GRAPHENE BASED LOW COST CATALYST FOR HYDROGEN GENERATION BY HYDROLYSIS OF SODIUM BOROHYDRIDE SOLUTION

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Submitted By

CHINMOY BAG

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Thesis on

GRAPHENE BASED LOW COST CATALYST FOR HYDROGEN GENERATION BY HYDROLYSIS OF SODIUM BOROHYDRIDE SOLUTION.

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Master of Chemical Engineering

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This project report is submitted towards the completion of Master of Engineering Degree in Chemical Engineering

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Declaration of originality and compliance of academic ethics

I hereby declare that this thesis contains literature survey and original research Work by the undersigned candidate, as part of his "***Master of Chemical Engineering***" studies. All information in this report have been acquired and conferred in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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Thesis Title:
Graphene based low cost catalyst for hydrogen generation by hydrolysis of sodium borohydride solution.

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CERTIFICATE OF RECOMMENDATION

This is to certify that Mr. Chinmoy Bag , final year Master of Chemical Engineering (M.Che) examination student of Chemical Engineering Department , Jadavpur University, Examination Roll No. M4CHE1609 , Reg No. 128888 of 2014-2015, has completed the project work titled "GRAPHENE BASED LOW COST CATALYST FOR HYDROGEN GENERATION FROM HYDROLYSIS OF SODIUM BOROHYDIRDE SOLUTION" under the guidance of Prof. Kajari Kargupta during his Master Degree Curriculum. This work has not been reported earlier anywhere and can be approved for submission in partial fulfilment of the course work.

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ABSTRACT

Graphene bedded nano-composites are prepared to boost hydrogen generation from sodium borohydride solution and numerous assessments have been done to improve performance of nano-hybrids. Graphene is the only allotrope of carbon, which has 2-D crystalline morphology that in term helps it to have extensive surface area so its alacrity is superior and any metal particles like silver, cobalt etc can be hybridized easily on it. Current investigation recommends that hydrogen production from Sodium Borohydride using novel metal base graphene catalyst can boost hydrogen formation rate notably. Among hydrides, it has been observed that Sodium Borohydride ($NaBH_4$) has acquired much concentration for portable hydrogen storage and generation due to its environmentally altruistic nature. In addition $NaBH_4$ has tremendous hydrogen content (~10.8 wt%) and excellent hydrogen production rate even at normal temperature applying low cost catalyst recommend to consider it as marvellous hydrogen yielding material. In this generation procedure there is no emission of green house gases so this is an eco friendly process.

Two types of graphene based catalysts were synthesised. These are – (1) mono metallic catalyst and (2) bi-metallic catalyst. Graphene-Cobalt (G-Co), Graphene – Silver(G-Ag) are in category of monometallic catalyst and bi-metallic catalyst are — $G_{1.07}Co_1Ag_{1.3}$, $G_{5.8}Co_{1.22}Ag_1$, and $G_1Co_{1.58}Ag_{1.06}$. All these catalysts are characterised using XRD, HRTEM, SEM and BET to understand the structure and morphology of the composites. Experimental results show that hydrogen generation rate is magnificently improved in existence of bi metallic nano-hybrid. The experiment was performed in different temperatures for each catalyst and the rate of reaction can be computed from stoichiometry. This data will further assist to determine the rate constant and order of the reaction. During kinetic study by curve, fitting some equation is suggested to predict what kind of pathway is followed to complete the reaction.

CHAPTER- I

Introduction

1. INTRODUCTION:

1.1. ABOUT HYDROGEN:

Hydrogen is one of the most abundantly available components in earth, roughly 75% of all baryonic mass [1]. It is the lightest element in the planet. In periodic table it comes as first element with symbol H and its atomic no is one with an atomic weight of 1.00794 u [2]. The most common isotope of hydrogen, termed protium (^{1}H), has one proton and no neutrons. Since hydrogen forms covalent bond readily with most non-metallic elements, so most of the hydrogen on earth prevails in molecular forms such as water or organic compounds [3]. In ionic compounds, hydrogen can configure in the form of a negative charge (i.e., anion) denoted as OH^- or as a positively charged (i.e. cation) species denoted by the symbol H^+ . In STP hydrogen has these physical properties like colourless, tasteless, non-toxic, odourless and non-metallic. It is highly combustible diatomic gas. On burn in air it produces water and heat. As it, produces heat so it can be used as fuel.

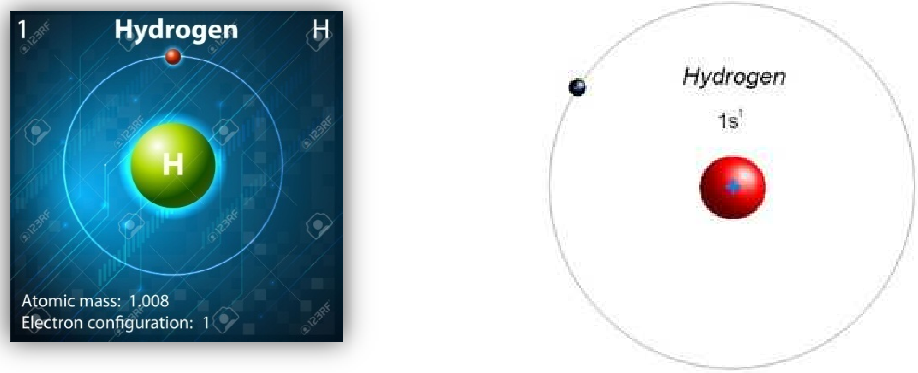


Figure 1: Molecular configuration of hydrogen

1.2. HYDROGEN AS FUEL:

Hydrogen is called as zero emission green fuel because on burn with oxygen it produces only water and release energy . Reaction is given below ---

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + 232\ KJ/mol$$ [4]

The above reaction is carried out either in electrochemical cell or internal combustion engine to power electrical devices or vehicles. In our planet hydrogen is locked up in the form of water, organic matter or in hydrocarbon so main challenge is to extract hydrogen efficiently from these compounds. Currently Hydrogen is mainly produced from steam reforming process[5] or by combining high temperature steam with natural gas. Electrolysis is the way of hydrogen production but this method needs huge energy so is not economical. Hydrogen can be used as renewable energy only when the effective hydrogen generation method can be developed.

1.3. ADVANTAGE OF HYDROGEN AS FUEL:

Many researches are going on all over the world to generate a clean, reliable and sustainable energy source. Hydrogen has the potential fulfil this demand and it is consider as the key solution for green energy. The main advantages of Hydrogen as fuel are ---

- During burning of Hydrogen ,no green house gas generate i.e. it does not pollute our environment so it is considered as green fuel.
- In planet source of hydrogen composite from where we can extract hydrogen is endless.
- It is very efficient fuel source than the traditional source of energy. Its calorific value (141790 KJ/Kg)[6] is higher than other fuel.

1.4. DIFFERENT METHODS FOR PRODUCTION OF HYDROGEN:

In present scenario hydrogen is produced largely by steam reforming technology for bulk production. It is recognized one of the most dominate method for direct production of hydrogen from hydrocarbon in industry. Other methods like electrolysis, thermolysis, photo catalytic water splitting, bio hydrogen routes and so on are also used to generate hydrogen .All these methods are described below—

- STEAM REFORMING:

In industry bulk hydrogen is produced mainly by steam reforming [7] of methane or natural gas. The efficiency of hydrogen generation from natural gas is approximately 80% and for other hydrocarbons it can vary from 30 to 65%. For the process, high temperature steam (700-1100 ^{o}c) reacts with methane in presence of nickel catalyst and produce syngas and hydrogen [8]. In second stage , low temperature steam 360 ^{o}c converts carbon monoxide into carbon dioxide and produce additional hydrogen. This reaction is known as water gas shift reaction. Commercial catalyst used for this reaction has been reported as 74.2% Fe_2O_3, 10.0% Cr_2O_3, 0.2% MgO (remaining percentage attributed to volatile components)[9]. Reactions are given below---

(i) $CH_4 + H_2O \rightarrow CO + 3\,H_2$ ----(high temperature reaction)
(ii) $CO + H_2O \rightarrow CO_2 + H_2$ -----(low temperature reaction)

- PLASMA REFORMING:

Plasma reforming is another good alternative method for hydrogen generation from liquid hydrocarbon (C_nH_m). Another name of plasma reforming is Kvaerner carbon black[10]. This process (CB & H) was developed in 1980 by a Norwegian company that help to produce hydrogen and carbon black from liquid hydrocarbon efficiently. Main advantage of this process is that carbon dioxide is not produced here . Among all the usable energy systems it is observed that the feed contains approximately 48% hydrogen and 40% is activated carbon and 10% in superheated steam.

ELECTROLYSIS:

Electrolysis is the process by which we can split water into oxygen and hydrogen using electricity[11]. The main disadvantage of this process is that it is very expensive but as we are getting hydrogen from water, which is readily available resource so the electrolysis method is gaining interest among scientists. There are three main types of cells named polymer electrolyte membrane cells (PEM), solid oxide electrolysis cells (SOECs), and alkaline electrolysis cells (AECs)[12].For high temperature electrolysis around 800 ^{o}c SOECs are needed. PEM cells are commercially used for low temperature electrolysis (below 100^{o}c). At present the best process of electrolysis has the efficiency of 50-80% that means for the production of 1 kg hydrogen (40 KWh/Kg) it requires 50-79 KWh electricity. Therefore, this process needs much modification for future application.

THERMO CHEMICAL CYCLE:

It is a process, which combines of both heat and chemical reaction to split water[13]. The chemical compound used in this process is continuously recycled so the term cycle is associated here. Sulphur-Iodine cycle(S-I cycle) is well known model of thermo chemical cycle which is almost 50% efficient. This method needs very high temperature approximately 950 ^{o}c and sulphur or iodine is not consumed by the process rather they are recycled. Another example of thermo chemical cycle is copper-chlorine cycle (Cu-Cl cycle) that comprises of four steps for production of hydrogen by water splitting with the help of chemical reaction around 530^{o}c temperature. The four reactions in the Cu–Cl cycle are listed as follows:

1. $2\ Cu + 2\ HCl(g) \rightarrow 2\ CuCl(l) + H_2(g)$ (430–475 °C)
2. $2\ CuCl_2 + H_2O(g) \rightarrow Cu_2OCl_2 + 2\ HCl(g)$ (400 °C)
3. $2\ Cu_2OCl_2 \rightarrow 4\ CuCl + O_2(g)$ (500 °C)
4. $2\ CuCl \rightarrow CuCl_2(aq) + Cu$ (ambient-temperature electrolysis)

Net reaction: $2\ H_2O \rightarrow 2\ H_2 + O_2$

BIOLOGICAL ROUTE:

Microbial electrolysis cell is a apparatus to produces potential difference with the help of bacteria. It is that device by which electro-hydrogenesis or dark fermentation can be performed to produce hydrogen biologically. Bio-catalysed electrolysis happens in presence of algae, reed sweet-grass, rice and tomato, which are acting like biocatalyst.

Similarly, we can generate hydrogen from wastewater or plant by microbial fuel cell. The waste plant parts are fermented and acetic acid is produced. Bacteria consume this acetic acid releasing protons, electrons, carbon dioxide etc. Protons pass through the ion exchange membrane and join with electron to produce hydrogen.

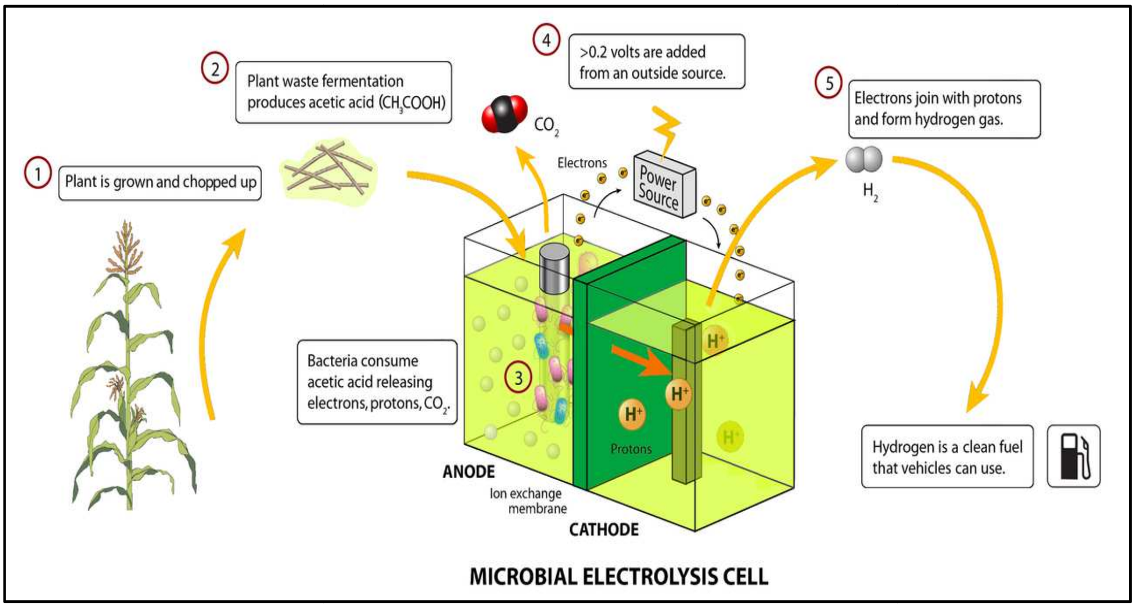


Figure 2: **Microbial Electrolysis Cell**[14]

1.5. HYDROGEN FROM HYDRIDES:

Hydrogen is recognized as one of the grater substitute of fossil fuel but it has some difficulties like storage and safety. Many researches are going on to overcome storage problem but still so far the report says that only 5 wt% Hydrogen storage can be done for fuel cell use which is very less .In current scenario various chemical hydrides have gained attention as an important alternative to reversible approach for on-demand Hydrogen generation. Among various metal hydrides, Sodium Borohydride is rich of Hydrogen and in water it releases hydrogen at normal temperature . This hydrogen generation rate can be increased significantly by using metal catalyst or even can be decreased by adding alkaline stabilizer. Therefore, it is very effective for on-demand hydrogen generation. Sodium borohydride based hydrolysis system has many advantages that help it to be used as portable hydrogen sources, including good reaction controllability, low temperature, safe fuel storability, no environmental pollution and no requirement of pre treatment to supply for PEMFC.

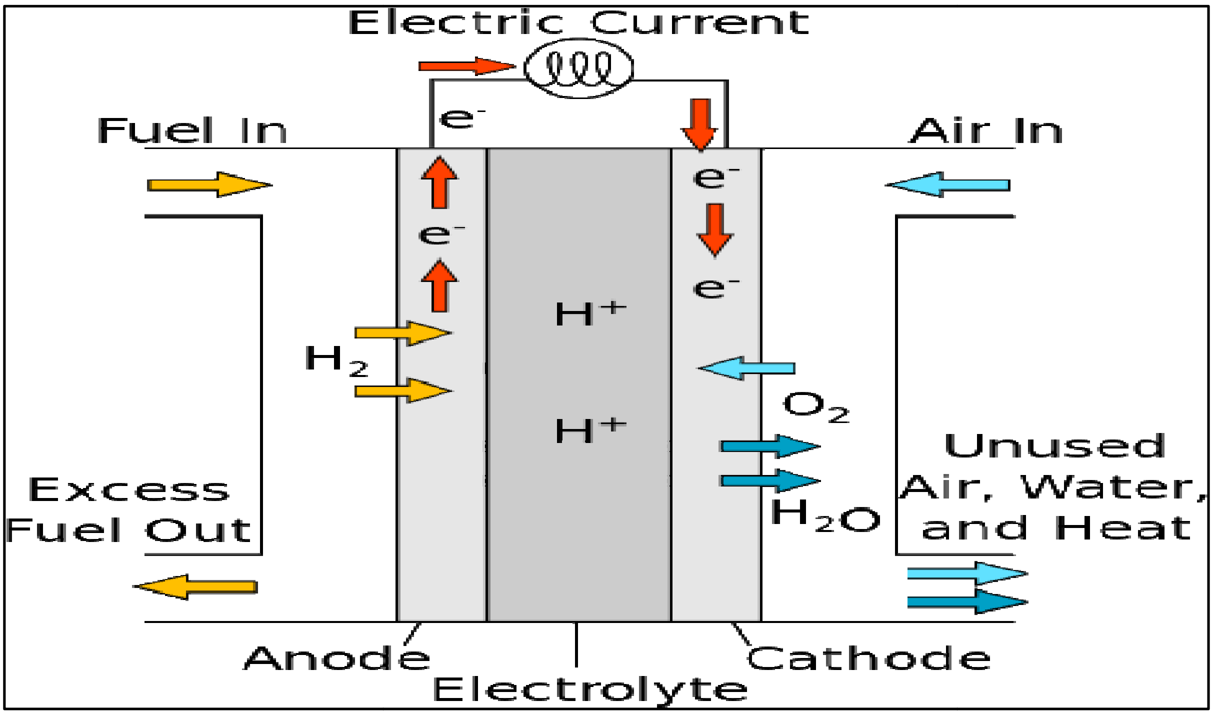


Figure 3: Application of hydrogen in PEMFC [15]

1.6. HYDROGEN GENERATION BY CHEMICAL REACTION:

The demand for green and clean energy is growing day by day and hydrogen has the potential to fulfil this demand so extensive researches have been going on to develop novel metal catalyst to improve the performance of hydrogen generation. After the invention of graphene, many metal catalysts have been prepared by impregnating in graphene sheet and the result improved. This successful change in catalyst is due to some excellent properties of graphene like large surface area (2630 m^2/g), high thermal conductivity (~5000W/m K),single layer of sp^2 hybridized carbon sheet[16].

In fuel cell reduced graphite oxide can be used as electrode due to its flexible structure and high conductivity. Study reveals that partial oxidation of graphite oxide with platinum helps to increase ECSA value. Another composite of Graphene with Cobalt or Silver is also an efficient catalyst for hydrogen generation from $NaBH_4$ solution. Instead of mono metallic catalyst if we use graphene based bi metallic nano composite for hydrogen formation the generation rate will increase further due to the increase of electron transfer pathways inside catalyst.

Schlesinger et al. [17] established that hydrolysis of one mole of $NaBH_4$ produces four moles of hydrogen gas and one mole of water-soluble Sodium meta borate ($NaBO_2$) with some exothermic reaction. The corresponding stoichiometric equation can be written as:

$$NaBH_4 + 2\,H_2O \xrightarrow[\text{50 c}]{\text{Catalyst}} NaBO_2 + 4H_2 + 210\text{ Kj}$$

1.7. NANOCOMPOSITES OF GRAPHENE:

As discussed in earlier section graphene has large surface area due to its 2-D structure compare to other allotropes of carbon so by impregnating different metal particles in it various nanohybrid of graphene is formed. This nanohybrid can be used as catalyst for hydrogen generation. Metal like cobalt, silver, platinum, nickel etc when bonded with graphene sheet show significant improvement in hydrogen generation rate. As the graphene is the main material for this project so let discuss about graphene in details ----

GRAPHENE:

Among different allotropes of Carbon like graphite, charcoal, carbon nanotubes and fullerenes, Graphene is the basic structural element whose atoms are bonded by hexagonal pattern in 2-D crystal. Like polycyclic aromatic chain of hydrocarbon, graphene is also considered as large aromatic hydrocarbon sheet [18]. The most attractive feature of graphene is that its reactivity. Due to 2-D structure, the end carbon atoms are available for reaction whereas for carbon nanotube or other allotropes of carbon this is not possible because of their 3-D structure. In 2013, scientists at Stanford University have reported that one-atom thick graphene sheets are hundred times more reactive than thicker sheets. Therefore, functionalisation of graphene sheet can be done easily.

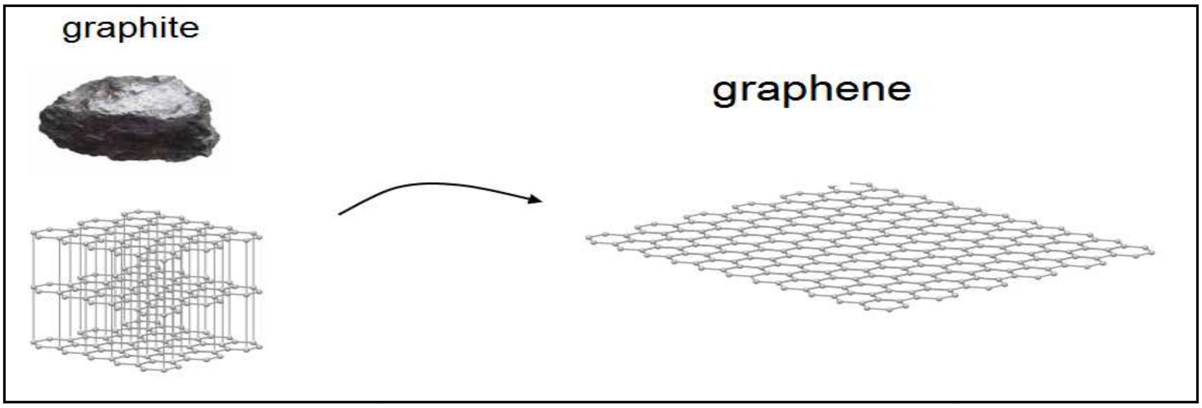


Figure 4: Graphene is an atomic-scale honeycomb lattice made of carbon atoms[19]

PROPERTIES OF GRAPHENE :

Structure: Graphene is a very stable material because of its tightly packed carbon atom. It has sp^2 hybridization – the orbits are s, p_x and p_y together form sigma bond and the final p_z electron is responsible for π-bonds which hybridize together to form π-band and π* band[20]. These bands are responsible for the half-filled band that permits free-moving electrons. Graphene can do self-adjustment of holes in its sheets, when resolved to molecules containing carbon, such as hydrocarbons and on bombarding with natural carbon molecules, the atoms entirely coordinate into hexagons by completely filling the holes.

Chemical: All the carbon atoms especially edge atoms of graphene are available for the chemical reaction as it has 2-D structure. Graphene has the maximum number of edge carbon atoms that can easily take part in any reaction. The onset temperature of reaction between the basic level of lone-layer graphene and oxygen gas is below 260 °C (530 K).[21] It burns at very low temperature [e.g. 350 °C or 620 K)]. It can be commonly modified with oxygen- and nitrogen-containing functional groups and resolved by infrared spectroscopy and X-ray spectroscopy. However, it is a critical task to determine the structures of graphene and requires well controlled reaction of oxygen and nitrogen functional groups on graphene sheet. In 2013, Stanford University physicists disclosed that single-layer graphene is chemically very reactive (almost 100 time) than thicker sheets graphite [22].

Electron transport : At normal temperature graphene has very high electron mobility as reported more than 15000 $cm^2 \cdot V^{-1} \cdot s^{-1}$[23]. More over from experimental measurement of conductance shows that the hole and electron mobility is almost same due to symmetry. Mobility does not depend on the temperature in between 10 K to 100 K, that proves dominant scattering mechanism has some defect. Uneven distribution by the acoustic phonons of graphene essentially reduces room temperature mobility to 200,000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ at a carrier density of 10^{12} cm^{-2}[24], which was later demonstrated and is 10 greater than copper. The resistivity of the graphene sheet at room temperature has been reported as 10^{-6} $\Omega\cdot\mathrm{cm}$ which is less than the resistivity of silver. However, on SiO_2 substrates uneven distribution of electrons by optical phonons have a larger repercussion than scattering by graphene's intrinsic phonons. This restricts the mobility to 40000 $\mathrm{cm}^2\cdot\mathrm{V}^{-1}\cdot\mathrm{s}^{-1}$.[25]

OXIDATION: Graphene is oxidized by concentrated sulfuric and phosphoric acid for the preparation of nanohybrid of metal. Due to oxidation oxygen containing functional group are attached to the 2-D aromatic scaffold of graphene. This graphite oxide has excellent properties to serve as catalyst for renewable energy resource. These sheets, called graphite oxide paper, have a measured tensile modulus of 32 GPa[26]. Catalyst of graphene is prepared by incorporating novel metal particles in it. Hub et al. discussed the electro catalytic activity toward the oxygen reduction and glucose oxidation of a graphene/Au nano ensemble that had a more advanced catalytic activity than Au nanoparticles or graphene alone. Liu et al. mentioned that the stretchable graphene nano-hybrid containing platinum nanoparticles that was synthesized via electrochemical reduction performed tremendous catalytic activity and showed well stability for the oxidation of methanol, which was considered to be used to improve electrical conductivity due to its high specific surface area .

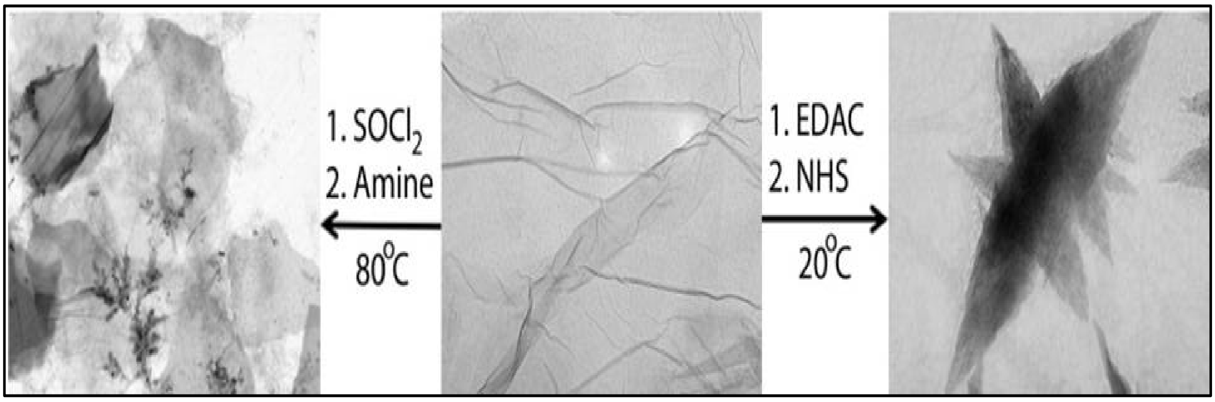


Figure 5: Image of single layer graphene oxide after heat and chemical treatment resulting in star like structure or sheet folding [27].

CHAPTER -II

Aim and Objective of the work

AIM AND OBJECTIVE OF THE WORK:

2.1. The main aim of the work is

1. Development of Bi-metallic Graphene based Catalyst to enhance Hydrogen generation from Sodium Borohydride ($NaBH_4$) and water reaction.

2.2 .The objectives of the work are –

1. Synthesis of Graphene sheet and characteristic study of the sheet.
2. Preparation of mono metallic catalyst – Graphene/Cobalt
3. Preparation of mono metallic catalyst – Graphene/Silver
4. Preparation of Bi metallic catalyst – Graphene/Cobalt/Silver
5. Characteristic analysis of these nano catalysts by XRD, HR-TEM, SEM and BET.
6. Hydrogen generation from Water and $NaBH_4$ using the prepared Catalysts.
7. Study of the reaction rate kinetics and activation energy

CHAPTER III

Literature Review

LITERATURE REVIEW :

3.1. INTRODUCTION :

It is very important to study various literature before go into the experimental work as this will make experimental work smooth by determining some significant parameters in the field of our experiment. To get the information about experiment many journal had been studied and indentified some important features, which may have some significant effect on the performance of those catalyst for hydrogen generation , various journals that are conducted all over the world in last few years have been studied. Few of these are given below---

JOURNAL NAME	GENERATION METHOD	EXTRACT
1. International journal o f hydrogen energy 4 0(2015)176 0e1773	Improved hydrogen production from sodium borohydride solution using graphene-supported Co-Ni as catalysts.	1. The electrocatalytic activity of the manufactured catalysts towards the oxidation of BH_4^- ions was investigated by two analytical methods namely linear sweep voltammetry (LSV) and cyclic voltammetry (CV) . 2. Among the different electro-catalysts G-Co-Ni (~4.5:1:1 weight ratio) gives the maximum value of electro active surface area (ESA ¼ 518.6 m^2/gm). G-Co-Ni reveals enhanced mass specific activity (msa: 750-900 A g^{-1}) favouring the direct oxidation of BH_4^- ions and oxidation of H_2 generated by catalytic hydrolysis of BH_4^- ions comparing with G-Ni (msa: 130-160 A g^{-1}) and G-Co (msa: 120-130 A g^{-1}) catalysts.

2. Fuel Processing Technology 92 (2011) 1606–1610	Hydrogen generation by hydrolysis of KBH_4 using carbon supported Ni–B, Co–B and Co–Ni–B catalysts.	1. Impregnation of commercial activated carbon in cobalt and/or nickel salt solution is the method for the synthesis of Ni–B, Co–B and Co–Ni–B catalysts supported by activated carbon(AC) in different Co/Ni mass ratios and later on reduction of metal salts by sodium borohydride at room temperature. 2. Co–B/AC has tremendous potential as active catalytic among Ni–B/AC, Co–B/AC and Co–Ni–B/AC catalysts. It is seen for bimetallic boride catalysts supported by activated carbon show high catalytic activity with the increase of Co/Ni mass ratio.
3. Journal of Alloys and Compounds 509 (2011) 7016–7021	Hydrolysis of alkaline sodium borohydride solution by Cobalt–nickel–phosphorus supported on Pd-activated TiO_2 (Co–Ni–P/Pd-TiO_2) is one of the cost-effective process for hydrogen generation.	1. Electro less impeachment was considered one of the most promising method for catalyst preparation . The Co–Ni–P particle which did not cotain electron was deposited on Pd-coated TiO_2 . 2.SEM along with EDX shows agglomerated particle like morphology in which primary particles size is in the range of 20 to 30 nm. 3. This catalyst has excellent reusable property, 86.4% of its initial catalytic activity even at fifth run.

4. Fuel 90 (2011) 1919–1926	Hydrogen generation from sodium borohydride fuel by Co and clay-based supported catalysts.	1. Catalyst was developed by Co- and clay. Three raw clays were taken from soil in Lebanon. Once purified and annealed, they could be a good supports for catalyst. It had been analysed that kaolinite and illite were the main composites which showed to be promising catalyst due to their sizable specific surface areas (58.0 and 67.1 m^{2} /g) and also for the high reactivity of the 15 wt.% Co catalysts (i.e .$NaBH_4$ conversions of 100% and hydrogen generation rates up to 31 L (H_2) min^{-1} g^{-1}(Co). 2. Raw clays from the Lebanon's soil are taken and purified. Among others, 15 wt.% Co–BC and 15 wt.% Co–RC are prepared by impeachment of metal salts by chemical reduction method. Both entirely converted to SB at 60–80^{o}C and HGRs is measured upto 31 lit (H_2) min^{-1} g^{-1}(Co) .

5. Catalysis Today 170 (2011) 33–39	Ni–Co–B catalyst advanced hydrogen production by hydrolyzing $NaBH_4$ solution for in situ supply of hydrogen to the portable fuel cells	1.Catalyst was prepared by two-step technique. First of all, chemical reduction was carried out to synthesise the precursors and in second step, heat treatment was done to adjust crystalline structure. 2.XPS analysis indicates multiplex metal borides have high catalytic activities in compare to simple mixture of Ni–B and Co–B . 3.At 400 ^{o}c temperature this catalyst can generate 708 ml/ min/ gm catalyst so hydrogen can be supplied for a 115 W portable PEMFC continuously.
6. International journal o f hydrogen energy 3 4 (2 0 0 9) 2 8 9 3 – 2 9 0 0	hydrogen is generated by hydrolysis of alkaline solution of $NaBH_4$ with the help of Co–Ni–P–B catalyst	1.Tetra metallic catalyst Co-Ni-P-B was prepared by chemical reduction of nickel and cobalt salt .Due to synergic effect caused by each chemical element this catalyst was giving the highest activity for H_2 generation. Activation energy of this catalyst was reported as 29 kj/mol. 2.Role of metalloids(P and B) was investigated by varying B/P molar ratio keeping Co/(Co+Ni) molar ratio constant at 0.85. With the increase of B/P ratio H_2 generation rate also increase but after a certain value of B/P ratio (2.5) H_2 generation rate starts to fall.

7. Journal of Colloid and Interface Science xxx (2012) xxx–xxx	Hydrogen is generated in controlled way from hydrogen storage material ($NaBH_4$) using efficient catalyst.	1.Hydroxyapatite (HAP) with cobalt ion is considered as novel, durable and inexpensive catalytic support material. Crystal HAP in comparison with amorphous gives better hydrogen generation rate. 2.H_2 generation rate significantly increased for Co immobilized single crystal HAP supports as compared to amorphous and calcium deficient HAP supports.
8. International journal of hydrogen energy 37(2012)1014e 1020	Hydrogen formation by hydrolysis of Al-Li-Bi-NaCl mixture with pure water. $Al + 3H_2O \rightarrow Al(OH)_3 + 3/2\ H_2$ $2Al + 4H_2O \rightarrow 2AlOOH + 3H_2$	1. Al-Bi-Li mixtures were processed by a milling method, using sodium chloride salt as the milling-assisted agent . On the other hand Li has capability to improve the hydrolysis rate significantly for Al-based mixtures by forming $BiLi_3$ and AlLi phase during milling process. Al based mixture containing 3 wt% Li shows higher hydrogen generation rate.

9. Journal of Power Sources 219 (2012) 60e64	Development of Mg-Al mechanical alloy material for hydrogen production from seawater. $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$ $2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$	1. Hydro reactive Mg-Al mechanical alloy has been produced by milling technique that required very high energy. 2.For 4 hrs of milling hydrogen generation rate form hydrolysis of sea water reaches to 397 ml/min/gm. Total hydrogen generation is 97.1% of the theoretical yield. 3.Milled Mg-Al material has lower starting oxidation temperature than unmilled Mg-Al blend.
10. Energy 38 (2012) 205e211	Hydrogen preparation from hydrolysis of MNH_2BH_3 and NH_3BH_3/MH (M= Li, Na) for fuel cells based unmanned submarine vehicles application.	1. Hydrogen generation rate of LiH/AB and NaH/AB by hydrolysis are 1.8 and 1.7 equiv. respectively, lower than those of $LiNH_2BH_3$ and $NaNH_2BH_3$ hydrolysis (3 equiv.) and lower than the theoretical maximum values of LiH/AB and NaH/AB (4 equiv.) 2. Mechanism of $LiNH_2BH_3$ and $NaNH_2BH_3$ hydrolysis is the combination of H^+ and OH^- ions of water with the polarized $LiNH_2BH_3$ or $NaNH_2BH_3$ molecules.

3.2. STUDY OF CHARACTERIZATION METHODS:

3.2.1. X-RAY Diffraction (XRD):

X-ray diffraction (XRD)[28] is a powerful analytical device used to determine unknown crystalline materials as well as unit cell dimension. Many properties of solid like magnetic, ferromagnetic, optical, electrical etc depend on the crystalline structure of the material. Therefore crystalline of a material plays an important role for characterization study . Besides this , some solids are found to form by many crystallites or grains of varying size and are termed as polycrystalline. It is founded many inorganic solids are polycrystalline along with most common metals, many ceramics, rocks and ice. Arbitrary diffraction lines are observed during XRD of polycrystalline material due to random orientation of grains. The interaction of the incident rays with the sample may produces constructive interference or a diffracted ray depending on the conditions and this can be determined by Bragg's Law ($n\lambda=2d \sin \theta$)[29].This law developes the relation between wave length of electromagnetic radiation to the diffraction angel and the lattice spacing in crystalline sample. These diffracted X-rays are detected; processed and computed .All possible diffraction directions of the lattice should be evaluated by scanning the sample in the range of 2θ angles as the powdered material has random orientation. Conversion of the diffraction peaks to d-spacing endorses to get identification of the mineral because each mineral has a unique set of d-spacing. So identification of mineral present in sample is accomplished by comparing the d-spacing with the standard reference patterns.

Strength of XRD : Some advantages of XRD are given below –

- It is a very rapid (< 20 min) technique to identify unknown mineral.
- Ambiguity is not a problem for determination of unknown material.
- Sample preparation is not a difficult task for XRD.
- Each individual substance has unique diffraction pattern so data interpretation is comparatively easier.

3.2.2. HR- Transmission Electron Microscopy (HRTEM):

High resolution transmission electron microscopy[30] is powerful tool to analyse material properties in atomic level. At present, the highest point resolution achievable in phase contrast TEM is around 0.5 A^{o}[31]. At this microscopic level individual atoms of a crystal and its defaults can be analysed effectively. For 3D mapping several views ,taken from different angels have been combined to get 3D image. This technique is called as electron crystallography. In case of TEM a beam of electrons is allowed to interact with the ultra thin specimen as it transmits through it, which results in a formation of image. This image is magnified and focused onto an imaging device such as fluorescent screen or photographic film layer and it can be identified by a sensor such as a CCD camera. TEM is capable to give very high resolution image (about 1000 times) compare to light microscope as the electrons exhibits short de Broglie wave length. This empowers the user of instrument to analyse every minute detail—even at a very small scale like single column of atoms, which in the comparison of the smallest resolvable object in a light microscope is thousands times smaller. TEM plays a major role in scientific fields like physics, chemistry , biology and in cancer research. Others important sectors like virology, materials science, environmental and pollution control, nanotechnology and semiconductor technology where TEM is associated with dignity.

At smaller magnifications, it is observed that TEM image is not vivid due to absorption of electrons in the material which has large thickness .At higher magnifications, complex wave interactions modulates the intensity of the image and for the analysis of images a proficient person is needed. Alternate modes of use allow the TEM to observe intonation in chemical character, crystal orientation, electronic structure and permits to take image of sample by inducing electron phase shift or by regular absorption of electron.

3.2.3. Scanning Electron Microscope (SEM):

Scanning Electron Microscope is one type electron microscope by which surface topology and every ingridints of a sample can be analysed. A focused beam of electrons scans the sample and produced SEM image of resolution higher than 1nm[32]. Specimens can be examined in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and in a large range of cryogenic or exalted temperatures. It is observed that the maximum used SEM mode is detection of secondary electrons coming from atoms due to excitation by the electron beam. The fraction of secondary electrons that can be detected depends upon the angle at which beam scatters on the surface of specimen, i.e. on specimen topography. By scanning the sample and detecting the secondary electrons that are emitted from specimen, using a special detector and an image of surface topography can be viewed in display.

SEM can produce variety of signals including secondary electrons (SE), reflected or back scattered electrons (BSE), electron from X-rays for characteristic and light cathode luminescence (CL), current absorption(specimen current) and transmission of electrons. Secondary electron detectors are thought to be as basic equipment in every SEMs, but it is still a subject of improvement that a single machine would have detectors for all other possible signals[33]. Specimen must be electrically conductive at surface and be electrically grounded to stop the build up of electrostatic charge at surface. An interesting scheme has been adopted for nonconductive specimen. An ultrathin layer on the above surface of specimen, made of electrically conducting material by low-vacuum sputter coating or by high-vacuum evaporation. Currently for specimen coating metals is used like Au, Au/Pd alloy, Platinum, osmium, tungsten, iridium, chromium, and graphite. Additionally, coating given by heavy metals helps to increase signal/noise ratio for samples of low atomic number (Z). The improvement in SEM image arises for heavy metals coating due to enhancement in the emission of secondary electron for high-Z materials.

3.2.4. Bruner-Emmet-Taller (BET) Analysis:

BET analysis serves as an important analysis technique to determine specific surface area of any sample. Specific surface area of the powder sample can be measured by physical adsorption of a gas (non corrosive gases like Nitrogen, Argon, and carbon dioxide) on the surface of the solid and by calculating the amount of adsorbate gas corresponding to the monomolecular layer on the surface. Weak Van der waals force between adsorbate gas molecules and adsorbent surface area of test powder is the main reason for physical adsorption. The experiment is usually carried out at temperature of liquid nitrogen. Adsorbed gas amount is measured by volumetric or continuous flow procedure.

BET theory[34] is an extension of Langmuir theory[35] from monolayer adsorption to multi layer adsorption with the following hypothesis-

- Physisorption occurs infinite layer on the solid surface.
- There is no interaction between each adsorption layer.
- Langmuir theory is applicable to each layer.

The data are treated according to the BET adsorption isotherm equation -

$$\frac{1}{v\left[(p_0/p)-1\right]} = \frac{c-1}{v_{\mathrm{m}}c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}, \qquad (1)$$

Where

p and p_o denote the equilibrium and the saturation pressure of adsorbents respectively at the temperature of adsorption.

v symbolized the adsorbed gas quantity,

v_{m} stands for the monolayer adsorbed gas quantity

c indicates the BET constant.

$$c = \exp\left(\frac{E_1 - E_{\mathrm{L}}}{RT}\right), \qquad (2)$$

Where, E_1 stands for the heat of adsorption for the first layer, and E_L symbolizes for the second and higher layers adsorption and the value of E_L is almost equal to that of heat of liquefaction.

Equation (1) gives an adsorption isotherm[36] and can be plotted as a straight line with $1/ v[(p/p_o)-1]$ on the y-axis and $\varphi = p/p_o$ on the x-axis. This plot is visualized as BET graph. The above equation is a straight line equation but the linearity of this equation holds only in the range of $0.05<p/p_o<0.35$. Calculation of adsorbed gas quantity for monolayer indicated as v_m and the BET constant c can be easily figured out from slope A and intercept I values. The following equations can be used:

$$v_m = \frac{1}{A+I} \qquad (3)$$

$$c = 1 + \frac{A}{I}. \qquad (4)$$

The BET method is extensively used in surface science for the determination of surface areas in solids by physical adsorption of gas molecules with specified temperature and pressure. The total surface area symbolized by S_{total} and the specific surface area is denoted by S_{BET} and the corresponding equation can be given as:

$$S_{\text{total}} = \frac{(v_{\text{m}} N s)}{V}, \qquad (5)$$

$$S_{\text{BET}} = \frac{S_{\text{total}}}{a}, \qquad (6)$$

Where, v_m denotes the molar volume of the adsorbate gas, N is well known Avogadro's number, **s** indicates the cross sectional area of the adsorbent, V symbolizes the molar volume of the adsorbate gas, and a is the mass of the solid sample or adsorbent.

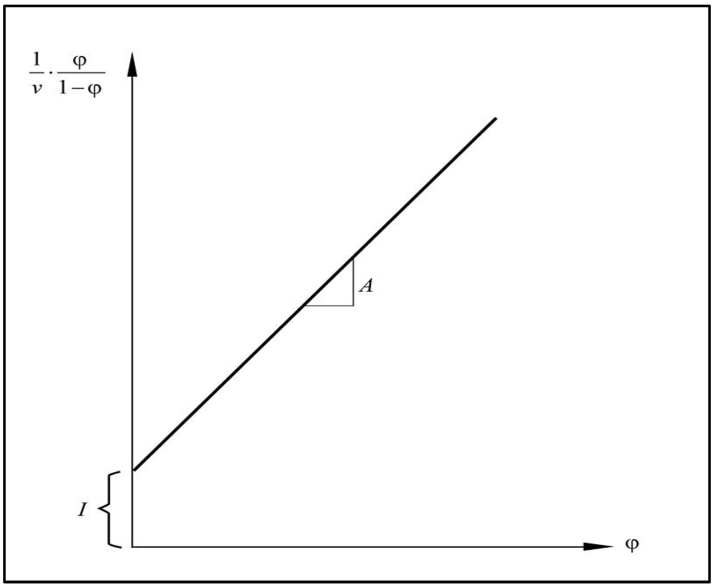


Figure 6: BET plot[37]

CHAPTER IV

Experimental Work

4.1. **INGREDIENTS AND GENERATION METHODS:**

4.1.1. **HYDROGEN GENERATION**:

There are multifarious methods to originate hydrogen like electrolysis of water, photo electro chemical water splitting, bio catalysed electrolysis, biological production and so on. Chemical itinerary of hydrogen generation from hydrolysis of Sodium Borohydride ($NaBH_4$) is considered one of the most persuasive and prudent method compare to the above mentioned methods as $NaBH_4$ contains high percentage of hydrogen (10.8 wt%) and yield immense hydrogen when hydrolysed. The reaction is given below –

$$NaBH_4 + (2+x)H_2O \xrightarrow{catalyst} NaBO_2 .xH_2O + 4H_2 \uparrow + 210\ Kj$$

The above presented catalytic reaction is carried out in a 50 ml cylindrical reactor where required amount of $NaBH_4$ (0.568 gm) and catalyst (30 mg) are preloaded .Then 10 ml water is added from top mouth of the reactor and the reactor is placed on the water bath where the desire temperature (60 ^oC) is to be maintained. As soon as sodium borohydride and catalyst mixture are exposed to water hydrogen formation will kickoff. The generated hydrogen is acceded to pass through silica drier to absorb water vapour if any and finally is collected in marked cylindrical vessel by water displacement method. During water deracination, the reading is taken with respect to time vs. volume, from which we can derive hydrogen generation rate. First experiment is done in absence of catalyst then monometallic catalyst and finally bi-metallic catalyst are used in distinctive temperature for each catalyst. From these three experimental results it can be easily evaluated in which case hydrogen generation rate is the fastest and the reading indicates bi metallic catalyst shows highest hydrogen generation rate.

The experimental set up is demonstrated below --

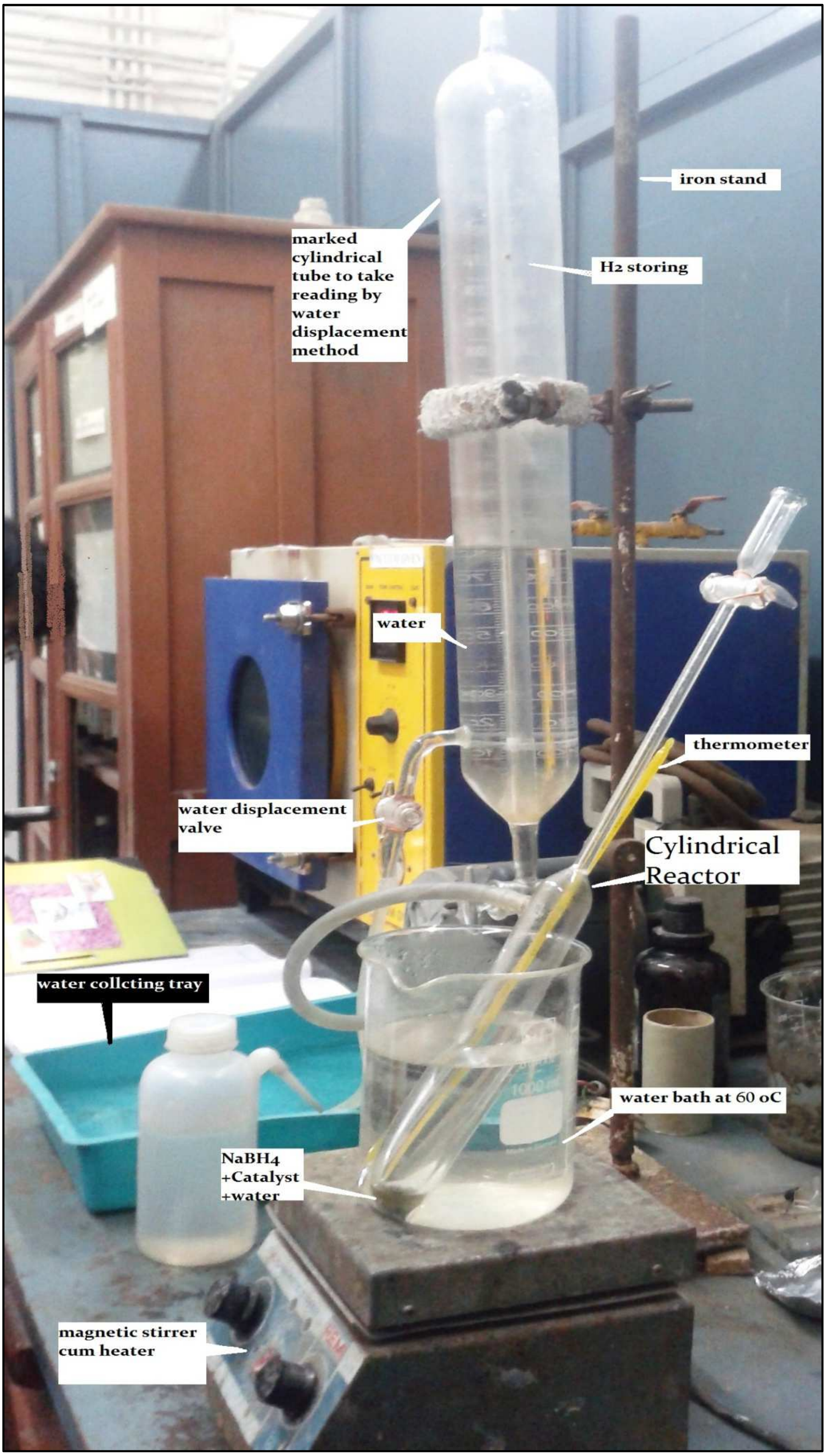


Figure 7: Lab scale experimental set up for H_2 generation from $NaBH_4$ solution

4.1.2. GRAPHITE OXIDE :

MATERIALS REQUIRED :

1. Graphite flakes –(Luba Cheme, extra pure 99.5% , 50 µm avg sizes, bulk density 20-30 gm/100 ml).
2. Sulphuric Acid(H_2SO_4)-(MERCK,98% concentration, density 1.84 Kg/lit)
3. Phosphoric Acid (H_3PO_4)- (MERCK,88% concentration ,density-1.75 Kg/lit)
4. Potassium Permanganate (KMnO$_4$)-(MERCK,99% purity)
5. Hydrogen Peroxide(H_2O_2)-(MERCK, 30% concentration)
6. Hydrochloric Acid(HCl)-(MERCK-35% concentration, density 1.18 Kg/lit)
7. Ethanol(C_2H_5OH)-(MERCK,99.9% purity,density 0.79 Kg/lit)
8. Distilled water

PREPARATION OF GRAPHITE OXIDE :

There are mainly three techniques available to synthesise graphite oxide like

1. Hummer's method[38]
2. Modified Hummer's Method
3. Improved Hummer's Method

Out of these three methods the latest, one i.e. Improved Hummer's Method is the best as it gives good quality Graphite oxide.

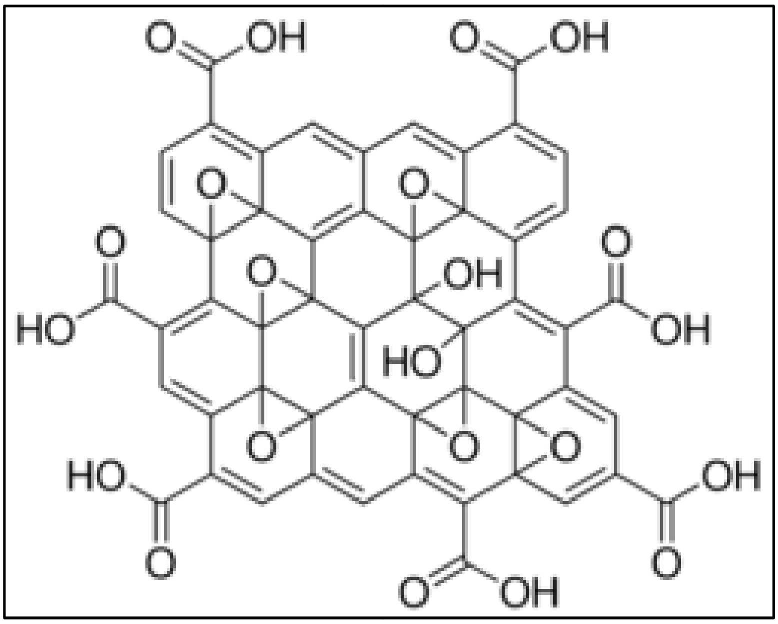


Figure 8:A model of graphite oxide[39]

IMPROVED HUMMER’S METHOD [40]:

This is the fastest conventional method of producing Graphite Oxide maintaining the high C/O ratio. The steps involved in this method are—

1. In a one litter biker, sulphuric acid[H_2SO_4 (98%)] 360 ml and phosphoric acid [H_3PO_4 (88%)] 40 ml i.e. in 9:1 ratio are taken.
2. Now Graphite powder is mixed into the acid mixture and whirled it for 15 min by magnetic stirrer (RPM = 450-500).
3. Then 18 gm Potassium permanganate ($KMnO_4$) is added very slowly(5min to add) to the above mixture with stirring. It is an exothermic reaction so temperature suddenly increased to 60^oC. Therefore, addition of $KMnO_4$ is done very cautiously with appropriate cooling arrangement.
4. After addition, just stirred the mixture for 15 min and kept temperature around 60^o c . When temperature starts to fall below 50^oC than heating should be provided to maintain the mixture temperature around 55-60 ^oC for 7-8 hrs.
5. After complete maintained of temperature, 400 ml cold water(10-15^oc) is added into the reaction mixture .
6. Then 6 ml Hydrogen Peroxide (H_2O_2) is added and the mixture is kept on ice bath overnight.
7. Next day yellowish, GO settled down. The above clear solvent is discarding slowly by siphon.
8. Then to wash the GO slurry 400 ml Hydrochloric Acid solution (3:1:1 vol ratio) added and kept the mixture for GO settle down.
9. After three hrs when GO settles down above clear liquid is discarded by siphon.
10. Again 400 ml distil water is added to the mixture and kept 4 hr
11. After 4 hr again above clear liquid is discarded and thick GO slurry is collected.

12. Then filtration is done by filter paper.
13. Finally, the wet GO is scarped from filter paper and keep in Vacuum Oven drier at 90^{o}c for 4 hrs.
14. Thus, the dried GO is collected and kept in sample bottle.

Pictorial view of all the steps are given below –

Fig 1: potassium permanganate

Fig 2: stirring of acid mixture, $KMnO_4$ & graphite powder

Fig 3: after completion of reaction

Fig 4: after overnight sedimentation

Fig 5: filtration of slurry GO

Fig 6: vacuum dried GO

4.1.3. PREPARATION OF G-Ag MONO METALLIC CATALYST:

Graphene-Silver (G-Ag) catalyst has the great potential to generate Hydrogen effectively and economically. Many researchers have tried to produce graphene based silver catalyst in different processes but the POLYOL method[41] seems to be simple and easier way.

MATERIALS USED:

1. Graphite Oxide (produced earlier)
2. Ethylene Glycol [$C_2H_4(OH)_2$]
3. Silver Nitrate [$AgNO_3$]
4. Sodium Borohydride [$NaBH_4$]
5. Distil water

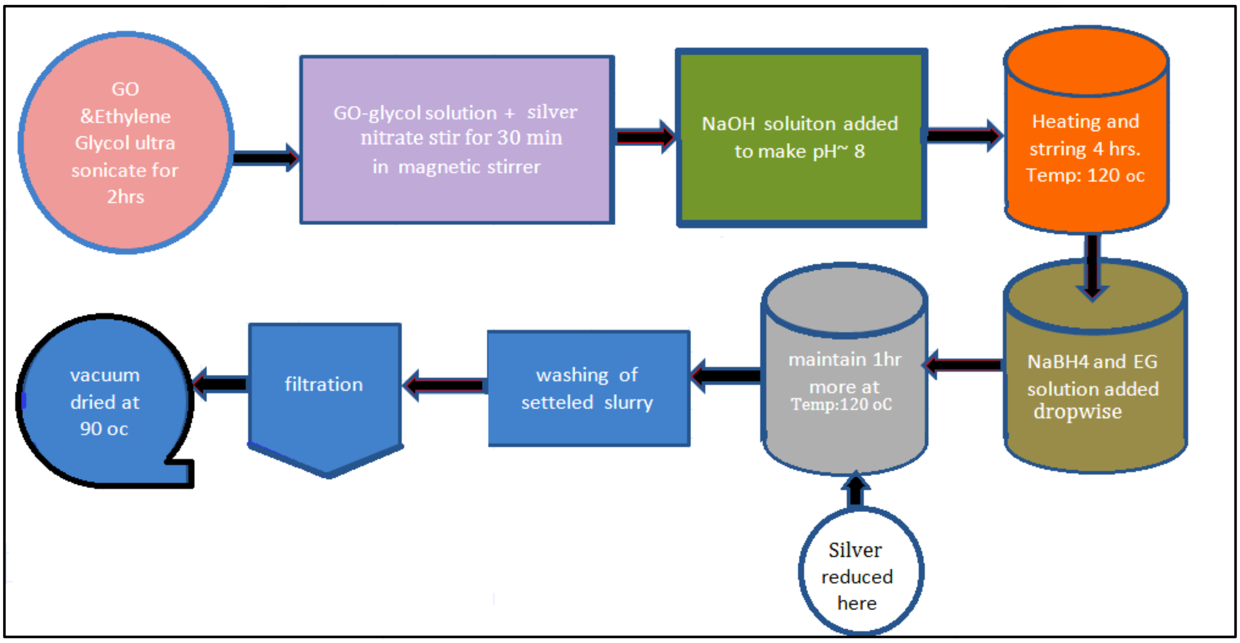
PREPARATION OF CATALYST (G-Ag) :

The steps involved in preparation of G-Ag catalyst are-

1. First Graphite Oxide (200 mg) and Ethylene Glycol (200 ml) in 1:1 ratio were ultra sonicated for 2 hrs.
2. Then Silver Nitrate was added into mixture and kept on the magnetic stirrer for stirring and heating.
3. Now 1(M) NaOH solution 50 ml approximately added to adjust the pH=7-8 of mixture.
4. Then temperature of the mixture was raised to 120 ^{o}C and maintained it for 4 hrs.
5. After maintenance ,Sodium Borohydride (100 mg)and Ethylene Glycol(5 ml) solution was added into the mixture and continued stirring another 1 hr maintaining temperature. 120 ^{o}c.
6. Then cool to room temperature and the solution was added drop by drop into a beaker that contained 500 ml distil water.

7. As $AgNO_3$ and GO were reduced to gray G-Ag nano hybrid heavier than water so precipitated which was separated by filter paper.
8. Thus the collected filtrate was kept inside vacuum drier around 85-90 °C for 6 hrs.
9. Finally, the dried G-Ag catalyst was stored in sample bottle.

This catalyst can be used to improve H_2 generation rate with cost effectively .



Schematic diagram for development of graphene silver nano ensemble .

4.1.4. PREPARATION OF G-Co MONO METALLIC CATALYST:

Graphene-Cobalt (G-Co) nano hybrid has the great potential to generate Hydrogen effectively and economically from sodium borohydride solution. Many researchers have tried to produce it in different processes but the POLYOL method seems to be simple and easier way.

MATERIALS USED :

1. Graphite Oxide (produced earlier)
2. Ethylene Glycol [$C_2H_4(OH)_2$]
3. Cobalt Nitrate Hexa hydrate[$Co(NO_3)_2.6H_2O$]
4. Sodium Borohydride [$NaBH_4$]
5. Distil water

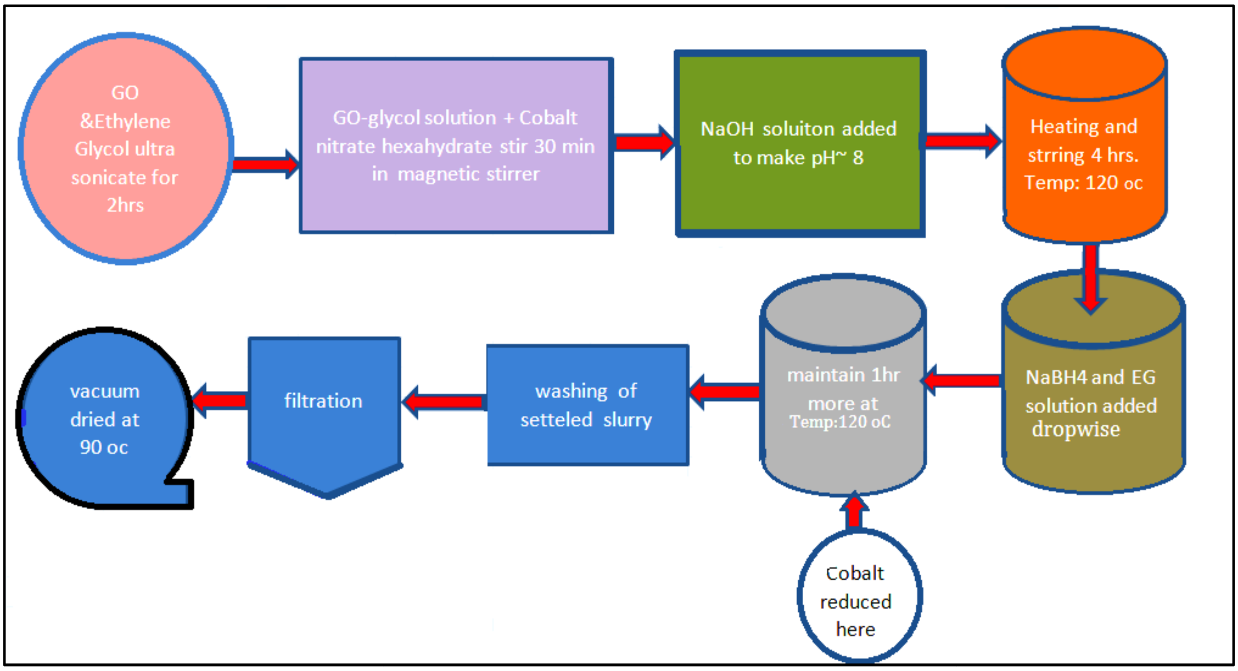
PREPARATION OF CATALYST (G-Co) :

The steps involved in preparation of G-Co catalyst are-

1. First Graphite Oxide (200 mg) and Ethylene Glycol(200 ml) in 1:1 ratio were ultra sonicated for 2 hrs.
2. Then Cobalt Nitrate Hexa Hydrate was added into mixture and kept on the magnetic stirrer for stirring and heating.
3. Now 1(M) NaOH solution 50 ml approximately added to adjust the pH=7-8 of mixture.
4. Then the temperature of the mixture was increased to 120 ^{o}c and maintained it for 4hrs.

5. After maintenance ,Sodium Borohydride (100 mg)and Ethylene Glycol(5 ml) solution was added into the mixture and continued stirring another 1 hr maintaining temperature. 120^{o}c.
6. Then cool to room temperature and the solution was added drop by drop into a beaker that contained 500 ml distil water.
7. As Co(NO$_3$)$_2$ and GO were reduced to blackish G-Co nano hybrid which is heavier than water so precipitated which was separated by filter paper.
8. Thus the collected filtrate was kept inside vacuum drier around 85-90^{o}C for 6 hrs.
9. Finally, the dried G-Co catalyst was stored in sample bottle.

G-Co catalyst can be used to enhance H_2 generation rate at cost effectively and it gives better result than G-Ag catalyst.



Schematic diagram of graphene cobalt nano composite preparation.

4.1.5. PREPARATION OF G-Co-Ag BI- METALLIC CATALYST:

Graphene-Cobalt-Silver (G-Co-Ag) catalyst shows the great strength to generate Hydrogen from water-borohydride solution effectively and economically. Many researchers have tried to produce it in different processes but the POLYOL method seems to be very simple and easier way to produce catalyst.

MATERIALS USED:

1. Graphite Oxide (produced earlier)
2. Ethylene Glycol
3. Silver Nitrate [$AgNO_3$]
4. Cobalt Nitrate Hexa Hydrate [$Co(NO_3)_2.6H_2O$]
4. Sodium Borohydride [$NaBH_4$]
5. Distil water

PREPARATION OF CATALYST (G-Co-Ag):

The steps involved in preparation of G-Co-Ag catalyst are-

1. First Graphite Oxide (200 mg) and Ethylene Glycol (200 ml) in 1:1 ratio were ultra sonicated for 2 hrs.
2. Then Silver Nitrate (200 mg) and Cobalt Nitrate Hexahydrate (200 mg) were added into mixture and kept on the magnetic stirrer for stirring and heating.
3. Now 1(M) NaOH solution 50 ml approximately added to adjust the pH=7-8 of mixture.
4. Then temperature of the mixture was raised to 120 ^oC and maintained it for 4 hrs.
5. After maintenance, Sodium Borohydride (200 mg) and Ethylene Glycol(10 ml) solution was added into the mixture and continued stirring another 1 hr maintaining temperature. 120 ^oc.
6. Then cool to room temperature and the solution was added drop by drop into a beaker that contained 500 ml distil water.
7. As $Co(NO_3)_2$, $AgNO_3$ and GO were reduced to gray G-Co-Ag nano hybrid which is heavier than water so precipitated which was separated by filter paper.
8. Thus the collected filtrate was kept inside vacuum drier around 85-90 ^oC for 6 hrs.
9. Finally, the dried G-Co-Ag catalyst was stored in sample bottle.

Practical images of steps involved for the preparation of bi metallic catalyst are stuck beneath—

Fig1: ultrasonication of GO & EG

Fig2: Ag and Co salt added

Fig3: 120 c temp. maintain 5 hrs.

Fig4: overnight settlement

Fig5: upper layer discard by siphon

Fig6: conc. slurry washing in DM

Fig7: settled nanohybrid in DM

Fig8: filtration of conc slurry

Fig9: filtrate collection

Fig10: wet $G_1Co_2Ag_1$ catalyst

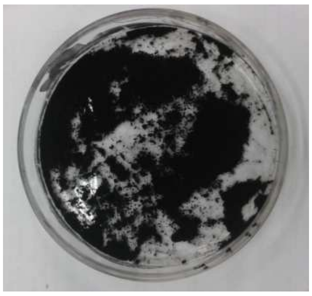


Fig11: catalyst after vacuum dried

Fig12: stored in sample bottle

This bi-metallic nano composite proves to be a good catalyst to improve hydrogen generation rate than mono catalyst due to higher surface to volume ratio of Co and Ag grain and electron transfer ways are increased due to bi metals compare to monometallic nano hybrid. Within this Bi-Metallic catalyst by changing the composition ratio of Silver and Cobalt, two more catalysts were prepared. Out of these three catalysts – $G_1Co_1Ag_1$, $G_{5.8}Co_{1.3}Ag_1$, $G_1Co_{1.58}Ag_{1.06}$ the last one displays highest hydrogen generation rate(0.11068 mol/ lit/min).

CHAPTER- V

Results and Discussions

5.1. RESULT AND DISCUSSION:

5.1.1. CHARACTERISATION OF THE CATALYSTS:

To embellish the hydrogen generation rate from sodium borohydride ($NaBH_4$) solution various combination and ratio of the compositions are tested. Due to this external adjustment, what kind of internal transformation is taking place can be identified by characterisation of the product. There are many characterisation equipments at present but due to our impediment to the availability of such equipments we did few characterisation tests like **XRD, HRTEM, SEM** and **BET.** These analyses reveal the internal morphology of the catalysts and help us to predict which composition is best suited for hydrogen generation from sodium borohydride solution .

Analysis of these characterisation are given below –

5.1.1.1. ANALYSIS OF XRD :

Fig-9 exhibits the XRD image of $G_1Co_{1.58}Ag_{1.06}$ nano- hybrid ploted 2θ vs. intensity. In most cases intense peak at around 8.4° corresponds to the GO is observed but as shown in Fig-9, the tiny spike at around $2\theta = 23.9^o$ indicates GO is successfully reduced to graphene .Generally a common broad peak that is observed at 24.3^o, can be attributed to the graphite structure (002) plane of the Graphene nano-sheet and here the peak value (23.9^o) we get is almost same. Lang Yang et.al mentioned that at Ag@Co/graphene microstructure diffraction peak at 38^o attributed to Ag(111) structure. Similarly, it is visible from XRD image a sharp peak around 39^o, which indicates silver existence in GCoAg nano-composite. In another journal Shubhanwita et al. described that for the sample of G-Co, two diffraction peaks at $2\theta = 51.5^0$, and 81.3^o are recognized, which can be marked as the (200), (311) planes of cobalt, respectively. Here also in Fig-9 it is evident that cobalt planes are corresponds to two diffraction peaks 65^o and 82^o. To briefly summarize the XRD result we can say GO forms a well-ordered layered structure of two bi metals silver and cobalt.

From the data of XRD, we can desist that during the formation of catalyst metal ions are infused into the layered GO sheets. Thus, G-Co, G-Ag and G-Co-Ag nano hybrids are formed by reducing GO sheet and crystal growth of metals. It is worthwhile to realise that impeachment of Co with Ag (in G-Co-Ag) results in the enhancement of the intensity of Ag (111) peak, which point outs the decrement of the corresponding crystalline grain size. For three different hybrids, the average crystal grain sizes of the Ag and Co nanoparticles /nanostructures are computed from broadening of the diffraction peak using Scherrer equation[42] :

$$d = \frac{0.9\lambda}{\frac{\beta 1}{2}\cos\theta}$$

Where , d is the average particle size in nm, **λ** stands for the wavelength of 1.54056 Å used in X-ray ,θ is the angle at the maximum of the peak (rad), and **β**$_{1/2}$ denotes the width of the peak in radians at half height. The estimated particle sizes of Ag and Co nano-clusters for three different hybrids are indexed in Table 1. It may be inferred that the crystalline grain sizes of both the Ag and Co are reduced in case of G-Co-Ag compared to G-Ag and G-Co, respectively.

Table 1: comparative analysis according to grain size of Ag and Co for different catalysts

Catalyst	Grain size from XRD	
	Ag	Co
$G_{1.12}Ag_1$	~36 nm	----
$G_{1.07}Co_1$	----	~24 nm
$G_1Co_{1.58}Ag_{1.06}$	~25 nm	~20 nm

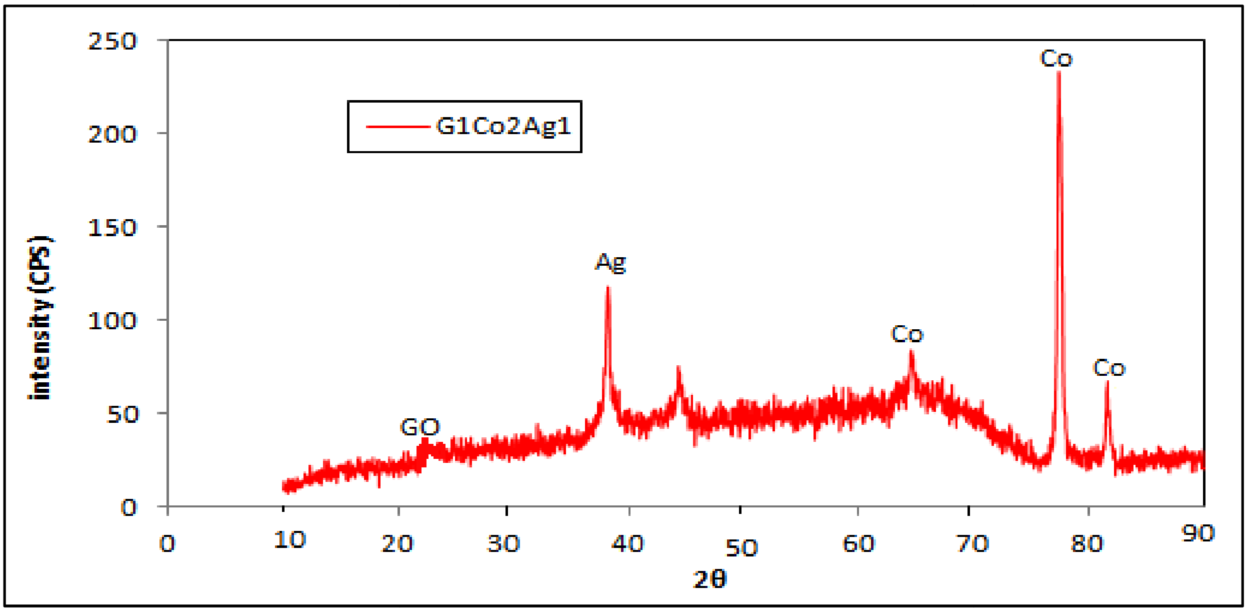


Figure 9: XRD Patterns of graphene-cobalt-silver ($G_1Co_{1.58}Ag_{1.06}$, red) nano-hybrid

5.1.1.2. SEM/EDX ANALYSIS:

Scanning Electron Microscopy (SEM) analysis is accomplished to gain the information about sample's surface topography and compositions. Fig-10 represents the SEM image for surface morphology of Graphene supported bi-metallic catalyst $G_1Co_{1.58}Ag_{1.06}$. The image reveals multi layer dispersion of Ag and Co on graphene sheet. It is evident that spherical shape particles are silver and irregular shape grains are cobalt. It is also apparent that particles are mutually distinct in diameter varying between 75 nm to 150 nm. Particles′ growth are only about few nano meters due to the use of strong reducing agent $NaBH_4$ during catalyst preparation which helped rapid reduction of silver and cobalt ion and thus it does not allow particles to grow in broad size. Besides all of these one fabulous fact happens i.e. particles are adhered to each other very densely by not allowing them to dispose of during hydrogen preparation. However, it is not possible to recognize which type of crystal structure is present whether face centred cubic(FCC) or hexagonal close pack (HCP).

The energy-dispersive X-ray (EDX) spectrum delineates in Fig-11, disclosed the presence of Co & Ag in G-Co-Ag nano-hybrid sample-2 ($G_1Co_{1.58}Ag_{1.06}$). EDX results revealed the presence of 43.32% Co and 29.23% Ag in the G-Co-Ag-2 sample. The metal content forecasted by EDX and estimated from the Atomic Mass Absorption Spectrophotometer assent nearly. Comparative analysis of percentage loading of metal components cobalt and silver in assorted catalysts is inured below –

Table 2: comparative study of metal loading of different catalysts

Name of catalyst	percentage of loading		
	Co	Ag	Graphene
G-Co (~1.07:1)	48.34	-	51.66
G-Ag (~1.12:1)	-	47.23	52.77
G-Co-Ag- 1 (~1.07:1:1.3)	31.21	35.34	33.45
G-Co-Ag- 2 (~1:1.58:1.06)	43.32	29.23	27.45
G-Co-Ag- 3 (~5.8:1.22:1)	15.24	12.45	72.31

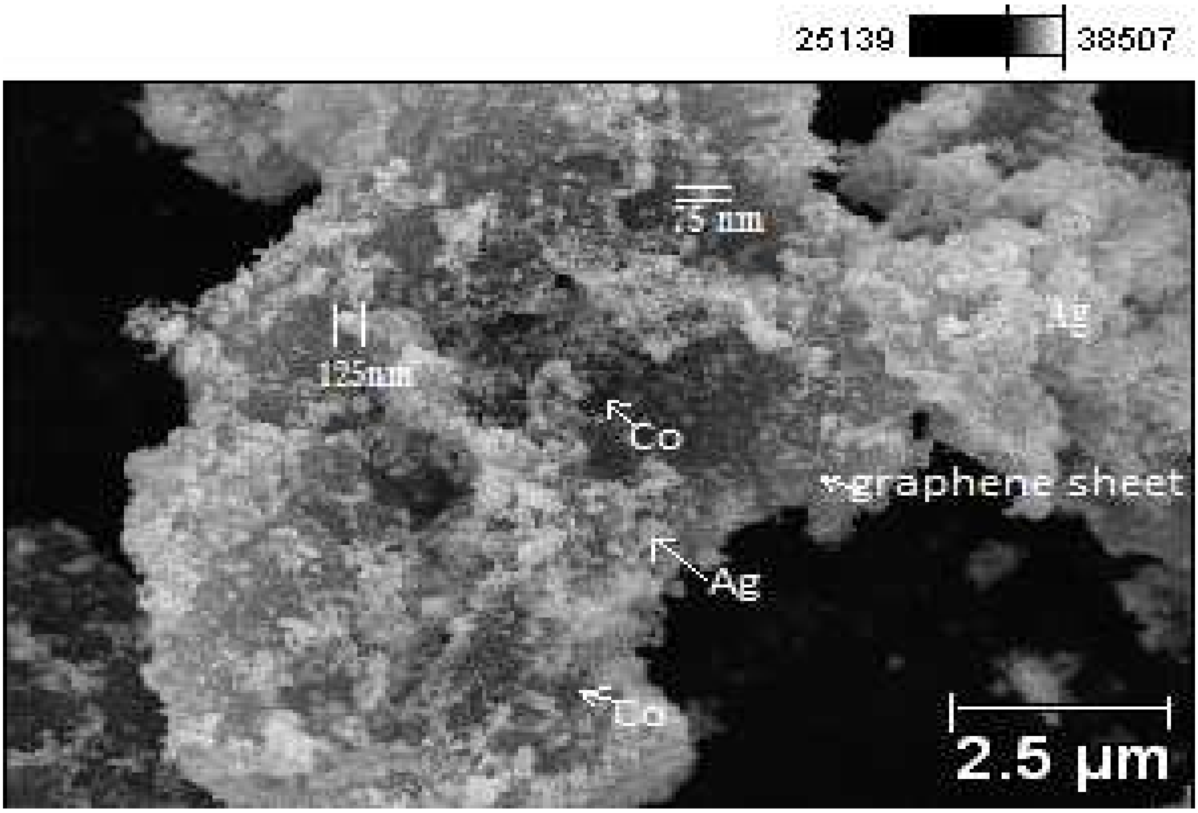


Figure 10 : SEM image of $G_1Co_2Ag_1$ nano-ensembles

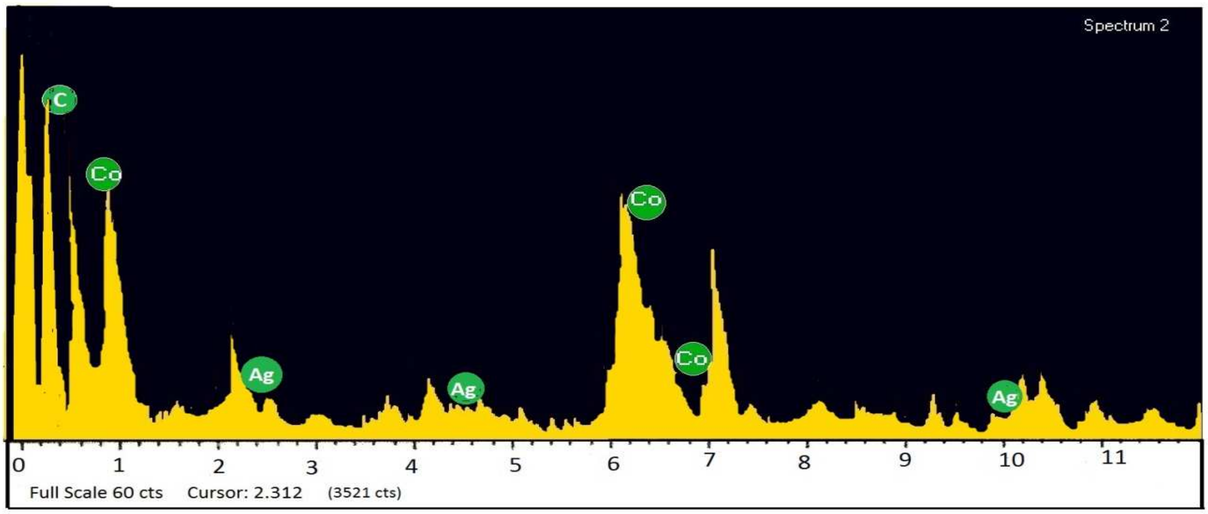


Figure 11: EDX spectrum of deposited Co and Ag metals in G-Co-Ag nano-ensembles

5.1.1.3. **HRTEM ANALYSIS:**

Fig-12 pageants the HRTEM image of G-Co-Ag nano-composite. This image illustrates about the dissemination of the particles on the graphene sheet and reveals the matrix like structure formation of cobalt and silver with graphene due to ferromagnetic and diamagnetic properties of the nano-particles . It is clearly visible from the image that Co and Ag agglomerates are in various sizes ranging from 10 nm to 40 nm. Here particles are randomly distributed on the surface and edges of graphene nanosheet . It is interesting to notice that no free metal nano particles are observable outside the graphene sheet. The Co-Ag nano-ensembles are not dispersed homogeneously rather they form various zones (as shown in image zone-I and zone-II) on graphene sheet .As in this sample ($G_1Co_{1.58}Ag_{1.06}$) cobalt is present in double quantity than silver so cobalt particles are observable throughout the graphene nanosheet but mainly inside that imaginary zone. Cobalt particles are ferromagnetic in nature so they attract silver particles and form Co-Ag agglomerates inside the imaginary zone. As silver particles are less in quantity, so outside that imaginary zone silver particles are rare.

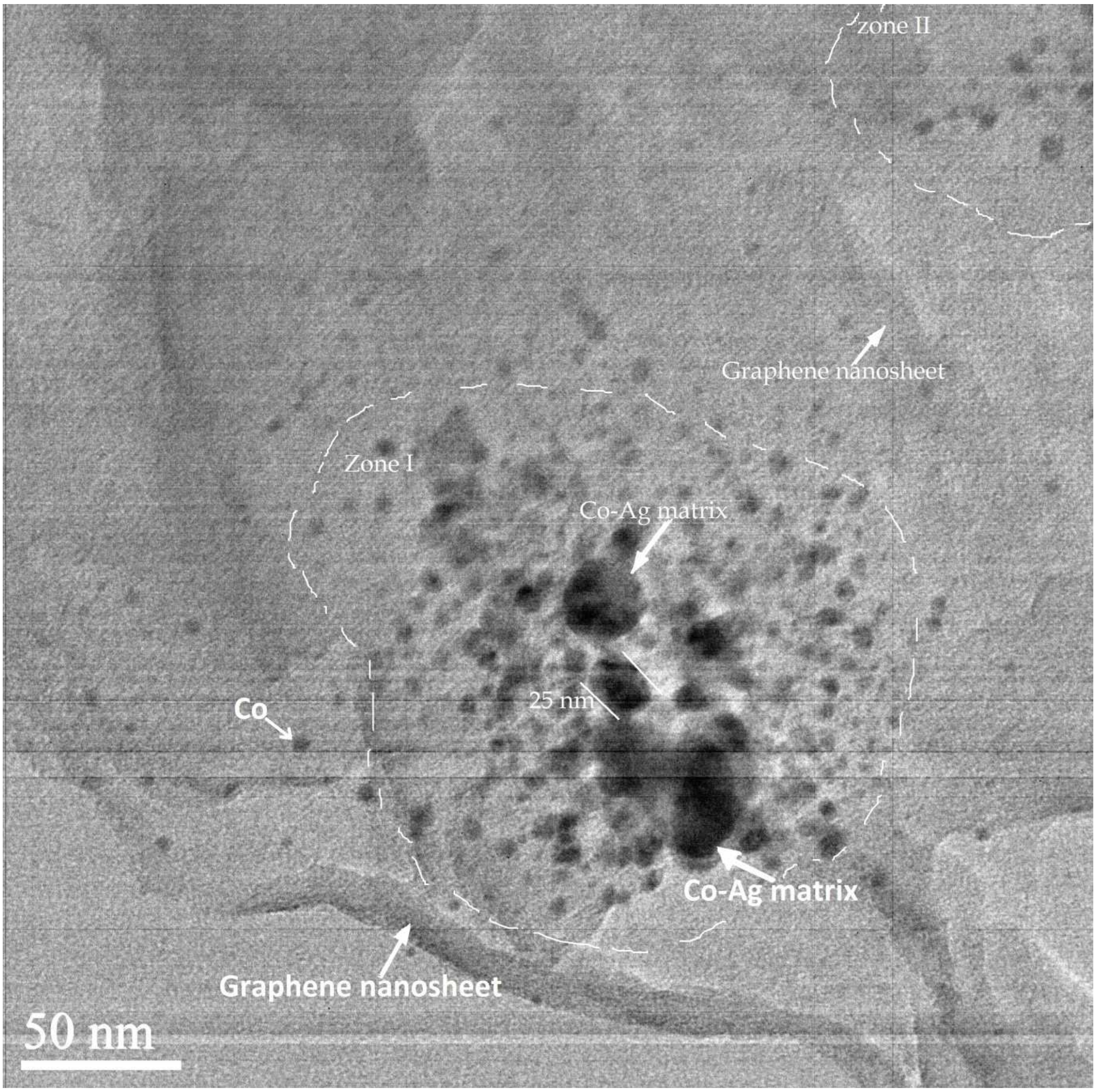


Figure 12: HR-TEM image of $G_1Co_{1.58}Ag_{1.06}$ nano composite

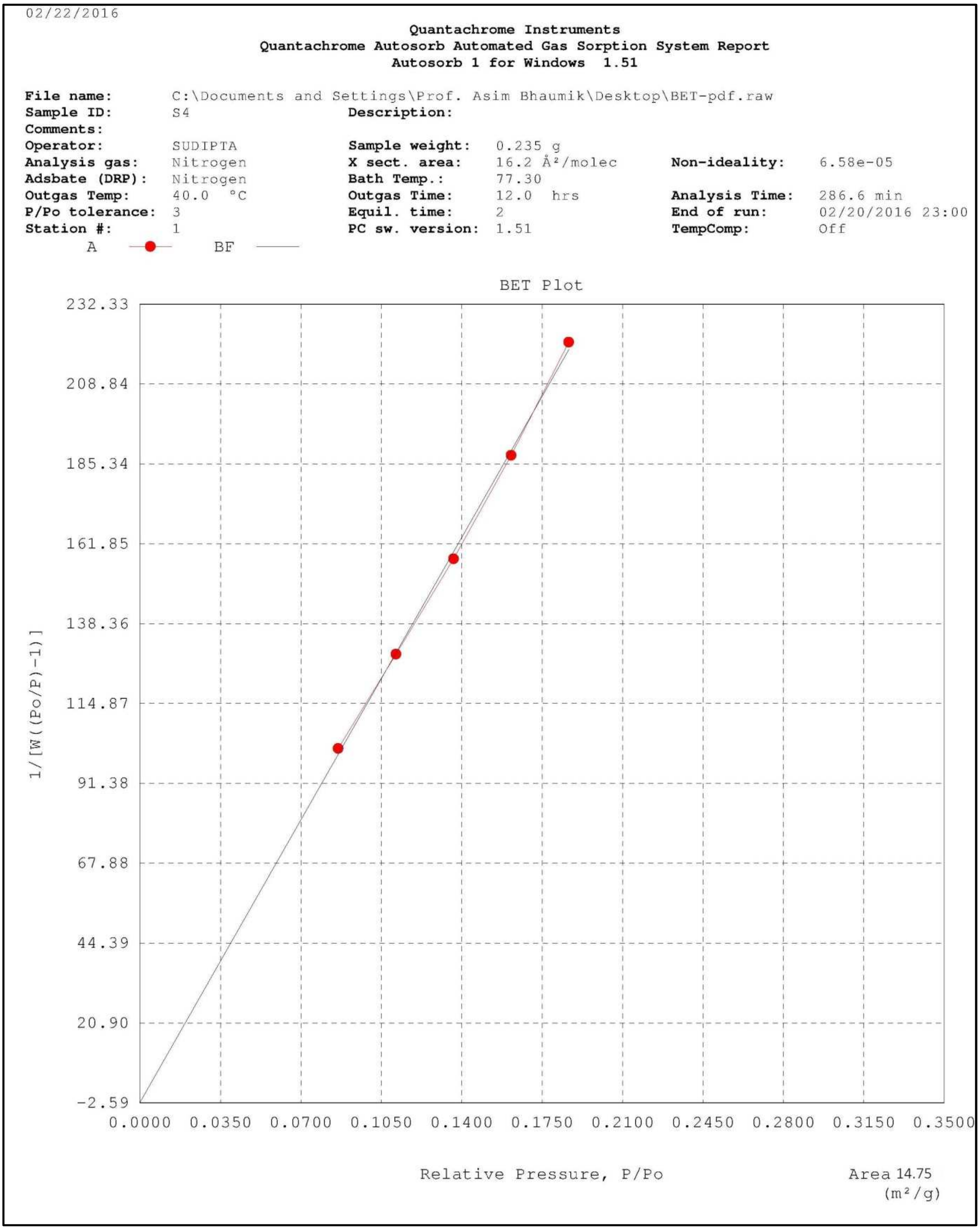
5.1.1.4. BET ANALYSIS:

BET analysis technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2 /gm gathering vital information in studying the effects of surface porosity and particle size in many reactions. The BET surface area measurement was made using a conventional BET multi-point nitrogen physisorption apparatus . Specific surface area of $G_1Co_{1.58}Ag_{1.06}$ sample is calculated from the basic BET equation –

$$\frac{1}{W(\frac{P_o}{P}-1)} = \frac{1}{W_mC} + \frac{C-1}{W_mC}(P/P_o)$$

In which, P_o = saturated vapour pressure of adsorbate gas
P = partial vapour pressure of adsorbate gas
W = weight of adsorbed gas
W_m = weight of adsorbed gas in monolayer
C = BET constant

In Fig-13, it is depicted $\frac{1}{W(\frac{P_o}{P}-1)}$ vs. P/P_o diagram from which we can determine slope $\frac{C-1}{W_mC}$ =1006.71 .Also from plot it is visible that the intersection ($\frac{1}{W_mC}$) has -2.59 value that in term help to evaluate C and W_m values as -387.69 and $9.95*10^{-4}$ gm respectively. Now total surface area (S_t) is calculated as 3.467 m^2 . Finally, the specific surface area (S) is determined 14.75 m^2/gm. In patent EP2224815 A1 it was mentioned that specific surface area of silver particles are generally within a range not exceeding about 20 m^2/gm with particle sizes of about 30 nm and Co (20% w/v)-Al_2O_3 with BET surface area is measured as 137.90 m^2/gm[43] .So it can be expected that cobalt and silver ensemble have BET surface within a range of 20 -140 m^2/gm, but from BET result we are getting BET surface area 14.75 m^2/gm which is less than the expected specific surface area. This unexpected result is coming probably due to the matrix formation of cobalt and silver on graphene sheet as visible in HRTEM image.



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02/22/2016
                         Quantachrome Instruments
          Quantachrome Autosorb Automated Gas Sorption System Report
                       Autosorb 1 for Windows  1.51

File name:       C:\Documents and Settings\Prof. Asim Bhaumik\Desktop\BET-pdf.raw
Sample ID:       S4                 Description:
Comments:
Operator:        SUDIPTA            Sample weight:   0.235 g
Analysis gas:    Nitrogen           X sect. area:    16.2 Å²/molec      Non-ideality:     6.58e-05
Adsbate (DRP):   Nitrogen           Bath Temp.:      77.30
Outgas Temp:     40.0  °C           Outgas Time:     12.0  hrs          Analysis Time:    286.6 min
P/Po tolerance:  3                  Equil. time:     2                  End of run:       02/20/2016 23:00
Station #:       1                  PC sw. version:  1.51               TempComp:         Off
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Figure 13: BET plot of $G_1Co_{1.58}Ag_{1.06}$ sample.

5.1.2. RESULT OF HYDROGEN GENERATION:

Two monometallic catalysts and three bi- metallic catalysts were synthesized and the characteristic study of these catalysts had been described in earlier chapter. Now to check how much they are effective, hydrogen is generated in lab by the hydrolysis of Sodium Borohydride [$NaBH_4$] in different temperatures. From this hydrogen generation data we can analyse reaction rate, activation energy, rate constant and various parameters related to rate equation. All these analysis are given below---

5.1.2.1. HYDROGEN GENERATION USING DIFFERENT CATALYSTS:

Given below in Fig-14, plot of H_2 volume vs. time using various catalysts in 50^{o}c temperature using same catalytic loading(30 mg). Data regarding this plot is given in Table1.

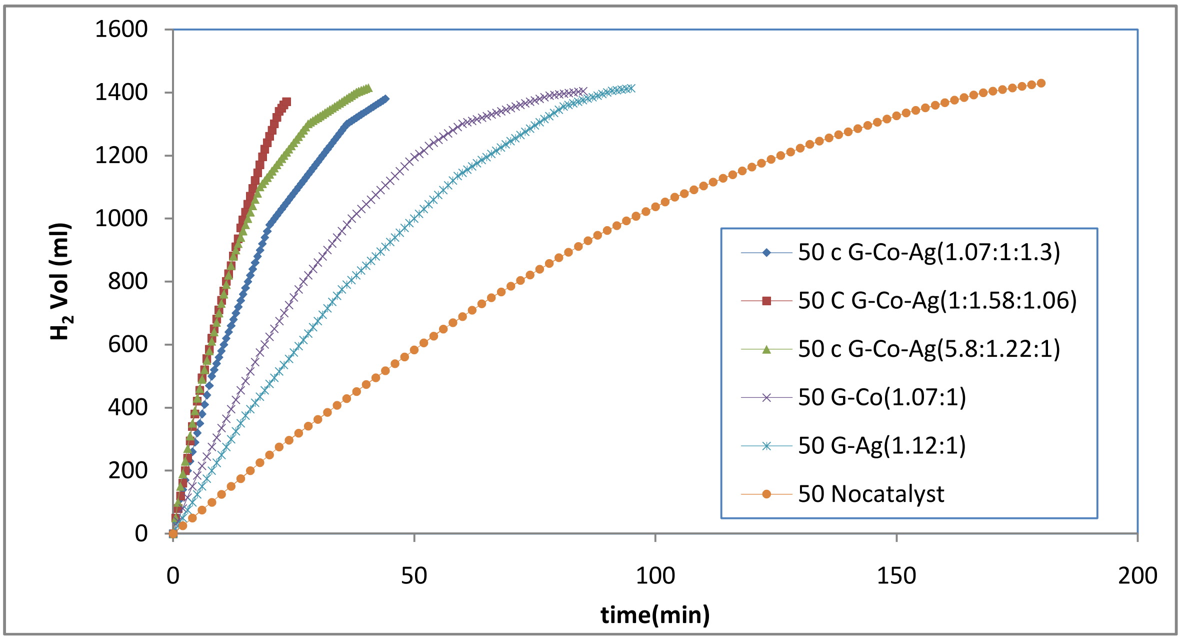

Figure 14: **Comparison study of different catalysts at 50^{o}c temperature**

The above figure clearly depicts that among various catalysts $G_1Co_{1.58}Ag_{1.06}$ produces hydrogen at much faster rate (1415 ml in 27.5 min) than the others do. Another inference we can draw from the above figure is that all the bi-metallic catalysts have higher reactivity than the monometallic catalyst as number of paths for electron transfer increases due to presence of bi-metallic monohybrids within the graphene sheet.

Table 1: H_2 generation data: time(min) vs. Volume of H_2 generation(ml) using different nano catalysts

Time (min)	Volume of Hydrogen generated (ml) at 50° c					
	Without catalyst	G-Ag(1.12:1)	G-Co (1.07:1)	G-Co-Ag(1.07:1:1.3)	G-Co-Ag(5.8:1.22:1)	G-Co-Ag(1:1.58:1.06)
0	0	0	0	0	0	0
5	62.5	125	185	320	430	420
10	125	250	335	580	730	740
15	187.5	375	485	780	980	1020
20	250	475	625	980	1140	1260
25	312.5	575	750	1080	1240	1395
30	375	675	860	1180	1320	1415
35	437.5	775	960	1280	1370	
40	485	850	1045	1340	1412	
45	537.5	925	1120	1390		
50	585	1000	1195	1420		
55	637.5	1075	1250			
60	685	1145	1300			
65	737.5	1195	1325			
70	785	1245	1350			
75	822.5	1295	1375			
80	860	1345	1394			
85	897.5	1375	1404			
90	935	1400				
95	977.5	1413				
100	1010					
105	1047.5					
110	1085					
115	1122.5					
120	1155					
125	1180					
130	1205					
135	1230					
140	1255					
145	1280					
150	1305					

155	1330					
160	1355					
165	1372.5					
170	1385					
175	1397.5					
180	1410					

As we compare earlier, hydrogen generation volume of different catalyst with respect to time similarly, a comparison study regarding the rate of the catalysts is shown in Fig-15 (Time vs. Rate)—

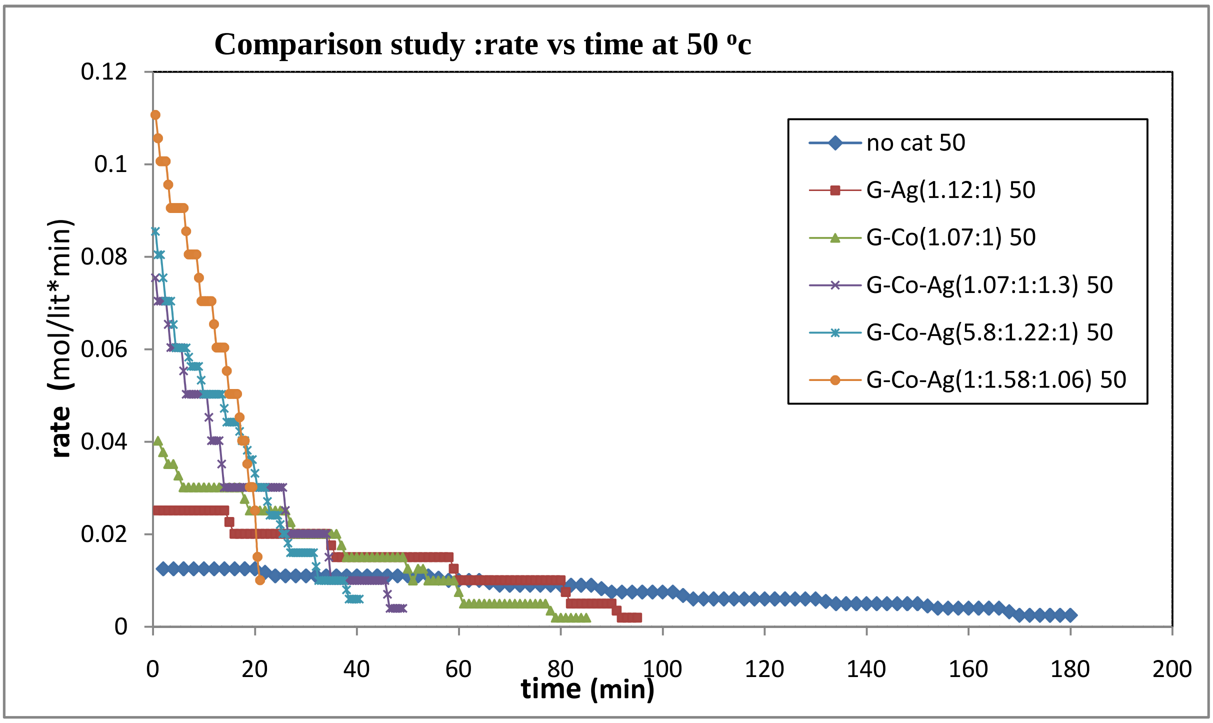

Figure 15: rate vs. time plot of various catalysts

It is apparently palpable from the above plot (Fig-15) the hydrogen generation rate is very slow if catalyst is not present in the borohydride solution and takes almost 180 mins to complete the reaction. On the other hand bi-metallic catalyst, G-Co-Ag in 1:1.58:1.06 wt ratio gives the highest hydrogen generation rate (0.11068 mol/lit/min) among the catalysts. It takes approx. 27.5 mins at 50^{o}c to complete the reaction.

5.1.2.2. ESTIMATION OF REACTION ORDER AND RATE CONSTANT:

We can estimate reaction rate and order by two methods . One is integral and other is differential method. Here reaction rate is analysed by differential method. In differential method reaction rate for nth order is written as ----

$r = (-dC/dt) = K*C^n$ taking log on both sides we get --

$\ln(-dC/dt) = \ln K + n \ln C$

where ,r = reaction rate

C= $NaBH_4$ concentration

K= rate constant

t = time

n = order of reaction

As the above equation indicates if we plot ln(-dC/dt) vs. lnC that gives straight line of which slope gives us reaction order n and the intercept gives lnK values and finally we can determine K value. Below is given ln(-dC/dt) vs. ln C plots of different catalysts:

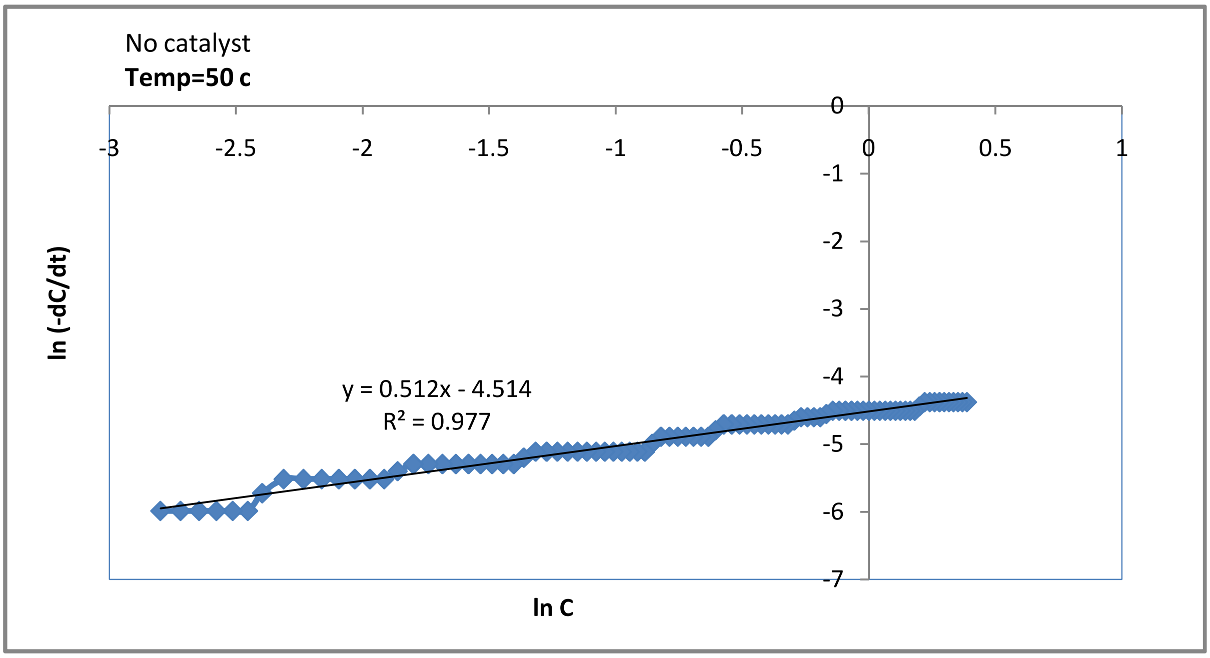

Figure 16: log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$, ln C at 50°c without catalyst in medium

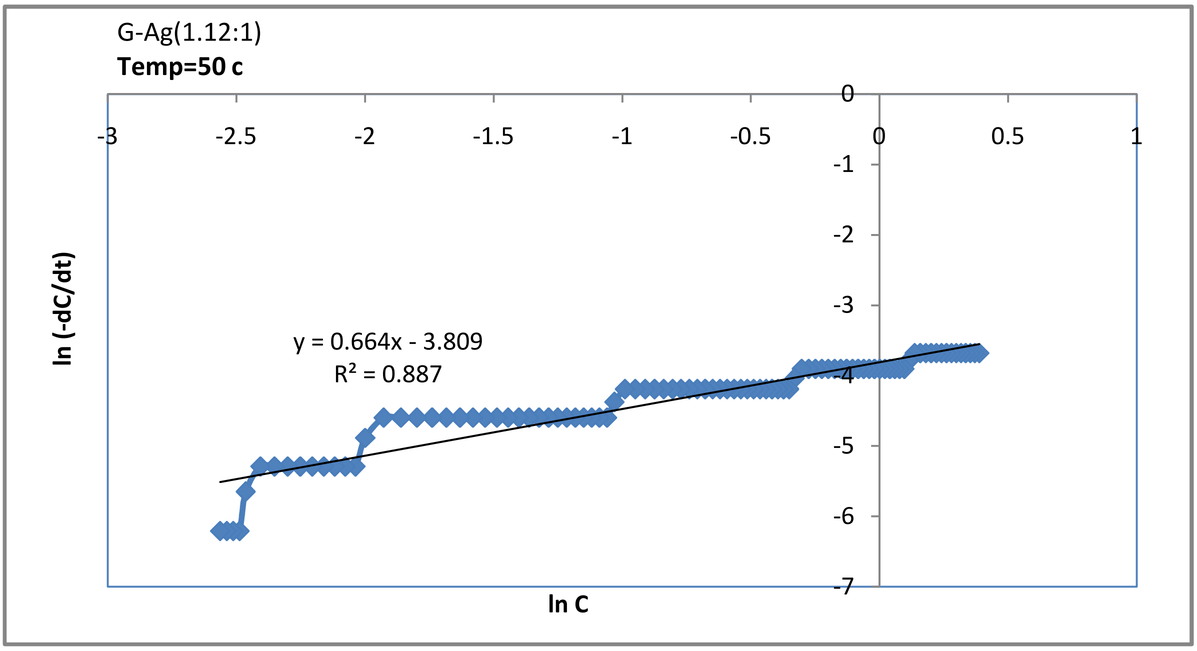

Figure 17: log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$, ln C at 50^oc using G_1Ag_1 as catalyst in medium

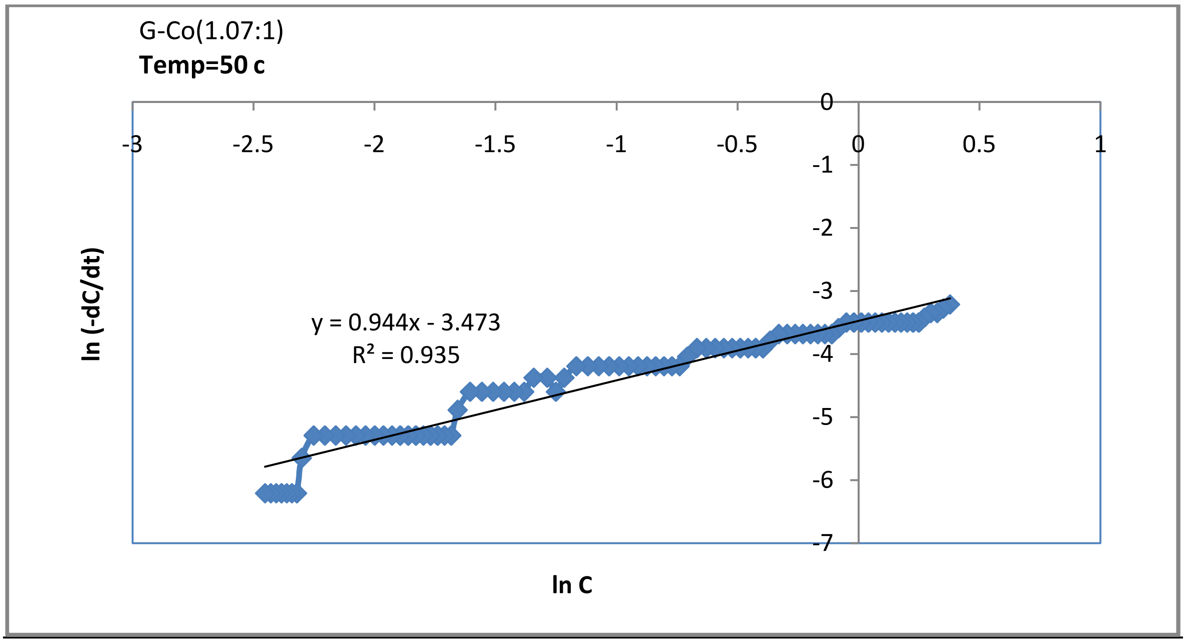

Fig 18: log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$,ln C at 50^oc using G_1Co_1as catalyst in medium.

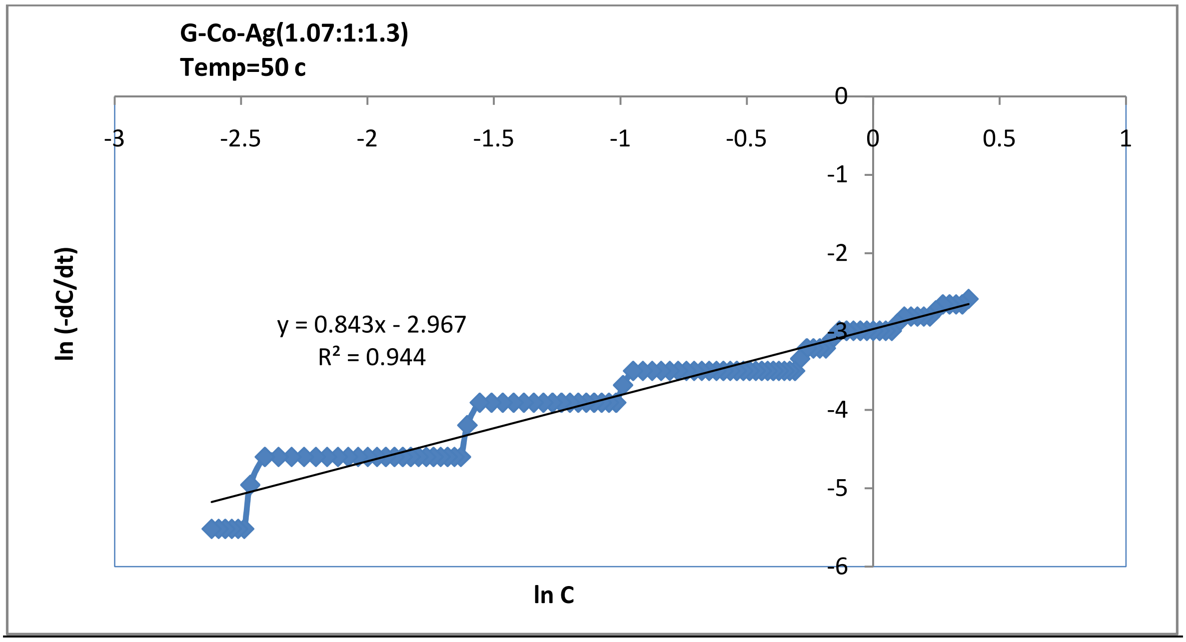

Fig 19: log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$,ln C at 50°c using $G_1Co_1Ag_1$ as catalyst in medium.

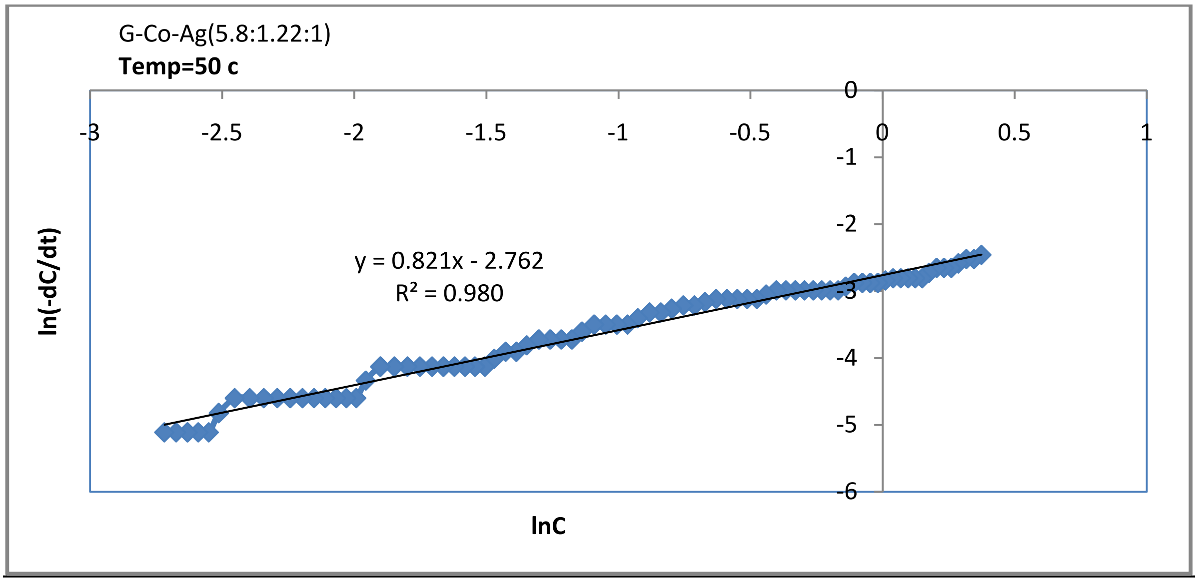

Fig 20: log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$,ln C at 50^{o}c using $G_{5.8}Co_{1.22}Ag_1$ as catalyst in medium.

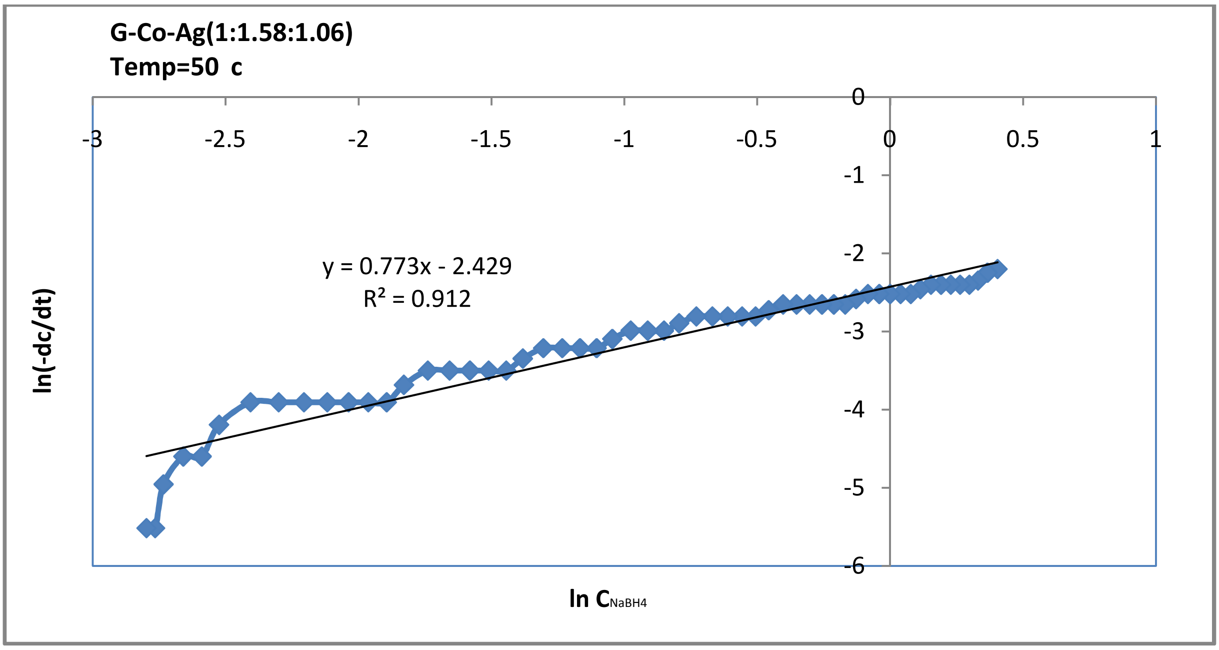

Fig 21: log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$,ln C at 50°c using $G_1Co_2Ag_1$ as catalyst in medium.

Table 2: order and rate constant values at 50 °C from above graphs

Catalyst	Order of Reaction(n)	ln K	Value of K
Without catalyst	0.5127	-4.515	0.011
$G_{1.12}Ag_1$	0.6643	-3.809	0.022
$G_{1.07}Co_1$	0.9441	-3.473	0.031
$G_{1.07}Co_1Ag_{1.3}$	0.8437	-2.967	0.051
$G_{5.8}Co_{1.22}Ag_1$	0.8214	-2.763	0.063
$G_1Co_{1.58}Ag_{1.06}$	0.7734	-2.429	0.088

ANALYSIS OF THE GRAPHS:

The rate of the reaction for the H_2 generation from $NaBH_4$ solution was studied using various catalysts at different temperatures. However, all the above graphs were given at 50 °C temperature because it was recognized that 50 °C is the feasible temperature for this reaction. Therefore, data at 50 °C temperature were given emphasised to analyse the rate parameters. Data obtained from experiments were used to plot the rate of decomposition of $NaBH_4$ versus the concentration of $NaBH_4$ present in the reaction medium at any time, t.

In first experiment H_2 generation was done in absence of catalyst and the data recorded was plotted in Fig-16. This plot gave the values 0.5127 and -4.5147 for slope and intercept respectively. As the plot is ln(-r) vs. ln C ,so slope actually gives reaction order i.e. n =0.5127 and intercept gives lnK = - 4.5147 i.e. K = 0.011. These data will be beneficial for further comparative study of various catalysts.

In 2nd and 3rd experiments H_2 generation were done by mono metallic catalysts i.e. G_1Ag_1 & G_1Co_1 and the corresponding graphs were plotted in Fig 17 and Fig 18 respectively. From Fig 17 we got slope 0.6643 i.e. order of the reaction is 0.6643 which is nearly same with previous one but the rate constant K= 0.022 which becomes double than the previous one. Similarly from Fig 18 we got order =0.9441 and rate constant = 0.031 which is three time than first value .So rate constant values are indicating that G_1Co_1 catalyst system has higher reaction rate than G_1Ag_1 catalyst system.

In 4th ,5th and 6th experiments H_2 was generated by using bi-metallic catalysts and form Fig 19,20 & 21 it is evident that the rate constant values are almost 5 to 8 time than the H_2 generation in absence of any catalyst. Another conclusion can be drawn that bi-metallic catalytic reactions are much faster than mono metallic catalytic reaction and among bi-metallic catalysts, $G_1Co_{1.58}Ag_{1.06}$ has the highest rate constant value (K=0.088).

5.1.2.3. CATALYST ACTIVITY MEASUREMENT BY ACTIVATION ENERGY:

Activation energy of a catalyst indicates how much energy we have to supply externally to start the reaction . High activation energy of catalyst indicates reaction will start at high temperature. Therefore, for development of any catalyst we have to build catalyst such a way so that it will have low activation energy.

CALCULATION OF ACTIVATION ENERGY :

From Arrhenius equation Activation energy is given as :

$K=k_o \ e^{-E/RT}$ taking log on both sides we get---

$\ln K = \ln k_o + (-E/R)*(1/T)$----(i)

Where ,E=activation energy

k_o= frequency factor

K= rate constant

R= universal gas constant

T=temperature in Kelvin

Now for nth order reaction rate equation can be written as :

$r = (-dC/dt) = K*C^n$ taking log in both sides we get—

$\ln(-dC/dt) = \ln K + n \ln C$ ------(ii)

From experimental result we have reaction rate value with respect to the change in concentration of the reactant. Therefore, from equation(ii) we can find lnK values in different temperatures. Now applying these two values i.e. lnK and (1/T) in equation (i) we can determine activation energy (E).

Below is given activation energy determination curve for **$G_1Co_{1.58}Ag_{1.06}$** catalyst ---

Table 3: Data from nth order model for curve ln K vs. 1/T to determine E

T (^oC)	**T (K)**	**1/T (K^{-1})**	**ln(K)**	Frequency factor **(k_o)**	**(-E/R)**	**E** (KJ/mol)
60	333	0.003003	-2.364	15835.34	-3967	32.985
50	323	0.003096	-2.429			
40	313	0.003195	-3.0264			
30	303	0.0033	-3.468			

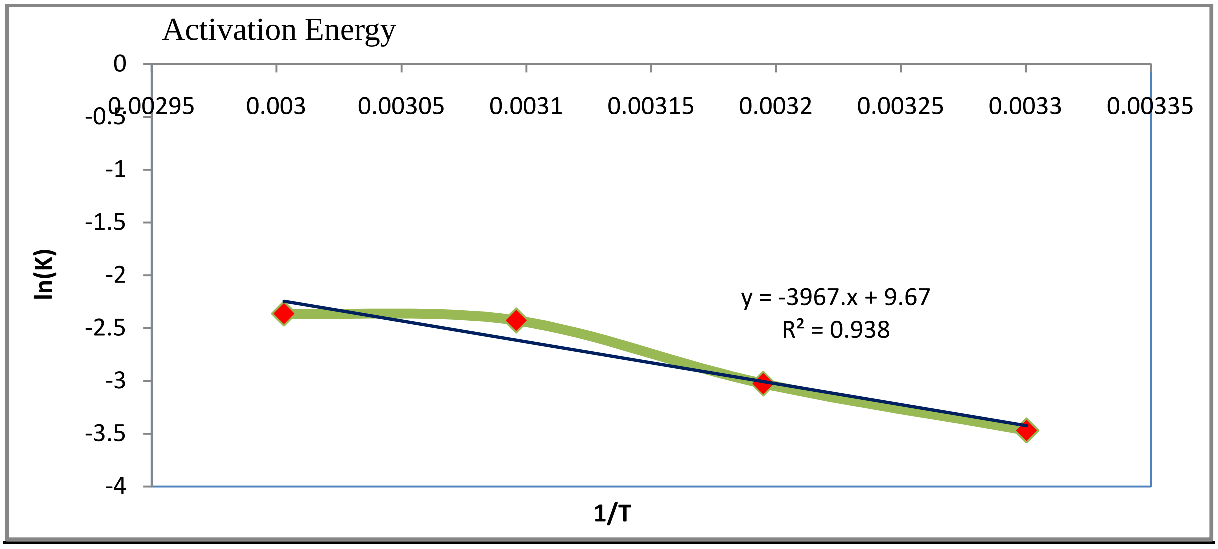

Fig-22: A plot ln K vs. 1/T of $G_1Co_{1.58}Ag_{1.06}$ catalyst

Table 4: Data from L-H model for curve ln K vs. 1/T to determine E

$T(^oC)$	T(K)	1/T (K^{-1})	lnK	Frequency Factor (K_o)	(-E/R)	E (KJ/mol)
60	333	0.003003	-1.30345	39065.7	-3979.4	33.085
50	323	0.003096	-1.89048			
40	313	0.003195	-2.07147			
30	303	0.0033	-2.28278			

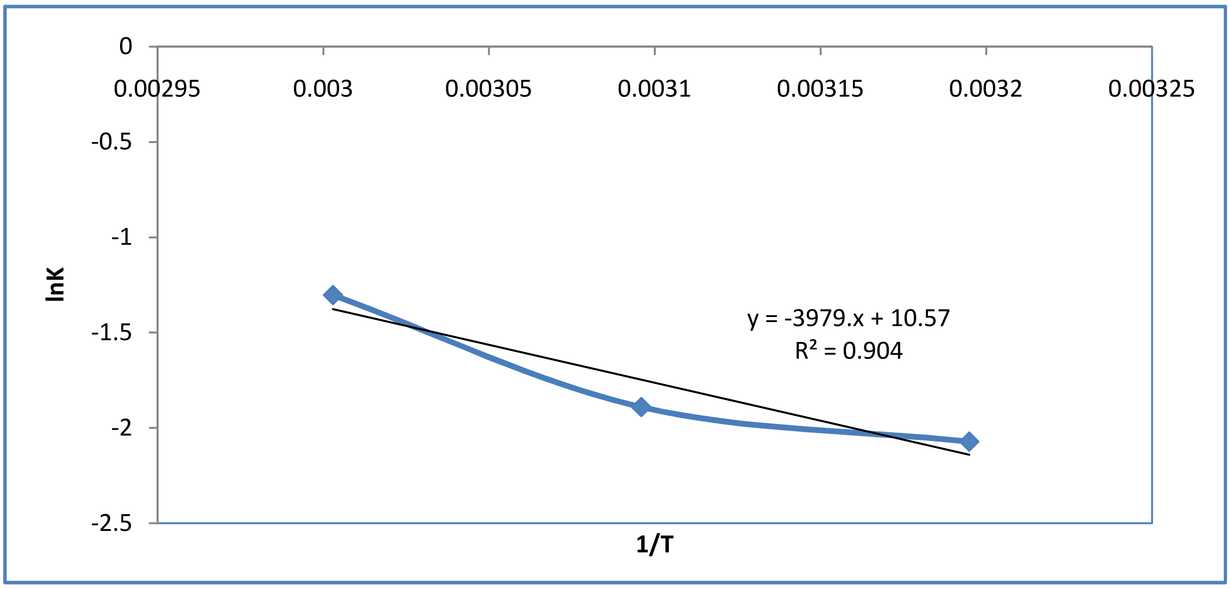

Fig-23: activation energy of $G_1Co_{1.58}Ag_{1.06}$ catalyst by L-H model

COMPARISON STUDY OF DIFFERENT CATALYSTS BY *E* VALUE :

As discussed earlier , activation energy of a catalyst is one of the key parameter by which we can select which one is better so a chart is prepared of the various catalysts which is given below—

Table 5: activation energy of different catalysts

CATALYST	ACTIVATION ENERGY (E) **(KJ/mol)**			
	n^{th} order model	R^2	L- H Model	R^2
Without catalyst	68.61	0.7035	57.824	0.9481
$G_{1.12}Ag_1$	52.81	0.7708	50.99	0.9252
$G_{1.07}Co_1$	47.55	0.786	47.27	0.9936
$G_{1.07}Co_1Ag_{1.3}$	40.67	0.903	39.75	0.9202
$G_{5.8}Co_{1.22}Ag_1$	37.29	0.955	35.05	0.9437
$G_1Co_{1.58}Ag_{1.06}$	32.98	0.9385	33.08	0.9045

Above values of R^2 from n^{th} order model clearly indicates that except bi-metallic nano composites, mono-metallic catalyst are not fitting properly. On the other hand, all values of R^2 in L-H model are perfectly fitted. Neglecting n^{th} order model values it can be inferred from L-H model that mono metallic catalyst system has higher activation energy compare to bi-metallic catalytic reaction and among bi-metallic catalyst $G_1Co_{1.58}Ag_{1.06}$ has minimum activation energy (33.08 Kj/mol) , so its reactivity is very high and prove to be a valuable catalyst.

5.1.2.4. KINETIC STUDY OF THE CATALYST $G_1Co_{1.58}Ag_{1.06}$:

Hydrolysis of 0.568 gm Sodium Borohydride ($NaBH_4$) is carried out at different temperatures from 30 to 60°c in presence of 30 mg $G_1Co_2Ag_1$ catalyst . The corresponding hydrogen ration rate is evaluated as a function of remaining Borohydride concentration. Hydrogen generation rate is recorded with time by the help of water displacement method in a marked cylindrical vessel of 2000 ml. Now from stoichiometric ratio remaining Borohydride concentration in reactor can be calculated with respect to time. From the log-log plot of $NaBH_4$ concentration vs. Rate at different temperatures, we can tally how the reaction rate constant and order are changing from temperature to temperature. 4 graphs at four temperatures are given below—

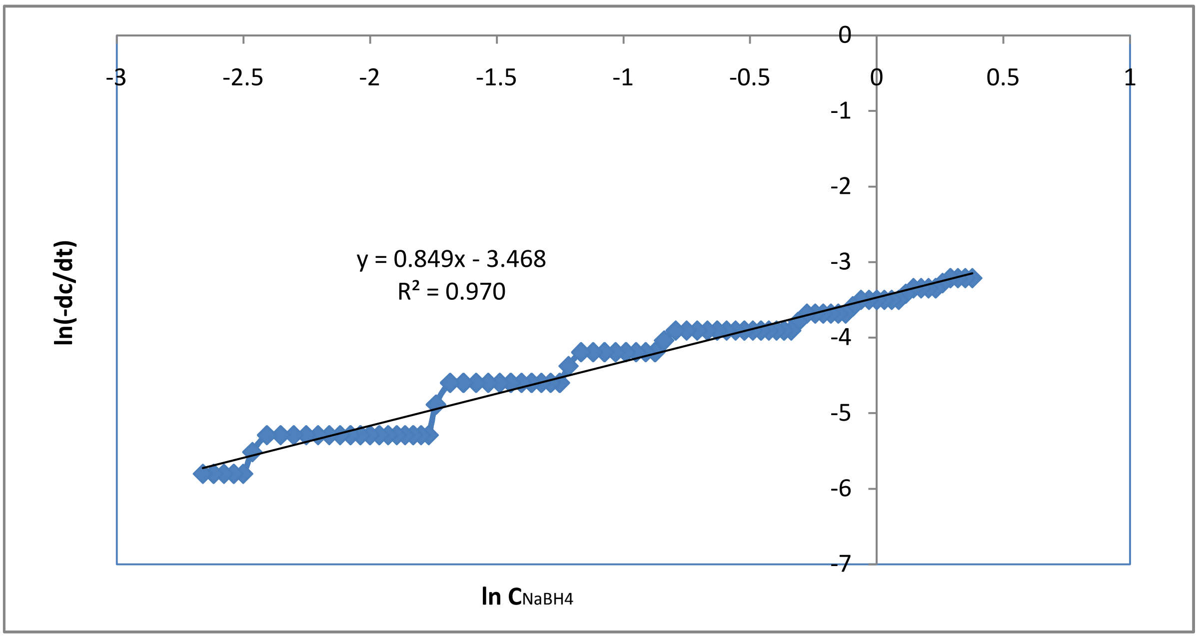

Fig 24 : log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$, lnC at 30^{o}c using $G_1Co_{1.58}Ag_{1.06}$ as catalyst in medium

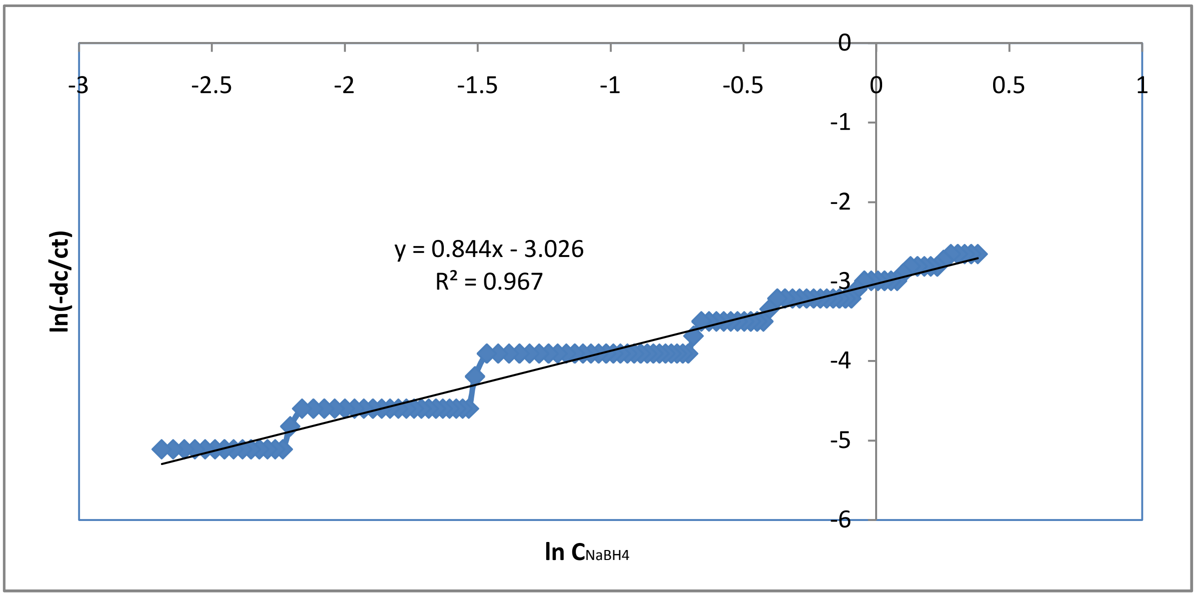

Fig-25 : log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$,ln C at 40^{o}c using $G_1Co_{1.58}Ag_{1.06}$ as catalyst in medium.

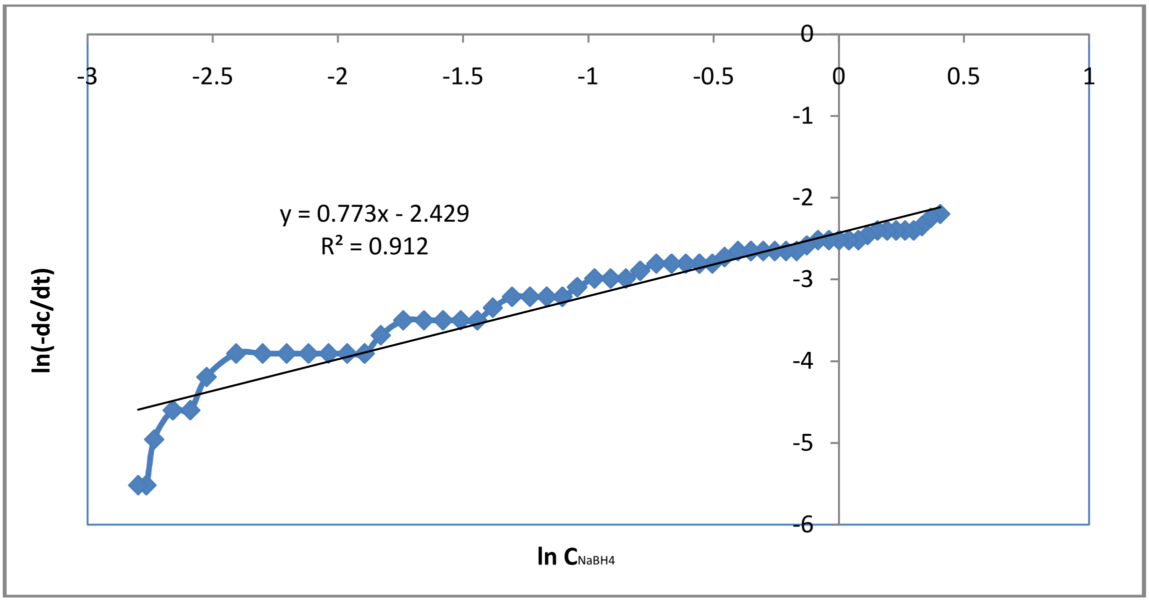

Fig-26 **:** log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$,ln C at 50^{o}c using $G_1Co_{1.58}Ag_{1.06}$ as catalyst in medium**.**

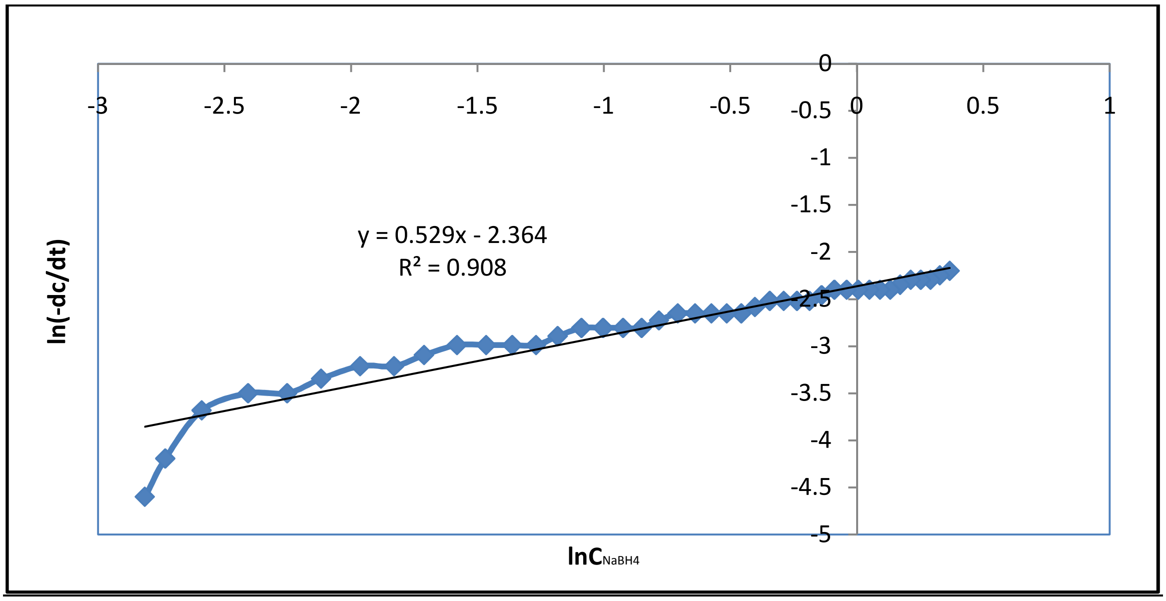

Fig 27 **:** log of Rate of decomposition of $NaBH_4$,ln(-dC/dt) vs. Concentration of $NaBH_4$,ln C at 60^{o}c using $G_1Co_{1.58}Ag_{1.06}$ as catalyst in medium.

Fig 23, 24, 25 & 26 provide the data of $G_1Co_{1.58}Ag_{1.06}$ nano-composite that is tabulated below -

Table 6: rate constant and order of $G_1Co_{1.58}Ag_{1.06}$ at different temperatures.

Catalyst	Temp (^{o}c)	Order(n)	Rate constant (K)
$G_1Co_{1.58}Ag_{1.06}$	30	0.849	0.031
	40	0.844	0.048
	50	0.773	0.088
	60	0.529	0.094
	70	0.531	0.090

In this reaction, temperature plays an important role to accelerate the rate of reaction .With the increase of temperature, rate constant (K) is also increasing that indicates higher temperature favours reaction rate. Table 6 data denotes that between 30 to 60 ^{o}c temperature rate constant gradually increased, especially from 40 to 50^{o}c increment of K value is remarkable. Interestingly, the values of rate constant at 60 &70 ^{o}c are almost same that means after 60 ^{o}c temperature there is no such significant impact of temperature in reaction rate .So it can be concluded that 60 ^{o}c is the optimum temperature and this phenomenon is common to the other catalysts also.

5.1.2.5. POSSIBLE KINETIC RELATIONS OF HYDROLYSIS REACTIONS :

Graphene was produced only in 2004 so relatively it is newer in the research field. Therefore, the graphene-based catalysts that I developed, kinetic study of the hydrolysis reaction of these catalysts were done, as it would help in future to produce catalyst that is more effective and to predict suitable reactor design.

Hydrolysis reaction of Sodium Borohydride is given as---

$NaBH_4(as) + H_2O(liq) \xrightarrow{catalyst} NaBO_2(aq) + 4H_2(gas)\uparrow$ -----------(1)

Possible Mechanism: (Zhang et al., 2012)

$2M + BH_4^- \rightleftharpoons MBH_3^- + MH$ ------------ (2)

$MBH_3^- \rightleftharpoons BH_3 + M + e^-$ ------------- (3)

$BH_3 + OH^- \rightarrow BH_3OH^-$ ------------- (4)

$M + e^- + H_2O \rightarrow MH + OH^-$ ------------ (5)

$2MH \rightarrow 2M + H_2 \uparrow$ ----------- (6)

At first $NaBH_4$ in aquas solution depleted to Na^+ and BH_4^- ions .These borohydride ions than came in contact to the active site of bi metallic catalysts constituting metal hybrids and then the electron on the BH_4^- ion with one hydrogen atom is transformed to the neighbouring atoms. The cycle of charge deportation moves on through the repeating reaction

$$BH_3(OH^-) \rightarrow BH_2(OH^-)_2 \rightarrow BH(OH^-)_3 \rightarrow B(OH^-)_4$$

via the same mechanism as (2)-(4). Finally the $B(OH^-)_4$ reacts with Na^+ to produce $NaBO_2$. During experiment, it had been observed that reactivity of bi metallic catalyst is higher than monometallic catalyst and for various catalytic compositions activity varies. So our aim is to understand what the reason behind this is. The possible reasons are the size of metal particles, well dispersion and no. of electron transfer path. For bi metallic catalyst due to presence of two metal particles, electron may transfer simultaneously by two parallel paths in some extend similar to Langmuir - Hinshelwood kinetics. To determine the kinetic relation between reaction rate and borohydride concentration we will take help of Curve Fitting Toolbox of MATLAB.

A. Proposed Kinetic Equation for $G_1Co_{1.58}Ag_{1.06}$:

Many kinetic equations have been proposed to grasp the experimental result in theoretical point of view. As it is a catalytic reaction, so surface area of catalyst is one of the key parameter. Besides that many other parameters like temperature, loading of catalyst, composition of catalyst also play an important role for the behaviour of the catalyst. Below are discussed few kinetic equations which are best fitted to the experimental result.

(1) Exponential curve fitting:

Like Michaelis and Menten model[44] in enzyme-substrate reaction, a reactant and unoccupied catalyst site complex is presumed to grasp the reaction nature. Catalyst has many active sites where reactants are absorbed and form a complex, which in turn converted into product (H) and active site (M) -----

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MA \overset{k_2}{\rightarrow} M + H$$

Where A is the reactant and M is unoccupied catalyst site and k_1, k_{-1}, k_2 is rate constants. The rate equations can be written as ---

$$r_{MA} = k_1 C_A C_M - k_{-1} C_{MA} - k_2 C_{MA}$$

$$r_H = k_2 C_{MA}$$

$$\text{If } C_M^0 \text{ is the total catalyat sites then, } C_M^0 = C_M + C_{MA}$$

$$\frac{dC_{MA}}{dt} = k_1 C_A C_M^0 - (k_1 C_A + k_{-1} + k_2) * C_{MA}$$

Here C_A is a function of time and can be calculated from experimental data. So further rearrangement gives

$$\frac{dC_{MA}}{dt} + (k_{-1} C_A + k_{-1} + k_2) * C_{MA} = k_1 C_A C_M^0$$

$$or, C_{MA} = \frac{\int [k_1 C_A C_M^0 * \exp\left(\int (k_{-1} C_A + k_{-1} + k_2) dt\right)] \mathrm{dt}}{\exp\left(\int (k_{-1} C_A + k_{-1} + k_2) dt\right)}$$

Thus, we can spot that exponential term emanates in rate equation because of non-equilibrium nature. Therefore, an exponential term associated rate equation for hydrogen generation is favoured as narrated below-

$$-\frac{dC_{BH_4^-}}{dt} = K * C_{BH_4^-} * \exp\left(-b * C_{BH_4^-}\right)$$

where $C_{BH_4^-}$ is concentration of BH_4^- , K is rate constant and 'a' is another constant. Rate is in the units of mol/(lit*min)

In Fig-27, exponential curve fitting of $G_1Co_{1.58}Ag_{1.06}$ catalyst at different temperatures are portrayed and corresponding values of rate constant are given in Table-6**.**

Table 7: different parameters' values for Exponential curve fitting of $G_1Co_{1.58}Ag_{1.06}$ catalyst.

Catalyst	Temp(°c)	K	b	R²
$G_1Co_{1.58}Ag_{1.06}$	30	0.0415	0.298	0.9903
	40	0.0555	0.0936	0.9857
	50	0.152	0.597	0.9957
	60	0.207	0.801	0.9908

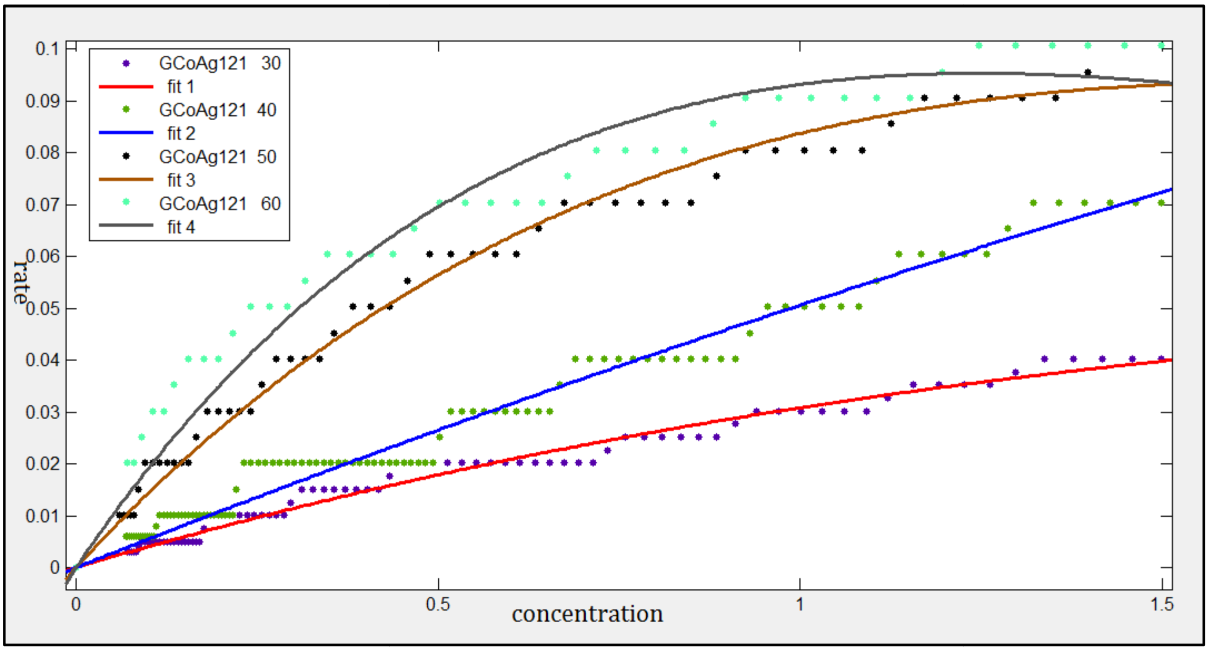

Fig 28: Exponential curve fitting of $G_1Co_{1.58}Ag_{1.06}$ at different temperatures**.**

(2) **Langmuir-Hinshelwood curve fitting :**

In 1916, Irving Langmuir established his model for the adsorption of species onto simple surfaces. Surfaces reaction is that type of reactions in which at least one step is the adsorption of one or more reactants. The reaction mechanisms and the rate equations involved in these types of reactions are extremely important for heterogeneous catalysis reaction [45].

If a reaction proceeds through this step: $A + S \rightleftharpoons AS \rightarrow \text{Products}$

Where, A is the reactant and S is an active site on the surface and the three rate constants are for the adsorption, desorption and reaction is k_1, k_{-1} and k_2 respectively. Now the overall reaction rate can be written as:

$$r = -\frac{dC_A}{dt} = k_2 C_{AS} = k_2 \theta C_S$$

where:

- r denotes the reaction rate, *conc./min*
- C_{AS} is the surface concentration of occupied sites, m^{-2}
- θ is the surface coverage, it is a dimensionless parameter
- C_s is the total number of sites (occupied or not), m^{-2}
- t is time, *min*
- k_2 is the rate constant for the surface reaction which is a rate determine step, s^{-1}.

  In case of limiting step reaction :

$$k_2 \ll k_1 C_A, k_{-1} \text{ so } \theta = \frac{k_1 C_A}{k_1 C_A + k_{-1}}$$

So Langmuir isotherm can be written as-- $r = \dfrac{K_1 k_2 C_A C_S}{K_1 C_A + 1}$

Where $K_1 = \dfrac{k_1}{k_{-1}}$; if we consider $k_2Cs = K$ and $K_1 = a$ then above equation can be arranged according to our practical experiment as---

$-\dfrac{dC_{BH_4^-}}{dt} = K * \dfrac{a * C_{BH_4^-}}{1 + a * C_{BH_4^-}}$; curve fitting graph and parameters value are presented below-

Table 8: Parameter's values of L-H kinetics of $G_1Co_{1.58}Ag_{1.06}$

Catalyst	Temp(°c)	K	a	R^2
$G_1Co_{1.58}Ag_{1.06}$	30	0.102	0.424	0.9911
	40	0.525	0.106	0.9857
	50	0.151	1.194	0.9975
	60	0.126	2.417	0.9978

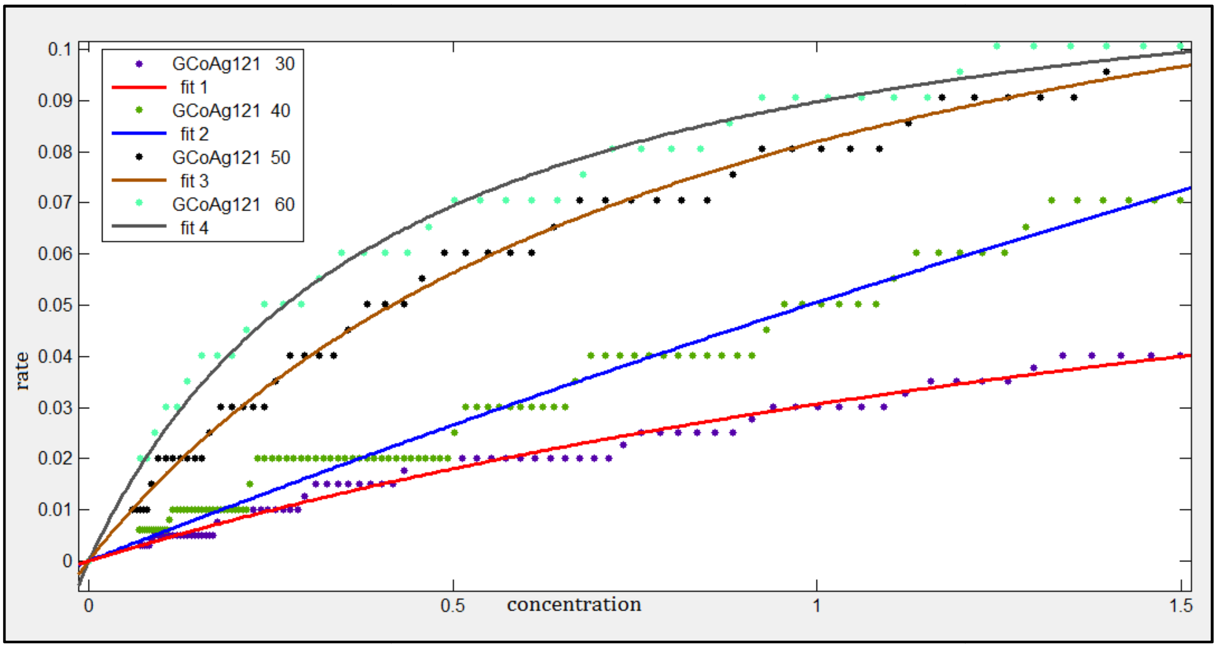

Fig29: L-H curve fitting of $G_1Co_{1.58}Ag_{1.06}$ at different temperatures.

Explanation of curve:

It is undoubtedly can be said from R^2 values (Table-8) that the speculated rate equation closely following the experimental result. Intent observation of K values i.e. product of surface reaction rate constant (k_2) and concentration of absorption site(C_s) reveal at 40 °C it has maximum value. On the other hand, $a=K_1=k_1/k_{-1}$ exhibits lowest value i.e. complex (AS) formation rate (k_1) becomes very slow at 40 °c. At 60 °c temperature though K=0.126 very low but at this temperature a=2.417 highest among the others. Large value of 'a' implies complex(AS) formation rate(k_1) is rapid but small value of K signals product formation rate (k_2) is very slow i.e. it is indeed rate determine step. Except 30 °c temperature 'a' is increased decently with the raise in temperature, affirms at higher temperature borohydride (BH_4^{--}) easily stuck to active site of catalyst and form borohydride-active site complex which later on oxidising yield H_2 and boron oxide (BO_2^-).

(3) Combine model of exponential and L-H :

From above two models, it can be extracted that hydrogen generation mechanism is following exponential as well as L-H model, but L-H model suited little bit better. Let us combine these two models and find out whether it is suitable or not. Combine model of exponential and L-H is written below---

$$-\frac{dC_{BH_4^-}}{dt} = \left(\frac{K*a*C_{BH_4^-}}{1+a*C_{BH_4^-}}\right) * \exp\left(-b * C_{BH_4^-}\right)$$

Table 9: Different parameters value for combine model of exponential and L-H of $G_1Co_2Ag_1$ catalyst.

Catalyst	Temp(^{o}c)	K	a	b	R^2
$G_1Co_{1.58}Ag_{1.06}$	30	-1.639	-0.0648	0.2959	0.9903
	40	0.9184	0.0383	0.3909	0.9648
	50	-0.9424	2.56	0.5663	0.9955
	60	-0.9226	2.689	0.804	0.9908

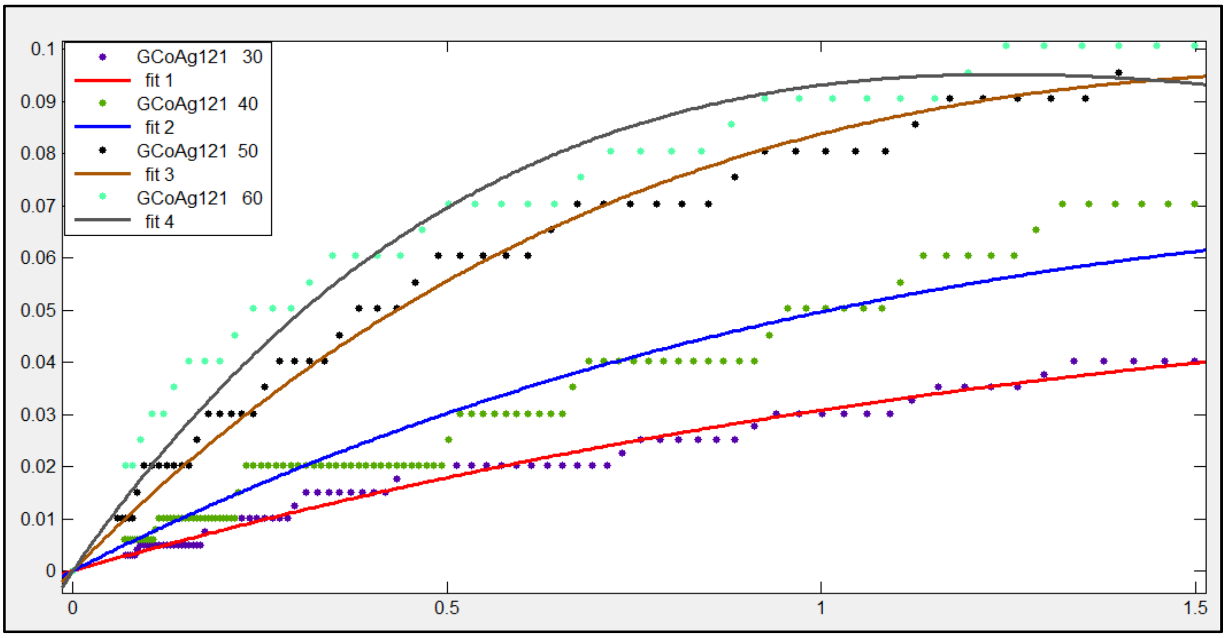

Fig 30: combined model curve fitting of $G_1Co_{1.58}Ag_{1.06}$ catalyst at different temperatures.

Explanation of curve:

R^2 values from Table-9 reveal that combine effect of Langmuir-Hinshelwood and exponential term is not fitting well like previous ones. Besides that most K values (except 40 ^oC) are coming in negative, practically it is impossible. So the simulated model cannot be considered for curve fitting.

(4) Two parallel L-H curve fitting:

As Langmuir-Hinshelwood model is fitting well for this reaction so an extended modelling equation i.e. parallel L-H model has been tested and the rate equation is given below--

$$-\frac{dC_{BH_4^-}}{dt} = K * \left[\frac{a*C_{BH_4^-}}{1+a*C_{BH_4^-}} + \frac{b*C_{BH_4^-}}{1+b*C_{BH_4^-}}\right]$$

Table 10: Different parameters value for two parallel L-H kinetics of $G_1Co_{1.58}Ag_{1.06}$

Catalyst	Temp(°c)	K	a	b	R^2
$G_1Co_{1.58}Ag_{1.06}$	30	0.04775	1.663	0.21	0.8112
	40	0.0339	22.06	0.6746	0.8381
	50	0.0587	89.93	0.5839	0.6951
	60	0.06782	318.8	0.6534	0.5997

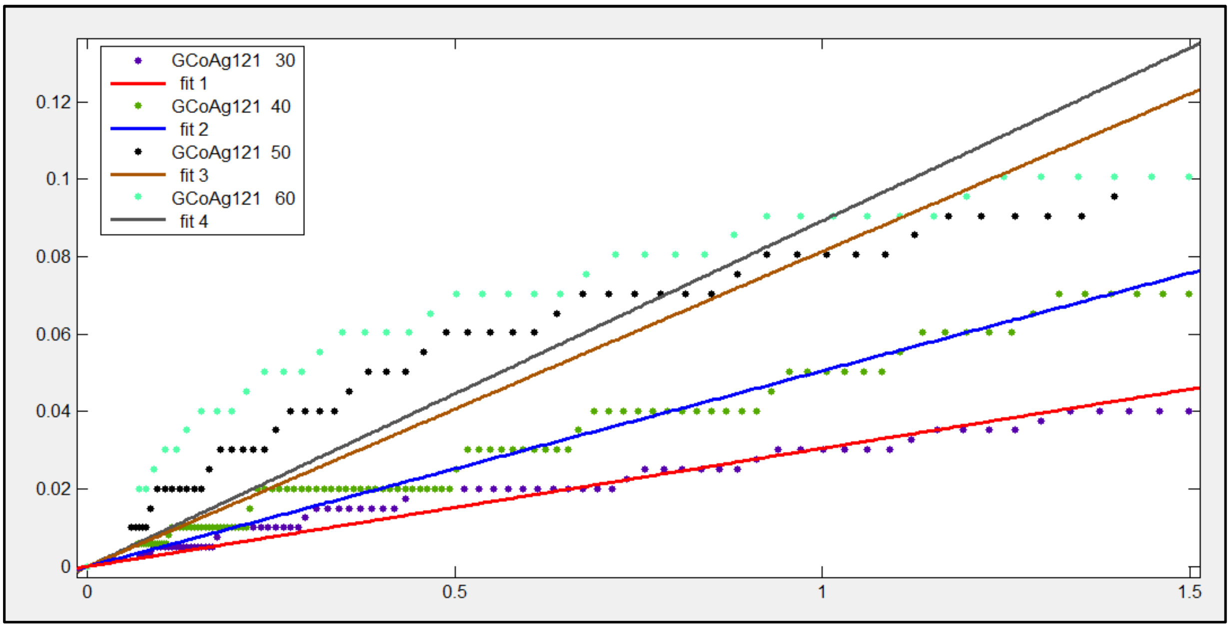

Fig-31: Two parallel L-H curve fitting of $G_1Co_{1.58}Ag_{1.06}$ at different temperatures.

Explanation of curve:

It can be stated from correlation co-efficient (R^2) values in Table-10 that the postulated model equation is not at all fitting with the experimental result and with the increase in temperature curve fitting is more deteriorating. Fig-31 shows how modelling curve is not following the practical trajectory. Probable reason of this may be at higher temperature metal particles coalescences and form single matrix which prevents propagation of two simultaneous reactions . So parallel L-H model shows poor fitting.

(5) Fitting for n^{th} order reaction:

When mechanism of the reaction is not known, we often attempt to fit the data with an n^{th} order rate equation of the form --

$$-\frac{dC_{BH_4^-}}{dt} = K * \left(C_{BH_4^-}\right)^n$$

Table 11: constants values of n^{th} order fitting $G_1Co_{1.58}Ag_{1.06}$

Catalyst	Temp(°c)	K	n	R^2
$G_1Co_{1.58}Ag_{1.06}$	30	0.0302	0.7823	0.9917
	40	0.0502	0.9069	0.9871
	50	0.0806	0.6055	0.9946
	60	0.0888	0.4482	0.9974

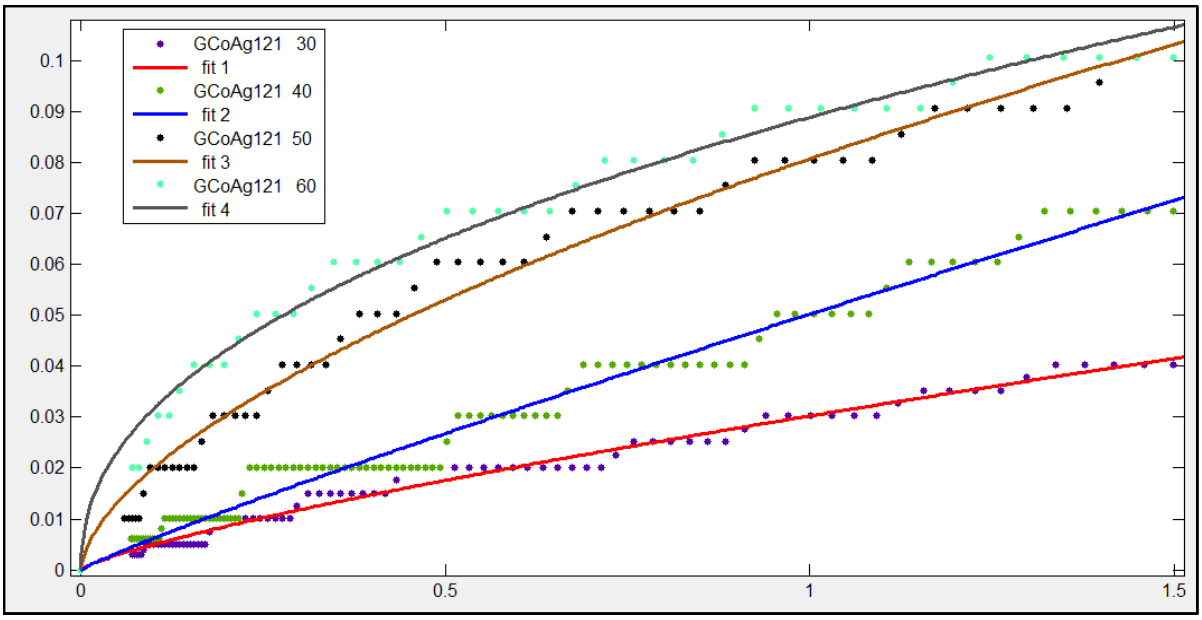

Fig 32: Fitting for n^{th} order reaction of $G_1Co_{1.58}Ag_{1.06}$ at different temperatures.

Explanation of curve:

From Table-11, it can be concluded that the order of the reaction (n) is less than one and when order falls in between zero to one it follows Langmuir-Hinshelwood model discussed earlier. Another interesting feature is that rate constant is increased with temperature i.e. higher temperature prefers fast reaction rate. One curious feature of this rate equation having order less than one can be stated that the reactant concentration will fall to zero and then become negative at some finite time. Since the real concentration cannot fall below zero we can not perform the integration beyond this time for n<1. In addition, as a consequence of this feature in real system the observed fractional order will shift upward to unity as reactant depleted.

B. Extract of Kinetics Study:

Among all the predicted kinetic models it is evident from curve fitting data and graph that L-H model is perfectly fitted with the experimental result. Therefore, the assumed reaction mechanism i.e. complex formation of borohydride and active site on catalyst may be right and the main reaction is taking place on the surface .Actually silver and cobalt particle forms different metal alloys on graphene sheet , which in term helps to bind borohydride ion (BH_4^-) in metal nano- matrix . As cobalt is transitional metal [d-block element, with general electronic configuration (n-1) d^{1-10} ns^{1-2}] so it has incomplete d-shell that helps it to be electro-chemically active towards borohydride by taking electron from borohydride ion. Absorbed electron may transfer from one metal grain to another and finally to the high conductive graphene sheet. As the number of electron transfer ways gets better in bimetallic catalyst so reaction rate also immensely improved.

Conclusion:

A terribly effective, reliable noble bimetallic nano-composite named as G-Co-Ag, is suggested to embellish hydrogen generation from hydrolysis of Sodium Borohydride under atmospheric situation. The investigation emphasizes on the comparative study of hydrogen formation from $NaBH_4$ using three different graphene based nano-hybrid catalysts, G-Co, G-Ag and G-Co-Ag. The catalysts were prepared applying chemical itineraries and delineated by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), High Resolution transmission electron microscope (HRTEM), Energy-dispersive X-ray spectroscopy (EDX), BET analysis and Atomic mass absorption spectroscopy. Both the HRTEM and XRD assessment disclosed the existence of bimetals Co and Ag on the graphene sheet really slash the grain size of Ag and Co compared to a monometallic nano-hybrid catalyst G-Co and G-Ag respectively. Moreover, in case of a bimetallic graphene supported catalyst the number of possibilities of electron movement of ions to adjoining metal atom increases, which may enhance its activity

Numerous kinetic model equations have been proposed for the hydrolysis of sodium borohydride ($NaBH_4$) supported by graphene based bimetallic nano-composite ($G_1Co_{1.58}Ag_{1.06}$) and equations are fitted with the experimental data by the help of MATLAB curve fitting tool. Here kinetic study has been done only for the best catalyst ($G_1Co_{1.58}Ag_{1.06}$) and among various models , Langmuir Hinshelwood model provides the best fit for hydrolysis reaction using $G_1Co_{1.58}Ag_{1.06}$ catalyst. The experimental rate curves for the reaction using $G_1Co_{1.58}Ag_{1.06}$ is found to be convex upward and with the raise in temperature, the curvature becomes more.

Lamentably with many probable experimental flaws during experimental work, we cannot eliminate these due to our limitation and many more experimental and theoretical efforts are required to grasp the phenomena of Graphene based bimetallic catalytic reactions more thoroughly.

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