (30)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	NiO	72 Hours	19%
50 ^{o}C	150mg	150 ml	NiO	72 Hours	28%
60 ^{o}C	150mg	150 ml	NiO	72 Hours	32%
Ultra Sonic Field (45 °C)	150mg	150 ml	NiO	6 Hours	39%

Table 4.12: : Experiment Conditions (Al 20µm+ NiO)

Temp	Aluminum (20)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	NiO	72 Hours	38%
50 ^{o}C	150mg	150 ml	NiO	72 Hours	43%
60 ^{o}C	150mg	150 ml	NiO	72 Hours	49%
Ultra Sonic Field (45 °C)	150mg	150 ml	NiO	6 Hours	64%

Table 4.13: : Experiment Conditions (Al 10µm+ NiO)

Temp	Aluminum (10)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	NiO	72 Hours	53%
50 ^{o}C	150mg	150 ml	NiO	72 Hours	66%

60 ^oC	150mg	150 ml	NiO	72 Hours	85%
Ultra Sonic Field (45 ℃)	150mg	150 ml	NiO	6 Hours	88%

4.9.4. Aluminum- Water Reaction in Presence of MnO

In the following experiments, magnesium oxide was added at various ratios and the 1:4 was found as best ratio to support hydrogen production. Table 4.14 till 4.17 shows conditions and results of experiment so conducted with MnO. If we compare the results with tables of no modifiers and NiO the results depicts no significant effect of MnO on hydrogen yield even in presence of ultra-sonic field. Yield at various temperatures has a minor increase, which is almost negligible

Table 4.14: Experiment Conditions (Al raw + MnO)

Temp	Aluminum (Raw)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^oC	150mg	150 ml	MnO	72 Hours	6%
50 ^oC	150mg	150 ml	MnO	72 Hours	9%
60 ^oC	150mg	150 ml	MnO	72 Hours	12%
Ultra Sonic Field (45 ℃)	150mg	150 ml	MnO	6 Hours	15%

Table 4.15: Experiment Conditions (Al 30 µm + MnO)

Temp	Aluminum (30um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^oC	150mg	150 ml	MnO	72 Hours	21%
50 ^oC	150mg	150 ml	MnO	72 Hours	29%
60 ^oC	150mg	150 ml	MnO	72 Hours	35%

Ultra Sonic Field (45 °C)	150mg	150 ml	MnO	6 Hours	41%

Table 4.16: Experiment Conditions (Al 20 µm+ MnO)

Temp	Aluminum (20um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 °C	150mg	150 ml	MnO	72 Hours	39%
50 °C	150mg	150 ml	MnO	72 Hours	45%
60 °C	150mg	150 ml	MnO	72 Hours	49%
Ultra Sonic Field (45 °C)	150mg	150 ml	MnO	6 Hours	66%

Table 4.17: Experiment Conditions (Al 10 µm + MnO)

Temp	Aluminum (10um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 °C	150mg	150 ml	MnO	72 Hours	55%
50 °C	150mg	150 ml	MnO	72 Hours	66%
60 °C	150mg	150 ml	MnO	72 Hours	87%
Ultra Sonic Field (45 °C)	150mg	150 ml	MnO	6 Hours	89%

4.9.5. Aluminum- Water Reaction in Presence of Co_3O_4

In the following experiments, Co_3O_4 was added at various ratios and the 1:4 was found as best ratio to support hydrogen production. Table 4.18 and 4.21 shows conditions and results of experiment so conducted with. The results depicts no significant effect of Co_3O_4 on hydrogen yield even in presence of ultra-sonic field as compared to previous experiments.

Table 4.18: Experiment Conditions (Al raw + Co_3O_4)

Temp	Aluminum (Raw)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	6%
50 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	9%
60 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	12%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	Co_3O_4	6 Hours	15%

Table 4.19: Experiment Conditions (Al 30 µm + Co_3O_4)

Temp	Aluminum (30um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	22%
50 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	31%
60 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	36%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	Co_3O_4	6 Hours	43%

Table 4.20: Experiment Conditions (Al 20 µm + Co_3O_4)

Temp	Aluminum (20um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	40%
50 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	47%
60 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	49%

Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	Co_3O_4	6 Hours	73%

Table 4.21: Experiment Conditions (Al 10 µm + Co_3O_4)

Temp	Aluminum (10um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	57%
50 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	67%
60 ^{o}C	150mg	150 ml	Co_3O_4	72 Hours	88%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	Co_3O_4	6 Hours	89%

4.9.6. Aluminum- Water Reaction in Presence of CoO

Table 4.22: Experiment Conditions (Al raw + CoO)

Temp	Aluminum (Raw)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	CoO	72 Hours	6%
50 ^{o}C	150mg	150 ml	CoO	72 Hours	9%
60 ^{o}C	150mg	150 ml	CoO	72 Hours	12%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	CoO	6 Hours	15%

Table 4.23: Experiment Conditions (Al 30 µm+ CoO)

Temp	Aluminum (30um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	CoO	72 Hours	23%
50 ^{o}C	150mg	150 ml	CoO	72 Hours	33%
60 ^{o}C	150mg	150 ml	CoO	72 Hours	37%

Ultra Sonic Field (45 ℃)	150mg	150 ml	CoO	6 Hours	44%

Table 4.24: Experiment Conditions (Al 20 + CoO)

Temp	Aluminum (20um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	CoO	72 Hours	41%
50 ^{o}C	150mg	150 ml	CoO	72 Hours	48%
60 ^{o}C	150mg	150 ml	CoO	72 Hours	49%
Ultra Sonic Field (45 ℃)	150mg	150 ml	CoO	6 Hours	75%

Table 4.25: Experiment Conditions (Al 10 µm + CoO)

Temp	Aluminum (10um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	CoO	72 Hours	57%
50 ^{o}C	150mg	150 ml	CoO	72 Hours	68%
60 ^{o}C	150mg	150 ml	CoO	72 Hours	89%
Ultra Sonic Field (45 ℃)	150mg	150 ml	CoO	6 Hours	89%

4.10. Aluminum- Water Reaction in Presence of $Ca(OH)_2$

When the same experiments were conducted using calcium hydroxide, the results as tabulated below in table 4.26 till 4.29 depicts an enhanced increase in hydrogen yield and an improved production rate. The presence of Ca(OH)2 has profound effect on yield especially as it gave 70% yield at 60 ^{0}C for raw Al as well.

Table 4.26: Experiment Conditions (Al raw + $Ca(OH)_2$)

Temp	Aluminum (Raw)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 °C	150mg	150 ml	$Ca(OH)_2$	72 Hours	50%
50 °C	150mg	150 ml	$Ca(OH)_2$	72 Hours	63%
60 °C	150mg	150 ml	$Ca(OH)_2$	72 Hours	70%
Ultra Sonic Field (45 °C)	150mg	150 ml	$Ca(OH)_2$	6 Hours	65%

Table 4.27: Experiment Conditions (Al 30 µm + $Ca(OH)_2$)

Temp	Aluminum (30 um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 °C	150mg	150 ml	$Ca(OH)_2$	72 Hours	88%
50 °C	150mg	150 ml	$Ca(OH)_2$	72 Hours	95%
60 °C	150mg	150 ml	$Ca(OH)_2$	24 min	100%
Ultra Sonic Field (45 °C)	150mg	150 ml	$Ca(OH)_2$	15 min	100%

Table 4.28: Experiment Conditions (Al 20 µm + $Ca(OH)_2$)

Temp	Aluminum (20 um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 °C	150mg	150 ml	$Ca(OH)_2$	72 Hours	95%
50 °C	150mg	150 ml	$Ca(OH)_2$	72 Hours	98%
60 °C	150mg	150 ml	$Ca(OH)_2$	21 min	100%

Ultra Sonic Field (45 ºC)	150mg	150 ml	$Ca(OH)_2$	14 min	100%

Table 4.29: Experiment Conditions (Al 10 µm + $Ca(OH)_2$)					
Temp	Aluminum (20 um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ºC	150mg	150 ml	$Ca(OH)_2$	72 Hours	96%
50 ºC	150mg	150 ml	$Ca(OH)_2$	72 Hours	98%
60 ºC	150mg	150 ml	$Ca(OH)_2$	18 min	100%
Ultra Sonic Field (45 ºC)	150mg	150 ml	$Ca(OH)_2$	12 min	100%

When fine aluminum powder 30µm, 20µm, and 10 um was used, the complete oxidation of aluminum powder took place at 60ºC in time as mentioned against each sample in respective tables. However at temperature 40 and 50ºC yield was obtained with in 35 minute but reaction was allowed to proceed further for 100% yield.

4.11. Reaction in Presence of LiOH

The results achieved in presence of lithium hydroxide as tabulated below in tables are not better than calcium hydroxide in term of yield however better generation rate was achieved with it.

Table 4.30: Experiment Conditions (Al raw + LiOH)					
Temp	Aluminum (Raw)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ºC	150mg	150 ml	LiOH	72 Hours	35%
50 ºC	150mg	150 ml	LiOH	72 Hours	39%
60 ºC	150mg	150 ml	LiOH	72 Hours	45%
Ultra Sonic Field (45 ºC)	150mg	150 ml	LiOH	6 Hours	60%

Table 4.31: Experiment Conditions (Al 30 μm + LiOH)

Temp	Aluminum (30 um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	LiOH	72 Hours	82%
50 ^{o}C	150mg	150 ml	LiOH	72 Hours	98%
60 ^{o}C	150mg	150 ml	LiOH	24 min	100%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	LiOH	15 min	100%

Table 4.32: Experiment Conditions (Al 20 μm + LiOH)

Temp	Aluminum (20 um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	LiOH	72 Hours	82%
50 ^{o}C	150mg	150 ml	LiOH	72 Hours	98%
60 ^{o}C	150mg	150 ml	LiOH	15 min	100%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	LiOH	10 min	100%

Table 4.33: Experiment Conditions (Al 10 μm + LiOH)

Temp	Aluminum (10 um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	LiOH	14 min	100%
50 ^{o}C	150mg	150 ml	LiOH	10 min	100 %
60 ^{o}C	150mg	150 ml	LiOH	7 min	100%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	LiOH	5 min	100%

4.12. Aluminum- Water Reaction in presence LiCl

It was tested on each aluminum sample but the results were not encouraging as compared to hydroxides under same conditions.

Table 4.34: Experiment Conditions (Al raw + LiCl)

Temp	Aluminum (Raw)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	LiCl	72 Hours	9%
50 ^{o}C	150mg	150 ml	LiCl	72 Hours	12%
60 ^{o}C	150mg	150 ml	LiCl	72 Hours	16%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	LiCl	6 Hours	18%

Table 4.35: Experiment Conditions (Al 30 µm + LiCl)

Temp	Aluminum (30 um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	LiCl	72 Hours	21%
50 ^{o}C	150mg	150 ml	LiCl	72 Hours	30%
60 ^{o}C	150mg	150 ml	LiCl	72 Hours	35%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	LiCl	6 Hours	41%

Table 4.36: Experiment Conditions (Al 20 µm + LiCl)

Temp	Aluminum (20um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	LiCl	72 Hours	40%
50 ^{o}C	150mg	150 ml	LiCl	72 Hours	45%
60 ^{o}C	150mg	150 ml	LiCl	72 Hours	50%

Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	LiCl	6 Hours	66%

Table 4.37: Experiment Conditions (Al 10 µm + LiCl)

Temp	Aluminum (10um)	Water (Degassed for ½ Hour)	Modifier (1:4)	Reaction Time	H_2 Yield %
40 ^{o}C	150mg	150 ml	LiCl	72 Hours	55%
50 ^{o}C	150mg	150 ml	LiCl	72 Hours	69%
60 ^{o}C	150mg	150 ml	LiCl	72 Hours	87%
Ultra Sonic Field (45 ^{o}C)	150mg	150 ml	LiCl	6 Hours	89%

Chapter 5: Results and Discussion

5. *In this chapter, the results so obtained will be discussed. The reaction will be discussed in stages: initial stage, induction stage, fast reaction stage and the final slow reaction stage.*

5.1. Reaction Explanation

5.1.1. Initial Stage

This stage starts when aluminum comes in contact with water. During this stage, the aluminum do not react with water due to presence of passive oxide layer present on aluminum which later on is removed by the modifier and ultrasonic effect. During this stage, the temperature of water also raises due to effect of ultrasonic field.

5.1.2. Induction Stage

This is the stage when the first bubble of hydrogen is produced and collected in measuring cylinder. During this stage, the aluminum layers starts to react with water and exothermic reaction takes place which increases the temperature of water present inside the vessel thus increasing the rate of reaction.

5.1.3. Fast Stage of Hydrogen Production

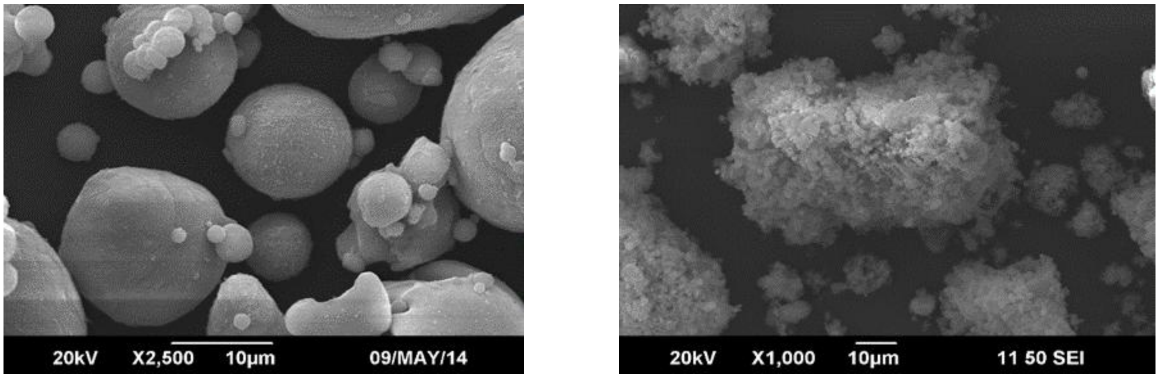
After the induction stage, a rapid production of hydrogen takes place due to two reasons. Firstly, the protective oxide layer is completely removed and all aluminum layers are in contact with water. Secondly, the exothermic effect so generated by aluminum-water reaction gives rise in temperature inside the vessel. Meanwhile the ultrasonic field also affects and does not allow formation of freshly produced aluminum oxide on aluminum particles. Hence a rapid reaction takes place inside the vessel after induction stage. This fast stage is the actual stage where most of the aluminum reacts with water

5.1.4. The Final Slow Stage

After the fast stage, a gradual slow stage is reached as most of the aluminum is consumed and negligible amount of aluminum so left is surrounded by aluminum oxide. This small amount will be remained unconsumed if the temperature range is below 45^{o}C.

5.2. Effect of Temperature and Ultra Sonic Field on Particle Morphology - Before and after Reaction

The most difficult part in generation of hydrogen from aluminum is its removal of passive oxide which come in contact as soon as aluminum is exposed in to atmosphere and presented on surface as smooth layer as shown in figure 5.1. It has been observed presence ultra-sonic field and temperature were very effective in removing desired layer and morphology of particles clearly depict an oxidation reaction took place on surface of particles as shown in figure 5.1. This can also be evident from the results that hydrogen yield increase as temperature increase / presence of ultra-sonic field as oxidation process enhanced.



(Before) **(After)**

Figure 5.1: Depicting effect of ultrasonic/temperature on 20 µm particles morphology before and after reaction

5.3. Effect of Ultra Sonic Field on Hydrogen Yield

As the experiments took under ultrasonic field they get separated from each other due to inherent capability of sonication waves and more surface area is exposed to reaction for oxidation process. This ultimately results in better yield/generation rates as shown in graph below (where absence of ultrasonic field is depicted by figure 0 and presence by figure 1)

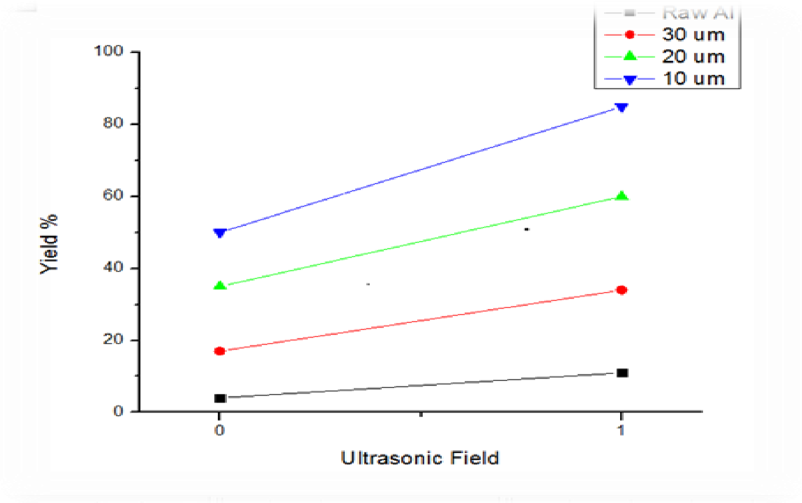


Figure 5.2: Effect of Ultra Sonic Field at Hydrogen Yield

5.4. Effect of Particle Size

Particle size has an inverse effect on hydrogen generation rate and yield. As the particle size is decreased the hydrogen generation rate increased and yield approaches nearly 100%. The reaction yield increased and almost doubled and reaction reached to stable state in less time when particle size was decreased. Which means small particle size favors maximum yield in less reaction time.

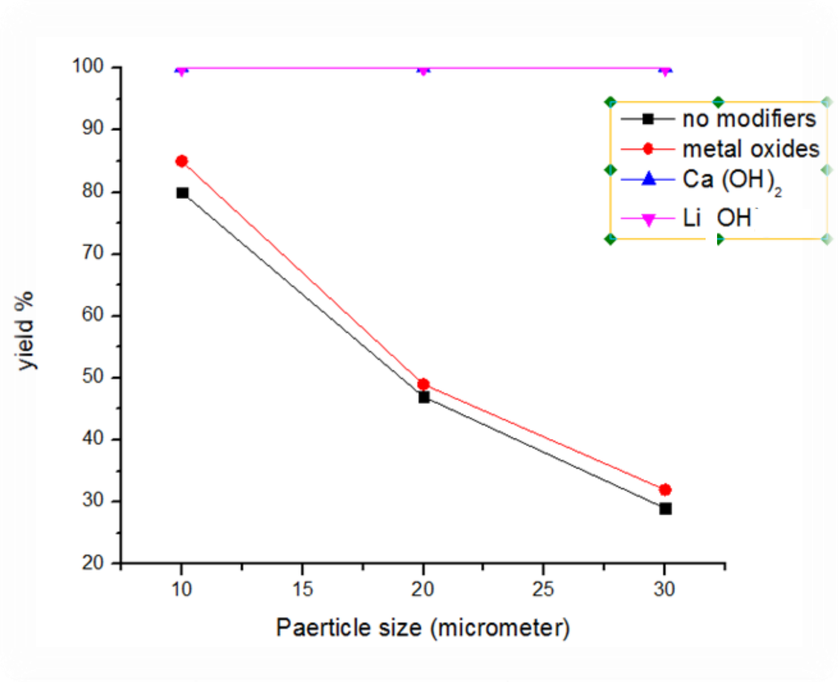


Figure 5.3: Effect of Particle Size at Hydrogen Yield at 60°C

5.5. Effect of Modifiers

The presence of modifiers in aluminum- water reaction has a positive effect on hydrogen production. The presence of metal oxides were remain ineffective as studied in literature primarily due to non-preprocessing. The presence of hydroxides has an enhanced impact on hydrogen generation and oxidation process of aluminum. The hydroxides reacts better then metal oxides/chlorides and helps in removing protective oxide layers so that fresh layer aluminum may come in contact with water. Calcium hydroxide proved to be more effective then lithium hydroxide in term of yield but better generation rate is achieved with later.

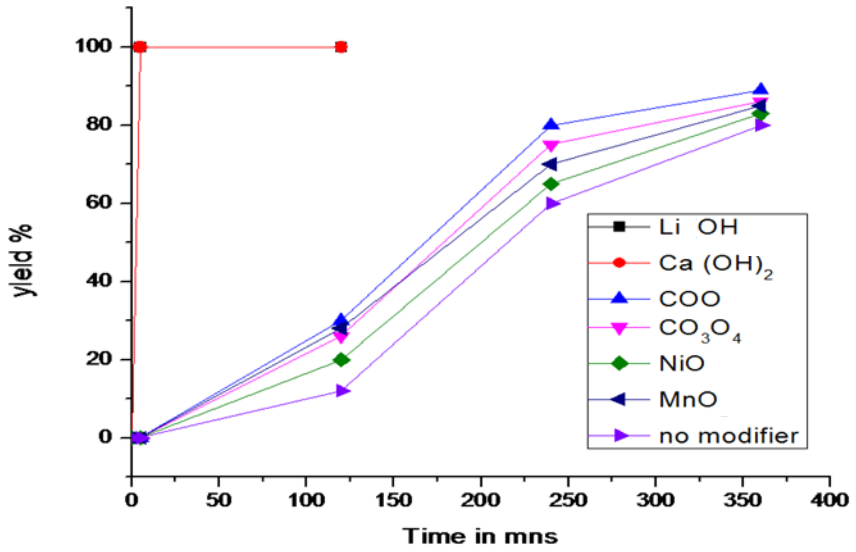
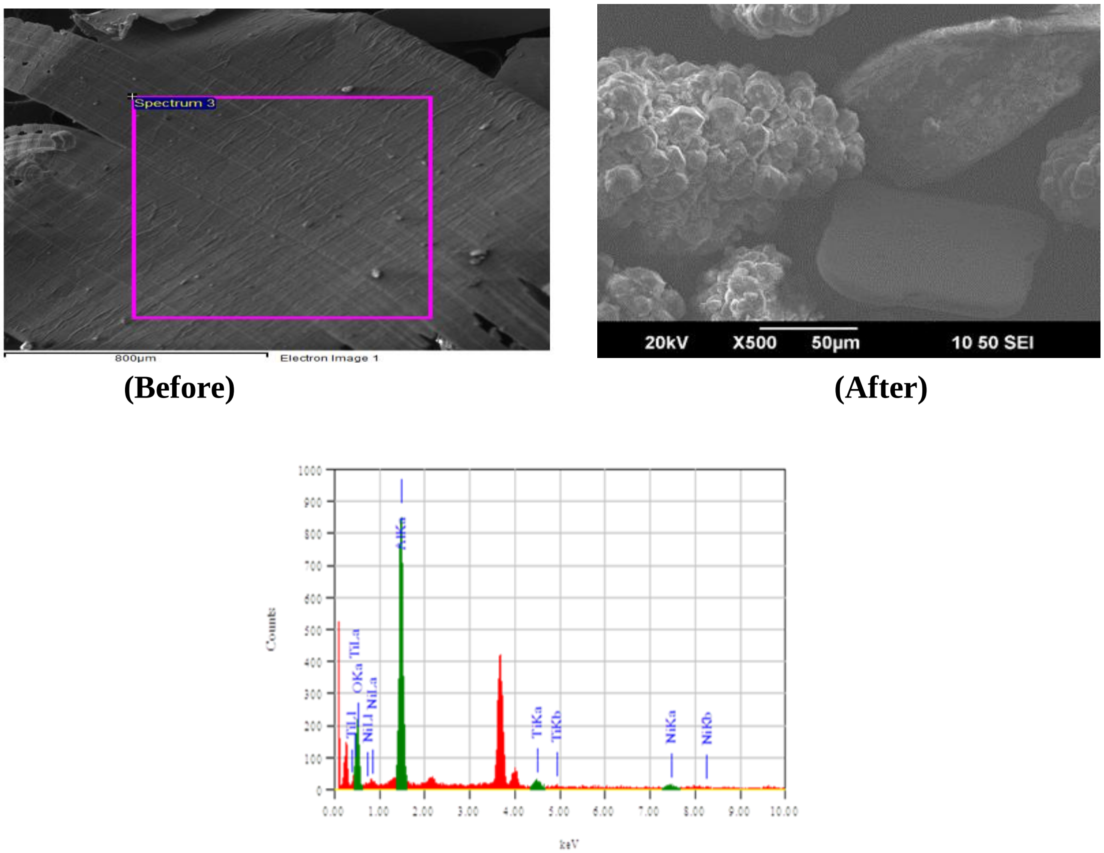


Figure 5.4: Effect of Modifiers on 10 µm at 45°C in ultrasonic field.

5.6. Characterization and Analysis of Reaction End products

5.6.1. SEM and EDS Results of Raw Aluminum Sample

The surface morphology and elemental analysis of raw aluminum and reaction end products was carried out on SEM (Figure 5.6) revealed that the surface of aluminum particles was smooth before the reaction and became porous and cracked during the oxidation process. They converted to irregular shaped small particles likely to be Al_2O_3 and Al $(OH)_3$ confirmed during XRD analysis. The oxidation process which took place during the reaction is also confirmed by EDS spectrum supporting oxidation reduction process.



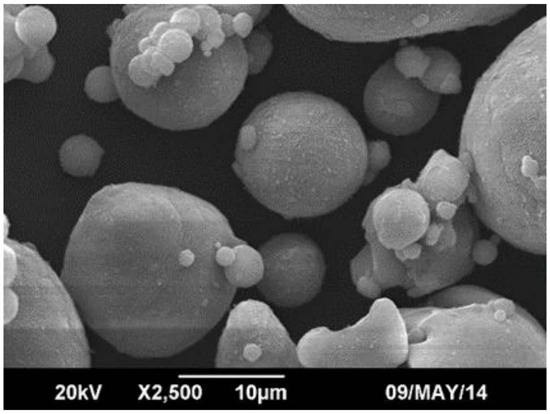
(Before) **(After)**

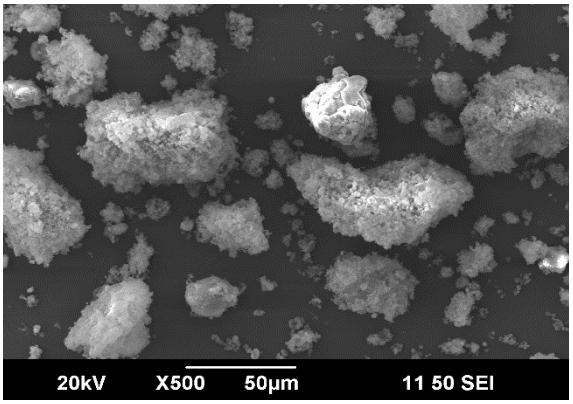
Figure 5.5: EDS Spectrum and SEM Images (Before and after reaction of Raw Al)

5.6.2. SEM and EDS Results of 30µm Aluminum Sample

In case 30µm aluminum powder and the spherical particles of aluminum sample either broke up into small pieces or changed shape due to re-crystallization under the influence of temperature and ultra-sonic effect. Where oxygen contents changed from 2% to 65% and similarly aluminum contents reduced to 21% from 94% confirms oxidation process.

BEFORE REACTION **AFTER REACTION**





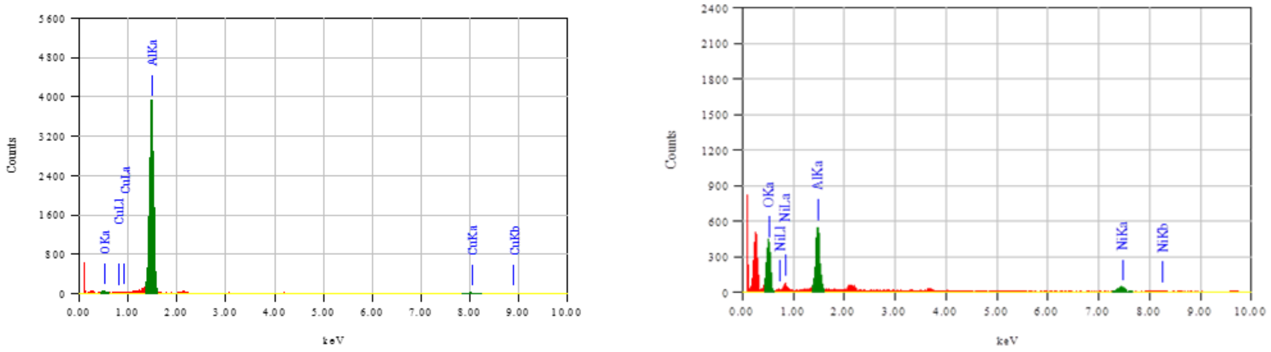
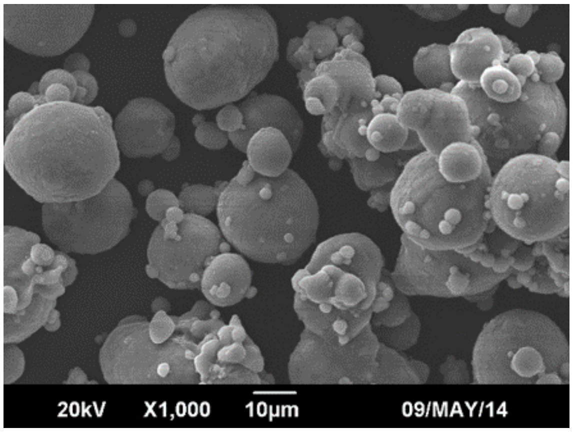


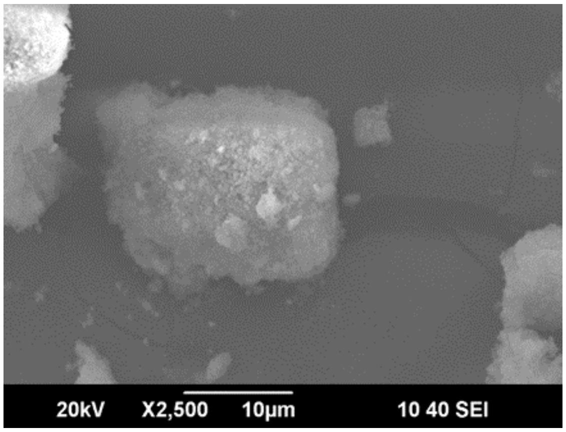
Figure 5.6: EDS Spectrum and SEM Images (Before and after reaction of 30 um)

5.6.3. SEM and EDS Results of 20µm Aluminum Sample

It revealed that the spherical particles of aluminum sample either broke up into small pieces, pits and cracks are clearly visible. The oxidation process which took place during the reaction is also confirmed by EDS spectrum where oxygen contents changed from 2% to 56% and similarly aluminum contents reduced to 30% from 95%.

BEFORE REACTION **AFTER REACTION**





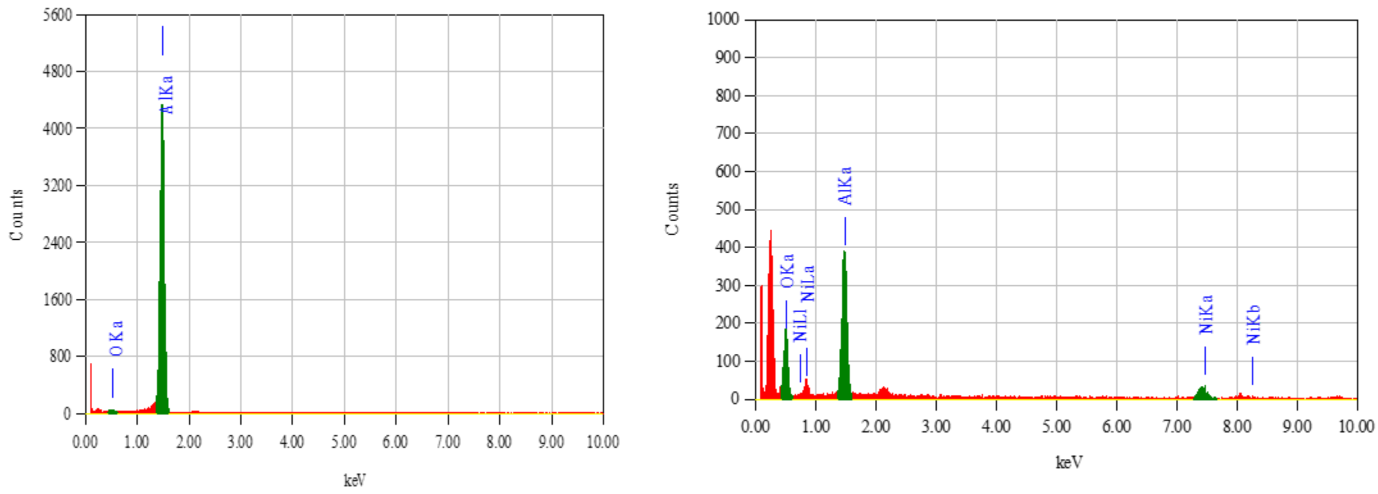
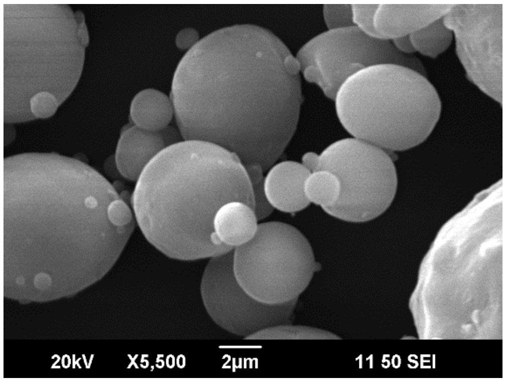


Figure 5.7: EDS Spectrum and SEM Images (Before and after reaction of 20 um)

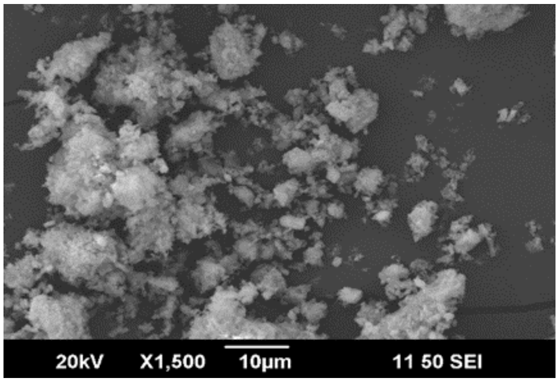
5.6.4. SEM and EDS Results of 10µm Aluminum Sample

The results were same as cracks and break up particles are also found again. The oxidation process which took place during the reaction is also confirmed by EDS spectrum where oxygen contents changed from 2% to 60% and similarly aluminum contents reduced to 14% from 97%.

BEFORE REACTION



AFTER REACTION



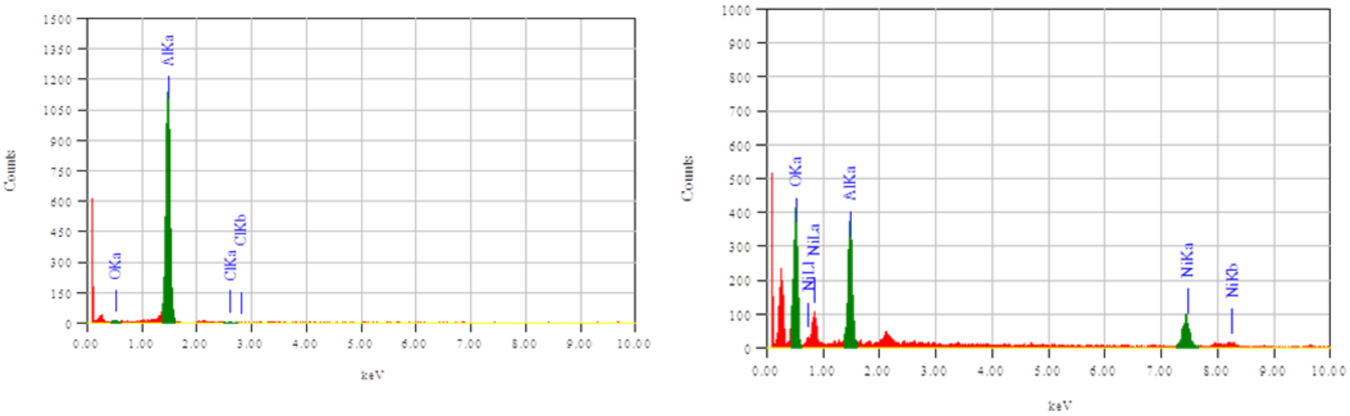


Figure 5.8: EDS Spectrum and SEM Images (Before and after reaction of 20 um)

5.7. XRD Analysis - End products of 10, 20, 30 µm and raw Aluminum Sample

Table 5.1: End products of 10,20,30 µm and raw Aluminum Sample

End Product	**Refference Code**	**Common Name**	**Chemical Formula**	**Crystal Structure**
10 um	01-077-0114	Aluminum Hydroxide	$Al(OH)_3$	Hexagonal
20 um	00-015-0136	Aluminum Hydroxide	$Al(OH)_3$	Hexagonal
30 um	00-015-0136	Aluminum Hydroxide	$Al(OH)_3$	Hexagonal

Raw Al	00-012-0401	Aluminum Hydroxide	Al (OH)$_3$	Monoclinic

5.7.1. Analysis of XRD Patterns

The XRD analysis of end products reveals that the mainly end products are forming during the aluminum water reaction which are Al (OH)$_3$ (Aluminum Hydroxide) which are confirming the reaction equation.

$$2Al + 3H_2O \rightarrow 2Al(OH)_3 + 3H_2$$

Moreover, the peaks of XRD analysis of all sample end products are similar according to peak positions but different in intensity of peaks. This is because of different morphology and particle size of end products.

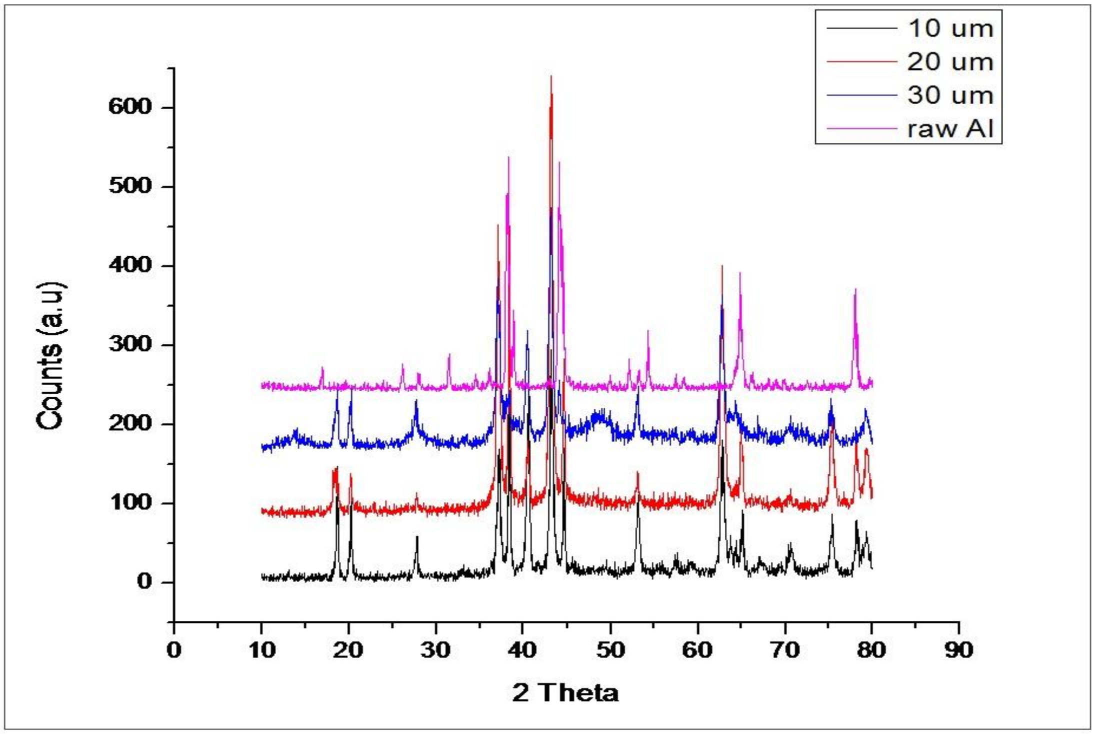


Figure 5.9: showing different morphology of end products

Chapter 6: Conclusions and Future Prospects

6. *This chapter explains the final outcome of the study and the further work which may be carried in future.*

6.1. Conclusions

- The presence of passive oxide layer on surface of Aluminum also known as alumina (Al_2O_3) is main cause of non-reactive behavior of Aluminum towards water.
- The reaction does not proceed on low temperatures till 35°C.
- Aluminum does react with water at temperature more than 35°C to produce hydrogen and the end products are alumina oxides and hydroxides.
- Modifiers play an important part in enhancement of hydrogen generation rate and yield like hydroxides, metal oxides, chlorides were effective.
- Conditions under which reaction take place has effective role in Aluminum water reaction as temperature and ultra-sonic field.
- Hydroxides immediately dissolve passive oxides layers on Aluminum surface in presence of temperature and ultrasonic field as well.
- Presence of ultrasonic field ensures 100% oxidation of aluminum in presence of modifiers.
- Aluminum oxide layers are detached from aluminum particle which changes the morphology of particles after oxidation process.
- Purity and small size of particles are better as compared to impure/large particles in high generation rate and yield in Aluminum water reaction.
- Chlorides and metal oxides without any pre-processing were not as effective as literature reviewed.
- Degassed water has positive effect on yield and generation rate.

- The end products of aluminum water reaction were Al $(OH)_3$ (Aluminum Hydroxide).
- Oxidation reduction process took placed confirmed by EDS.

6.2. Future Prospects

6.2.1. Hydrogen Storage

Hydrogen capturing and storage is considered as the most important aspect of hydrogen economy. Many materials are under study which may efficiently store hydrogen. To put hydrogen fuel system operative in daily life, hydrogen capturing, storage and transportation issues must be addressed thoroughly. In fact, without efficient and successful storage systems, a hydrogen economy will be hard to achieve [19, 20, 42, 43].

6.2.2. Integration of hydrogen in electricity generation sector

Presently the world is generating electricity from conventional methods in which chemical energy is converted to thermal energy then to mechanical energy and finally electricity is produced. In contrast to above, fuel cell is a fascinating technology which may convert chemical energy directly to electricity. Moreover, aluminum when reacts with water generates hydrogen and a considerable sum of heat that can generate a steam. Then the same steam along with hydrogen (by burning will generate more heat) can be used in turbine system to produce mechanical power [44-47].

6.2.3. Transport sector

Many analysts see hydrogen as future fuel due to its high efficiency, diminishing existing fossil fuels, environment concerns. Many developed countries has already made their long term and short term plans and implanting them in true spirit as well.

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