

Photocatalytic Conversion of Biomass Derived Oxygenated Compounds over Titania Supported Metal Catalyst

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Department of Chemical Engineering

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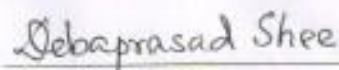
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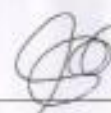
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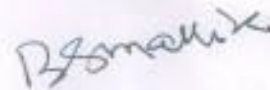
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Dedicated to

My Family

Abstract

Fossil fuels (coal, natural gas, crude oil) play an important role as an energy source and in the production of many chemicals. The world is completely dependent on this non-renewable energy source which can be depleted in very nearby future. Carbon dioxide one of the main sources of the greenhouse gases is emitted by the use of these fossil fuels. Global energy crisis and limited supply of petroleum fuels have rekindled the worldwide focus towards development of a sustainable technology for alternative fuel production. The advantage of biomass and its derivatives are they emit no net greenhouse gases because a natural cycle is maintained in which the carbon is extracted from the atmosphere during plant growth and released during H_2 production. In the class of alternative fuels H_2 is considered to be ideal, clean and climate-neutral with virtually zero emissions of air pollutants and carbon dioxide. H_2 is widely anticipated to be a key energy carrier within a future low carbon energy economy. Potential uses of H_2 as a fuel cell feedstock abound within the transport, remote and distributed generation sectors. It can be produced by various methods like steam reforming, electrolysis etc. which are highly energy intensive. The photo catalysis to split water molecule in the presence of sunlight is an alternative process of production of H_2 . In this process, oxygenated compound (known as sacrificing agent) which act as a hole scavengers is used as feedstock. These sacrificing agents are derived from biomass and the process is environmental friendly and low cost. Photo catalytic reactions were carried out in an outer-irradiation photo reactor using Ni, Cu, Cr, V, Mn, Co supported Titania as catalyst at ambient temperature. The Mesoporous Titania was synthesized using templating technique. The metal supported Mesoporous Titania and P25 Titania catalysts with different loadings were prepared using wet impregnation method. The prepared catalysts were characterized using XRD, BET, Pulse chemisorption, and TPR, FTIR, UV-VIS-NIR, TGA techniques.

Nomenclature

P25	Commercial TiO ₂
TiO ₂	Titanium Dioxide
TEOA	Triethanol amine
FTIR	Fourier transform infrared spectroscopy
TGA	Thermo gravimetric analysis
H ₂	Hydrogen
Meso Ti	Mesoporous Titanium Dioxide
h	Planks constant = 6.62×10^{-34} Joules sec
c	Speed of light = 3.0×10^8 meter/sec
λ	Cut of wavelength= 410.57×10^{-9} meters
3NiTi	3 wt% Ni loaded on P25
3CuTi	3 wt% Cu loaded on P25
3CrTi	3 wt% Cr loaded on P25
3VTi	3 wt% V loaded on P25
3MnTi	3 wt% Mn loaded on P25
3VmTi	3 wt% V loaded on Meso Ti
3NimTi	3 wt% Ni loaded on Meso Ti

List of Tables

- 1.1 Different routes for Hydrogen production
- 1.2 Semiconductors with band gap energies
- 2.1 Summary of literature review using different sacrificing agents and catalysts
- 3.1 Calculation of band gap energy
- 4.1 BET surface area of the synthesized catalysts
- 4.2 Band gap energy of different catalysts and supports

List of Figures

- Fig 1.1 Energy Consumption by Energy source
- Fig 1.2 Principle of water splitting using semiconductor photo catalyst
- Fig 1.3 Band positions of several semiconductors in contact with aqueous solution at pH 1 and their band gap energies.
- Fig 1.4 Mechanism of TiO₂ photocatalysis
- Fig 2.1 Overview of project
- Fig 3.1 Image of photo reactor
- Fig 3.2 Schematic of photo reactor
- Fig 4.1 Nitrogen Adsorption– desorption isotherm
- Fig 4.2 XRD Results
- Fig 4.3 TPR Results of bi-metallic catalysts
- Fig 4.4 UV-Vis-NIR absorption spectra for supports (P25 and Meso Ti) and catalysts 3NiTi, 3CuTi, 3CrTi, 3MnTi, 3VTi.

Fig 4.5 Different concentrations (weight %) of glucose on photo catalytic reaction.

Conditions: Weight of catalyst= 0.5gP25, temperature=ambient, magnetic speed=1200 rpm, Halogen lamps (2 lamps each of 150W)

Fig 4.6 Different weights of catalyst on photo catalytic reaction. Ambient temperature, magnetic speed=1200 rpm, Halogen lamps (2 lamps each of 150W)

Fig 4.7 Effect of various mono and bimetallic catalysts on photo catalytic conversion of glucose. Conditions: catalyst weight=0.5g, catalyst loading is 3 wt%, glucose =5wt%, magnetic speed=1200 rpm, at ambient temp, halogen lamps 2 (each of 150W)

Fig 4.8 Effect of various metals on TiO₂ (P25) support on photo catalytic conversion of glucose. Conditions: catalyst weight=0.5g, catalyst loading=3 wt % glucose =5wt%, magnetic speed=1250 rpm, at ambient temperature, Halogen lamps 2 (each of 150W)

Fig 4.9 Effect of various metals on mesoporous titanium dioxide support on photo catalytic conversion of glucose. Conditions: catalyst weight=0.5g, glucose =5wt%, magnetic speed=1200 rpm, at room temperature, halogen lamps 2 (each of 150W)

Fig 4.10 FTIR spectra of Fresh and Spent TiO₂ (P25) Support

4.11 FTIR spectra of Fresh and Spent Meso Ti Support

4.12 FTIR spectra of Fresh and Spent 3V/Ti catalyst

4.13 Gaseous product analysis by Gas Chromatogram

Contents

Declaration.....	Error! Bookmark not defined.
Approval Sheet	Error! Bookmark not defined.
Acknowledgements.....	iv
Abstract.....	vi
Nomenclature	Error! Bookmark not defined.
1 Introduction	
1.1 Background & Motivation	1-2
1.1.1 Fuel - Hydrogen	2-12
2 Literature Review	13-20
2.1 Summary	20-24
2.2 Objectives	25-26
3 Experimental Section	
3.1 Materials and Methods	
3.1.1 Preparation of Mesoporous Titania	27
3.1.2 Catalyst preparation by Wet Impregnation method	27-28
3.2 Catalyst Characterization	
3.2.1 BET surface area measurement and pore size distribution	28-29

3.2.2 X Ray diffraction	29
3.2.3 Temperature Programmed Reduction	29
3.2.4 UV-VIS Spectroscopy	29-30
3.2.5 FTIR Analysis	30
3.3 Photocatalytic Hydrogen generation	30-32
3.4 Analysis of Product	32
4 Results and Discussion	
4.1 BET surface area measurement and pore size distribution	33-35
4.2 X Ray diffraction	36
4.3 Temperature Programmed Reduction	37
4.4 UV-VIS-NIR	38-40
4.5 Photocatalytic H ₂ generation	
4.5.1 Effect of different concentrations of glucose in photocatalytic H ₂ generation	40
4.5.2 Effect of various metals on photocatalytic H ₂ generation	41
4.5.3 Effect of catalyst weight on photocatalytic H ₂ generation	42
4.5.4 Effect of supports on photocatalytic H ₂ generation	42-43
4.5.5 Effect of different metals on photocatalytic H ₂ generation	44

4.6 FTIR Analysis	47-50
Conclusions	51
Future Work	52
Reference	53--57

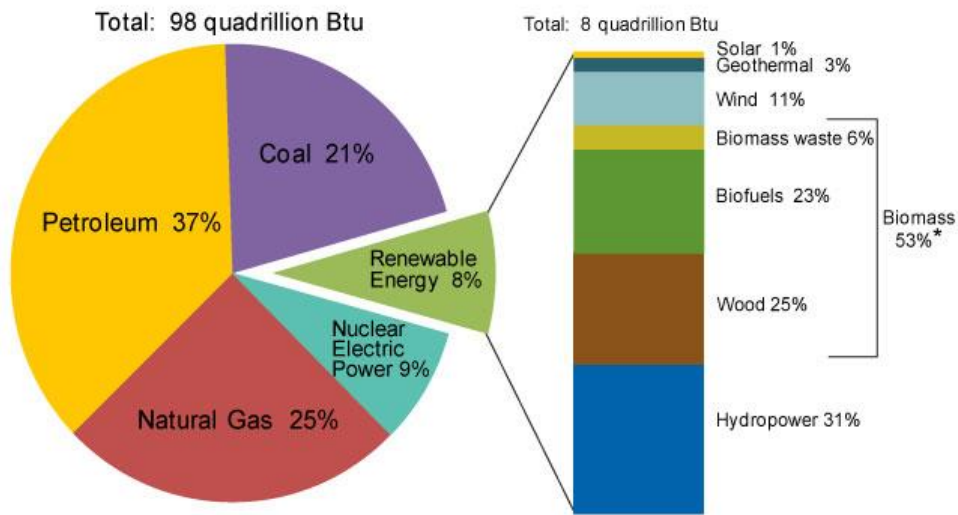
Chapter

INTRODUCTION

1.1 Background & Motivation

Fossil fuels (coal, natural gas, crude oil) play an important role as an energy source and in the production of many chemicals. The world is completely dependent on this non-renewable energy source which can be depleted in very nearby future [Yasuno Izumi et al., 2013]. Carbon dioxide one of the main sources of the greenhouse gases is emitted by the use of these fossil fuels. This tremendous increase in the CO₂ has an effect on the environment and causes the global warming [Momirlan et al., 2005]. The depletion of fossil fuel reserves and the environmental problem due to the excessive use of the fossil fuels accelerate the development of well-grounded technology for energy production. Again with the declining oil reserve the extraction of the remaining oil will be more complicated considering the economical and technological difficulties, and consequently the energy requirement for obtaining oil will become significantly higher than the energy output from fuel.

U.S. Energy Consumption by Energy Source, 2010



* Note: Sum of biomass components does not equal 53% due to independent rounding.
Source: U.S. Energy Information Administration, Monthly Energy Review, Table 10.1 (June 2011), preliminary 2010 data.

Fig1.1 Adopted from U.S Energy Consumption by Energy Source, 2010.

1.2 Fuel - Hydrogen

Modern society is looking for a clean, renewable, cheap and a possible alternative to fossil fuels. Many efforts are being made to fulfil the requirement using renewable energies like biomass, sun-energy, wind energy. Biomass which is one of the sources of renewable energy has been used for generating heat, electricity, and in the transportation of the fuels in liquid form. The advantage of biomass and its derivatives are they emit no net greenhouse gases because a natural cycle is maintained [X.Chen et al., 2008].

In the class of alternative fuels H_2 is considered to be ideal, clean and climate-neutral with virtually zero emissions of air pollutants and carbon dioxide. [R.Ramachandran et al., 1998]. H_2 is also the most abundant element in the universe and is contained in the large amounts of many chemical compounds, biomass and hydrocarbons. H_2 has been identified as a potential energy carrier [M.Ni et al., 2006]. H_2 can be produced in many ways. H_2 is widely anticipated to be a key energy carrier within a future low carbon energy economy. One of the forces driving changes in the international energy economy is an increasing concern about the implications of CO_2 release into the atmosphere. Global emissions of carbon dioxide are predicted to increase to 33.7 billion tonnes/year from 25.0 billion tonnes/year from 2003 to 2015. The use of H_2 as a potentially carbon-free fuel is one possible response to this situation. H_2 contains more energy per unit mass than any hydrocarbon fuel. Water is the only waste product when it is burnt in either a specially designed engine or a fuel cell.

Traditionally H_2 is produced from steam reforming which produces a large amount of CO_2 . Steam reforming of natural gas is a proven technology that can be used in for the production of H_2 . However, because of the associate to carbon emissions, and being an endothermic reaction which requires large amount of energy, large scale H_2 production based on natural gas cannot be considered as a clear or sustainable supply. The production of H_2 from the renewable energy sources is given much more importance [David B.Levin et al., 2009].

Among the various sources of renewable energy, biomass provides today the largest contribution to the worldwide energy supply. Biomass is formed by organic

compounds originally produced during the process of plant photosynthesis. Thus, biomass resources consume CO₂ from the atmosphere as part of their natural growth process. Since CO₂ in the atmosphere theoretically remains constant in this cycle, producing H₂ from biomass can be considered neutral in term of greenhouse gas (GHG) emissions [R. M. Navarro et al.,2008].Pyrolysis, Gasification, Liquification are the main process for the production of H₂ using the Biomass. H₂ can also be produced from the biomass derived components like Bio-ethanol, Bio-diesel and Bio-gas.

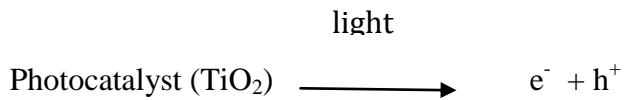
Among recent technology developed production of H₂ from aqueous phase reforming is one of the fine technology. Moreover the catalyst used in this process is not stable. In the long term H₂ can also be produced using steam reforming using oxygenated hydrocarbons like methanol, glycerol, glucose using a wide variety of temperatures and catalyst. [Davda et al., 2005].Another method available to produce H₂ is via Photolytic process. Photolytic process uses the light energy to dissociate the water to produce H₂ and oxygen. This process is in the early stage of research but offer long-term potential for sustainable H₂. The work is first pioneered by Akira and Fujishima in the early's of 70's using a metal oxide based semiconductor as a catalyst [L.S Al-Mazroai et al., 2007].

Table 1.1 Different route for H₂ production

H₂	production routes	Advantages	Disadvantages
Steam reforming of methane		Least expensive (48 % of world H ₂ produced by this route)	Generation of greenhouse gases and Endothermic reaction
Gasification of coal		Only competitive with methane reforming where natural gas is expensive.	Generation of Carbon dioxide, Less efficient.
From biomass		Less expensive raw materials.	Little contribution (4%) towards world H ₂ production.
Electrolysis		Cost effective for production of extremely pure H ₂ in small amount.	Electrolysis is very much expensive at large scale.
Solar and wind power based electrolysis		Less expensive than conventional electrolysis.	Still in developing stage.

Photocatalysis is defined as the phenomena in which the photons are used to accelerate the reaction [A.Fujishima et al., 2000]. Photocatalyst substrates are generally semiconductors due to their electronic structure. Semiconductors have a band structure in which the conduction band and the valence band are separated

from each other with a suitable width called Band gap or Band energy. When an energy equal or greater than that of the band energy is given the electrons and the holes are being generated in the conduction band and valence band respectively [A.Kudo et al., 2009].



These causes the redox reactions in which the water molecules are reduced to form H₂ by electrons and oxidized to form the Oxygen by the holes.

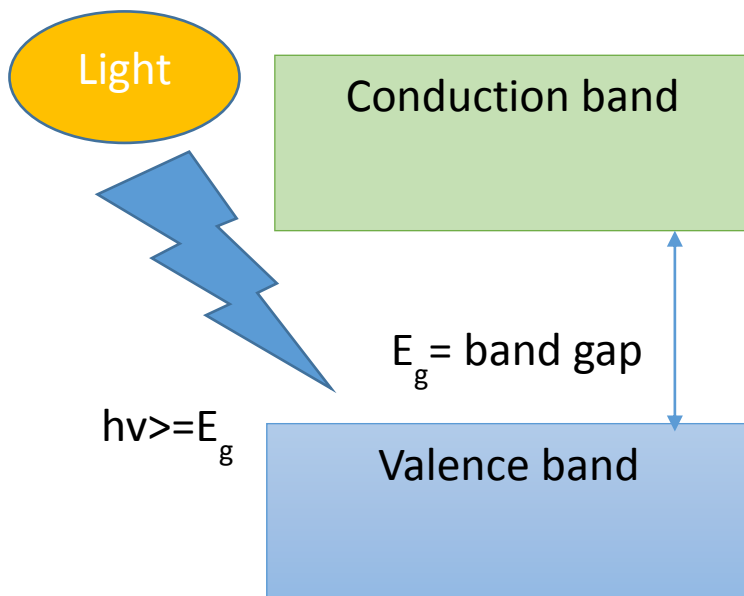


Fig.1.2 Principle of water splitting using semiconductor photocatalyst.

From last few decades after the inception of this process many oxide and non-oxide photo catalysts were discovered. The band gap of the semiconductor is the important. The bottom level of the conduction band has to be more negative than

the redox potential of H^+/H_2 and the top level of the valence band should be more positive than the redox potential of O_2/H_2O . Various semiconductors with their band gap energies is shown below in table 1.2.

Table 1.2 Semiconductors with band gap energies

Semiconductor	Band gap energy (eV)
SnO ₂	3.8
TiO ₂	3.0
ZnO	3.2
ZnS	3.7
CdS	2.5
GaP	2.3
WO ₃	2.8
Fe ₂ O ₃	2.3
SrTiO ₃	3.2

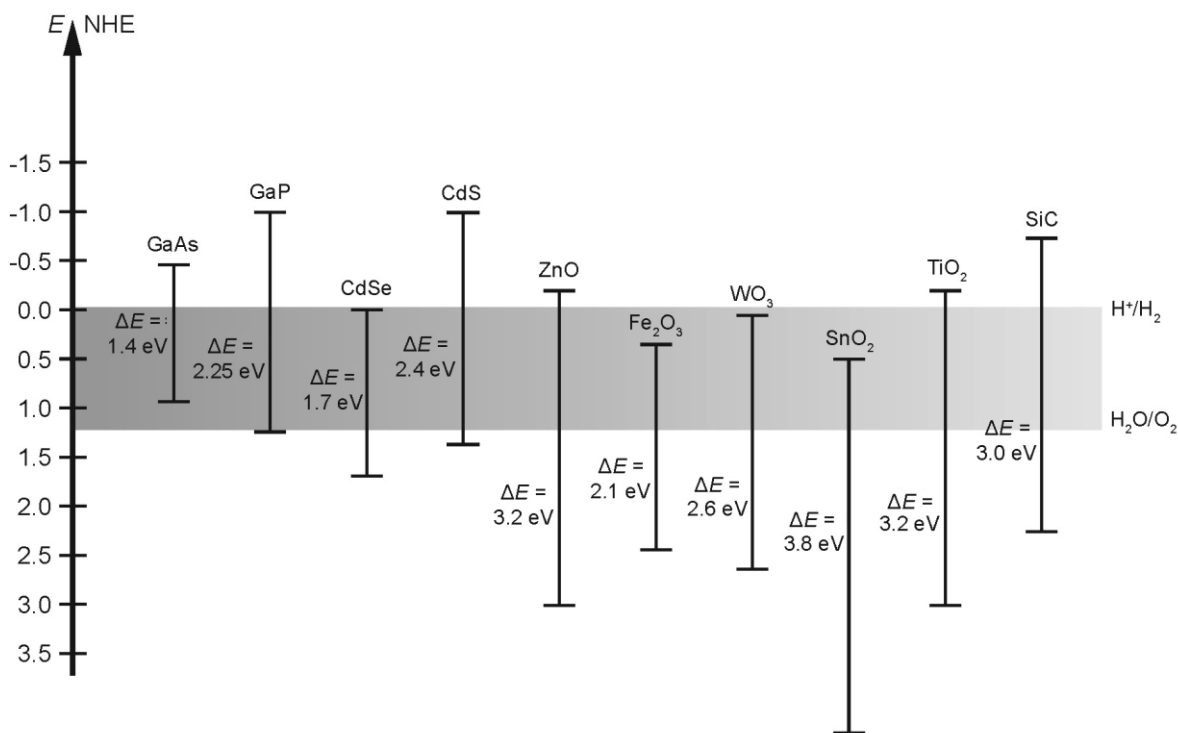


Fig 1.3 Band positions of several semiconductors adopted from [Marcos de et al., 2011].

Heterogeneous photo catalysts are solids that can promote reactions in the presence of light not being consumed in the overall reaction. Catalysts used in photo catalytic reactions are invariably semiconductor materials. The semiconductors used as photo catalysts include several metal oxides such as TiO_2 , ZnO , ZrO_2 , Fe_2O_3 , CeO_2 , WO_3 , etc. or even sulfides like CdS , ZnS , MoS_2 and CdS . An ideal photocatalyst should possess the following characteristics: i. photoactive; ii. have the ability to be excited with visible and/or near UV light; iii. Biologically and chemically inert; iv. Photos table (*i.e.*, not prone to photo corrosion); v. inexpensive

and vi.non-toxic. Furthermore, in order to a catalyst to be photo chemically active as a sensitizer, the redox potential of hydroxyl radical should lie in the band gap of the semiconductor.

Nonetheless, some of the semiconductor catalysts do not show long-term stability in aqueous media. Metal semiconductors such as CdS, CdSe and PbS are regarded as insufficiently stable for catalysis in aqueous media, since they readily undergo photo anodic corrosion, which can only be partly suppressed by the addition of sulfide and sulfite to the contacting solution. These materials are also known to show some toxicity. Although ZnO and TiO₂ have similar bandgap energies (3.2 eV), zinc oxide shows some instability in illuminated aqueous solutions, with Zn(OH)₂ being formed on the particle surface leading to the deactivation of the catalyst. WO₃ has also been investigated as photo catalyst [B.Ohtani et al., 1997]. However, it is generally less photo catalytic active than TiO₂.

Among the various catalyst discovered so far TiO₂ has received a high attention and been used widely as a photocatalyst because this catalyst has a specific characteristics like chemically stable, cost effective, resistive to corrosion, eco-friendly, widely abundance of material, non-toxicity.[K.Conelly et al., 2012, M.Ni et al., 2007].Moreover, TiO₂has a wide band gap energy of 3.0 ~ 3.2 eV which is prevents the utilization of the visible-light, which accounts the main source of the sun light. TiO₂ is active under UV light which consists 4% of the solar light [T.Ochiai et al., 2012]. Secondly, TiO₂ has other disadvantage like fast electron hole recombination. More recently, many efforts are been made to modify the

semiconductor photo catalysts to increase the efficiency and to suppress these fast backward reactions. Various kinds of modifications, such as deposition of the metal ion, adding of the sacrificial agents, doping of cation or anion, sensitization with organic dyes etc., enhances the activity of the semiconductor based photo catalyst [P.Gomathisankar et al., 2013]. The addition of the sacrificing agents which acts as an electron donors or hole scavengers, addition of carbonate salts and doping the photo catalytic production of the H₂ is enhanced reportedly [N.Luo et al., 2009, Meng et al., Nianjun et al.,2009, M.NI et al., 2007].

When the photo catalytic reaction is carried out in an aqueous solution such as Methanol, Glucose and sulphide ion, [N.Luo et al., 2009 GuoPeng et al., 2008, P.Gomathisankar et al., 2013] the photo generated holes irreversible oxidize the reducing reagent instead of reducing the water. It enriches electrons and enhances the production of H₂. Using sacrificing agents from renewable sources like biomass and abundant compounds in nature as reducing reagents is one of the reason for making this process an ideal with high H₂ selectivity [A.kudo et al., 2009]. When these oxygenated hydrocarbons are used as sacrificing agents they act as electron donors which enhances the yield of H₂.

The other method used to enrich the selectivity of H₂ is by deposition of the metal ions and transition metals as Pt, Pd, Rh, Au, Ag, Ni, Cu [K.Conelly et al., 2012, H.Yan et al., 2009, S.Ikeda et al., 2001]. The challenging factor in TiO₂ is bang gap narrowing and decreasing the electron-hole recombination rate. Doping is one of the technique used to overcome this issue up to some extent. Doping means adding or injecting an impurity to the material. Dopants will form the mid gap states

between the conduction and valence bands and lowers the band gap. It will act as electron and hole traps, which reduces the surface recombination [Adriana 2008]. By incorporation of Metal dopants like Mo, Nb, Fe, Ru, Au, Pt, Pd, Ni, Mn, Cu, Co, V and Non-metal dopants like N, S, C, B, P, I, F [Ariana 2008, R.Aashinet al 2009]. When TiO₂ is doped with a metal ion a new energy level is produced in the band gap. The Fermi levels of these metals are comparatively low when compared to that of the TiO₂. The photo generated electrons in the conduction band is transferred to the conduction band of the metal or transition metals and thus the trapping of the electrons is done to inhibit the electron-hole recombination which results in enhancing the photo activity. The mechanism of the metal ion and non-metal ion doping is shown in the Fig.1.3

Quite a good amount of researchers are working hard for the tunable band gap of TiO₂ to enhance the activity. Most research has been done on metal loading Pt, Pd, Rh, Au, [K.Conelly et al.,2012, P.Wei et al., 2013, H.Yan et al., 2009] since these are very expensive an alternative, cheap metals like Ni, Cu, Ag are also been thoroughly investigated [L.Kokporka et al., 2012] and expected to be the promising materials to improve the photo catalytic activity.

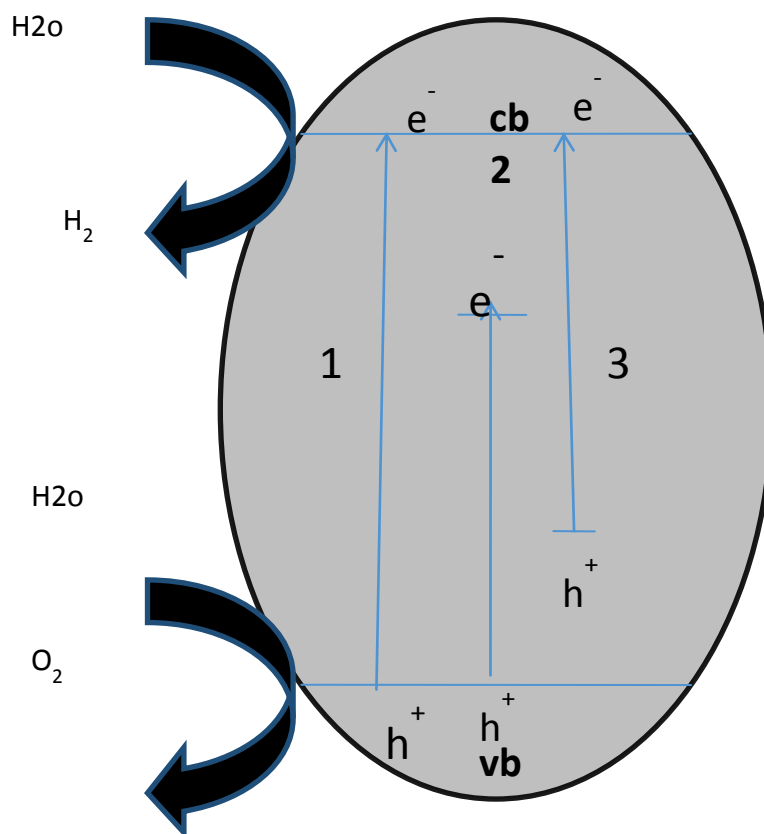


Fig 1.4 Mechanism of TiO₂ photocatalysis: 1:- $h\nu_1$: pure TiO₂; 2:- $h\nu_2$: metal doped TiO₂; 3- $h\nu_3$:non-metal doped TiO₂ (adopted from A.Zaleska, 2008).

Chapter2

LITERATURE REVIEW

N.Luo et al [[N.Luo et al., 2009](#)] studied the effects of different doping atoms on TiO_2 . They studied the effect of Nitrogen (N) and Boron (B) doped on TiO_2 for the production of H_2 using oxygenated compounds like glycerol, glucose and sucrose. These oxygenated hydrocarbons are acting as sacrificing agents in the production of H_2 under visible light. The photo catalytic reaction was performed using different concentrations of glycerol. They reported that the amount of H_2 produces with pure water without the aid of any sacrificing agent was low, but with the addition of glycerol, the H_2 evolution increased with the irradiation time. From the results, it was found that the glycerol produced higher amounts of H_2 when compared to that of glucose and sucrose under same conditions.

The photo catalytic production of H_2 with metal deposition on TiO_2 using aqueous glucose solution was studied by P.Gomathisankar et al [[P.Gomathisankar et al., 2013](#)]. In this they reported that the H_2 production was very little with pure TiO_2 . On simultaneous aid of metal deposition and from glucose which acts as feed and electron donor, the H_2 production was increased significantly. They deposited Au/Pd on TiO_2 . They reported that the metal-deposition significantly promoted the electron transfer and suppressed the recombination of photo generated electrons and holes. Under the optimal conditions with Au and Pd depositions the evolution of H_2 is about 203 and 362 times more than that of the pure TiO_2 .

The production of the H₂ over TiO₂ nanoparticles with mesoporous structured catalyst with the aid of different sacrificial agents such as methanol (CH₃OH), CH₂O, Na₂S was studied by H.Yi et al [H.Yi et al., 2007]. Among all the sacrificing agents used they reported that the methanol is more efficient when compared with the rest. The evolution of H₂ increased with the increase in the concentration of methanol. Pt loaded TiO₂ has shown the better result when compared to that of bare TiO₂.

Zheng XJ et al [Zheng XJ et al., 2010] photo catalytic H₂ production from acetic acid under Cu/SnO₂. The catalyst was prepared using simple co-precipitation method. The experiment was carried out at room temperature. The effects of CuO loading, concentration of acetic acid and production of H₂ was studied. They reported that when compared to pure SnO₂, the 33.3 mol% CuO/SnO₂ showed nearly twenty times enhancement in the H₂ production. They also reported that the method of catalyst preparation was simple and economical and will find many uses in the nearby future.

D.Jing et al [D.Jing et al., 2005] studied on the photo catalytic production of the H₂ using Ni doped mesoporous titania. They reported that the H₂ evolution from the aqueous methanol solution is mainly dependent upon the percentage of the Ni dopant. Doping of 1% of Ni showed the highest yield of H₂ wherein 3% of doping has the highest surface area for mesoporous titania but the selectivity of H₂ is comparatively low.

K.Connelly et al [K.Connelly et al., 2012] has conducted a couple of experiments with different phases of TiO₂ i.e., anatase and rutile phase and

compared with the P25 with and without Au metal loading using (0.5 vol%) of the ethanol as a sacrificing agent. The catalyst was synthesized by deposition-precipitation method. They reported the yield of rutile decrease while the yield of anatase increased with the increased Au loading. The quantum yield of the P25 was found higher than compared to anatase. This shows the synergistic effect of both the phases.

Nae-Lih Wu et al [[Nae-Lih Wu et al., 2004](#)] studied the effect of Cu particles on TiO₂ by Incipient-Wetness Impregnation method which is followed by the calcination at lower temperature (673 K) and reduction which led to the significant increment in the photo catalytic activity of TiO₂ for H₂ from aqueous methanol solution. They reported Cu containing TiO₂ catalysts is well known for the reduction of CO₂ but in the case of production of H₂ it is not so well known. The deposition with Cu particles on TiO₂ for the production of H₂ from methanol is greatly enhanced because they were oxidized and self-regulated to achieve the minimal valence for maximum activity.

Liu, Shou-Heng et al [[Liu, Shou-Heng; et al., 2012](#)] studied the behavior of the N-doped mesoporous TiO₂ nanoparticles for the photo catalytic water splitting in visible light. They reported the yield of H₂ is relatively high by doping with the N. They prepared N-doped mesoporous titania using evaporation induced self-assembly. They reported this enhancement of the H₂ production is due to the high mesoporous of samples and N-doping which made the catalyst active under the visible-light.

T.Kawai et al [T.Kawai et al., 1980] studied the photo catalytic conversion of H₂ from liquid methanol. The catalyst was prepared by mixing powdered TiO₂ with powder Pt, Pd or RuO in agate motor. RuO₂-TiO₂-Pt showed the highest yield of H₂ from methanol when compared to pure TiO₂ and individual metal ion depositions.

Y.Ikuma et al [Y.Ikuma et al., 2006] studied the effect of noble metal loading of H₂ by a TiO₂ photo catalyst. They used Pt incorporated on TiO₂. They used three different methods for the preparation of catalyst, H₂ reduction method, photo catalytic method and formaldehyde method. The highest rate of H₂ was produced in the formaldehyde method in which Pt is deposited on TiO₂.

T.Sreethawong et al [T.Sreethawong et al., 2005] has studied the Photocatalytic evolution of H₂ from water and methanol system with the Mesoporous TiO₂ catalyst by doping with different metals like Cu, Pd and Au. The catalysts were prepared using Single step sol gel process with the surfactant template. They reported the comparison of optimum loading contents of the cocatalysts was chiefly studied on the Mesoporous TiO₂. Among photo catalysts, 2 wt% Au supported on Mesoporous TiO₂ exhibited the highest photo catalytic H₂ evolution activity.

V.Lanese et al [V.Lanese et al., 2013] studied the production of H₂ through the photo reforming of the formic acid using Cu/TiO₂/Cl under UV simulated solar radiation at room temperature. They coupled Cu/TiO₂/Cl. They reported that the results with the aid of the combination of the system (Cu/TiO₂/Cl) with formic acid, and the interaction between these species gave an unexpected result. H₂ production is also observed at prolonged reaction times.

S.Xie et al [S.Xie et al., 2013] has described the H₂ production from solar energy driven glucose using TiO₂ nanowire arrays without the use of the expensive metals like Pt, Pd and Au. They used Ni (OH)₂ which showed good oxidizing potential for glucose. Electron-reduction through this process is effective approach for the production of H₂ using a sacrificial agent they stated.

G.Sadanandam et al [G.Sadanandam et al., 2013] studied cobalt doped TiO₂ photocatalyst for H₂ production using glycerol as sacrificing agent. Cobalt doped TiO₂ photo catalysts are prepared by impregnation method. Maximum H₂ production of 220 m mol h⁻¹ g is observed on 2 wt% cobalt doped TiO₂ catalysts in pure water under solar irradiation. A significant improvement in H₂ production is observed in glycerol: water mixtures; and maximum H₂ production of 11,021 m mol h⁻¹ g is obtained over 1 wt% cobalt doped TiO₂ in 5% glycerol aqueous solutions.

2.1 SUMMARY

Many researchers have put a great effort to enhance the yield of the H₂, which is considered to be clean fuel through the photocatalysis. The different types of photocatalyst has been shown in Table 1.2. In the class of semiconductors TiO₂ is been used as photocatalyst for various applications. The modification of the catalyst used in the photocatalyst plays a vital role. These modifications include noble or transition metal doping, adding sacrificial agents. The most commonly used metals for the doping are Pt, Pd, Ru, Au, Ni, Cu, Rh [T.Kawai et al., 1980, J.Greaves et al., 2006, D.Jing et al., 2005]. Many researches also produced catalysts with two different metals such as Pd-Au, Pd-Pt, Ni-Cu, Pt-Ru [T.Kawai et al., 1980], also showed a great result for the production of the H₂. The efficiency of these catalyst

depends upon the calcination temperature, amount of metal loadings, concentration of sacrificial agents, irradiation time and pH. Among the different types of the metal dopants Pt, Au, Ru are most commonly used due to their high production of H₂, and also reducing the backward reaction. So far many researchers discovered many sacrificing agents which considerable effect the H₂ production like methanol, ethanol, glucose, glycerol, acetic acid, 1-propanol, 2-propanol, 1-butanol, dimethyl formamide, trietanolamine [T.Sreethawong et al., 2007, P.Zeng et al., 2011, Nae-Lih Wu et al., 2004, J.Greaves et al., 2006, K.Connelly et al., 2012]. Among various types of sacrificial agents methanol is proved to be more efficient as an electron donor. Studies have also been carried out for non-metal doping of TiO₂ in which they used N, C, B, S, W. Among these N has been regarded as the best dopant [R.Aashi et al., 2009]. The combination of these dopants were also been studied by many of the researchers which showed a high selectivity for H₂.

Table 2.1 Summary of the literature using different sacrificial agents and catalysts

Sacrificing agents	Catalyst	References
Sulphite ion solution.	Fe ₂ O ₃ /ZnS & CdS	V.Preethi et al., 2013
Methanol	Au/TiO ₂	J.A.Ortega Mendez et al., 2014
Glycerol	Co/TiO ₂	G.Sadanandam et al., 2013

Triethanolamine (TEOA)	Ni@C/TiO ₂	P.Zeng et al., 2011
Methanol	Annealed TiO ₂	G.Xin et al.,2013
Methanol	Pd/TiO ₂ , Au/TiO ₂	L.S. Al-Mazroai et al., 2007
Methanol	Au/TiO ₂	J.Greaves et al 2006
Glycerol	Pt/TiO ₂	N.Luo et al., 2009
Ethanol	Au/TiO ₂	K.Conelly et al., 2012
Aqueous methanol	Cu/TiO ₂	Nae-lih Wu et al., 2004
-	N doped TiO ₂	R.Aashi et al., 2009
Methanol	Pt/TiO ₂	H.Yi et al., 2007
Methanol,	Pt/TiO ₂	T.Sreethawong et al., 2007
Ethanol,		
1-Propanol,		
2- Propanol,		
1-Butanol,		
Acetic acid,		
Ethylene glycol,		
Dimethyl formamide		

Acetic acid	CuO/SnO ₂	Zheng XJ et al., 2010
Glycerol,	N and B doped on	N.Luo et al., 2008
Glucose,	TiO ₂	
Sucrose		
Glucose	Au/TiO ₂ ,	P.Gomathisankar et al., 2013
	Pd/TiO ₂	
Methanol	Pt,Pd,RuO ₂ ,Rh /TiO ₂	T.Kawai et al., 1980
Methanol	Pt/TiO ₂	Tao et al.,
Glucose	NiO/TiO ₂ -SiO ₂	Mohammad et al., 2012
Glucose,	Pd/TiO ₂ ,	Xianliang et al., 2008
Sucrose,	Pt/TiO ₂ ,	
Starch	Au/TiO ₂ ,	
	Ru/TiO ₂ ,	

Rh/TiO₂,

Ag/TiO₂

Methanol	Ag, Au, Ag-Au/TiO ₂	G.L.Chiarello., et al 2010
Glucose	Ni(OH) ₂ /TiO ₂	S.Xie et al., 2013
Methanol	Ni/TiO ₂	D.Jing et al., 2005
Formic acid	Cu/ TiO ₂	V.Lanese et al., 2013
Methanol	Cu, Pd, Au/TiO ₂	T.Sreethawong et al., 2005
Methanol	Au/ TiO ₂	G.L.Chiarello et al., 2008
Methanol	Au/TiO ₂	G.Wu et al., 2008
Glycerol	Pt/TiO ₂	Vasileia M. Daskalaki et al., 2009

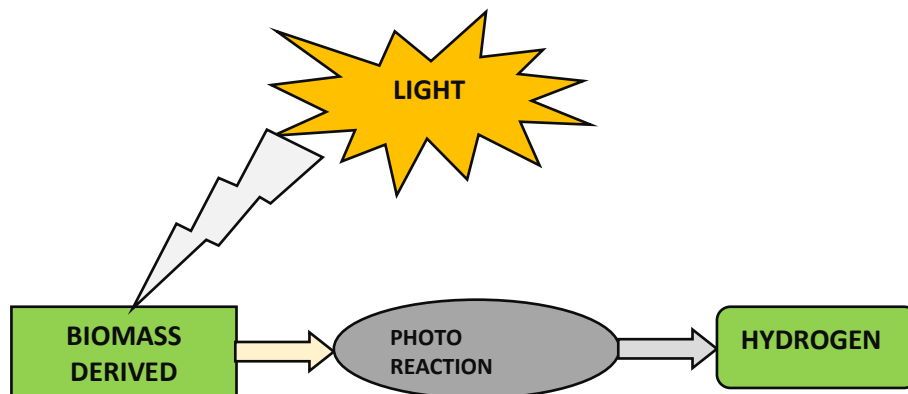


Fig: Overview of project

2.2 OBJECTIVES

Driven by increasing demand for energy and environmental problems there is a need to produce a clean fuel from renewable sources at relatively low cost. H₂ is proven to be a clean fuel having versatile applications in different fields. Production of H₂ through The unlimited solar energy is one of the recent technology developed. The yield of H₂ using this process need to be increased by incorporating less expensive and abundant metals which are economical. The proper modification of the semiconductor based catalyst TiO₂ increases the yield of H₂. The present investigation was focused on the development of metal incorporated Titania based Mesoporous material with tunable band gap energy using different types and concentrations of the oxygenated hydrocarbons. The specific objectives are as follows:

1. Synthesis of the Titania based Mesoporous oxide material.

2. Preparation of monometallic (Ni, Cu, Cr, V, Co, Mn) and bi-metallic (Ni-Cu) with different compositions supported on the synthesized supports. Metallic catalysts supported on pure P25 catalysts were prepared for comparison purpose.
3. Characterization of the catalyst and the support using BET, XRD, TPR, UV-Vis spectroscopy, FTIR spectroscopy.
4. The prepared catalysts were tested for the photo catalytic conversion of aqueous solution of glucose to H₂ in presence of halogen source. Various process parameters such as catalyst loading, concentration of glucose, catalyst composition, irradiation time, metal loadings were studied.
5. Catalyst deactivation studies were performed with the spent catalyst

Chapter 3

EXPERIMENTAL SECTION

3.1 MATERIALS AND METHODS

3.1.1 Preparation of MESOPOROUS TITANIA

The synthesis of Mesoporous Titania based catalyst was synthesized using a method as reported by Morris, Stacy M et al 2008. 98%+ titanium (IV) isopropoxide from (Sigma Aldrich) was used the source for the titania. About 4 g of Pluronic P123 from (Sigma Aldrich, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$) was dissolved in the 20 ml of anhydrous ethanol and the solution was stirred for 4 h. Then 20 mmol of titanium isopropoxide was dissolved in 10 mL of anhydrous ethanol and 3.2 mL of the 68-70 wt% of nitric acid (HNO_3) was added as a hydrolyzing agent. The titanium isopropoxide solution was stirred for 4 hr. Two previously solutions were combined together and 10 ml of anhydrous ethanol was used to completely transfer the titanium isopropoxide. The combined solution was continued to stir for 5 hr. The solvent evaporation was done at 333 K for 48 h in an oven. The resulting samples was calcined at 723 K in a furnace with a heating rate of $10^\circ\text{C}/\text{min}$ and held at final temperature for 4 h. The calcined material was designated as mTi, where m represents mesoporous and Ti as TiO_2 .

3.1.2 Catalyst preparation by Incipient-Wetness impregnation method

Several metal catalysts supported on the TiO₂ (P25) and synthesized mesoporous titania were prepared by using Incipient-Wetness Impregnation method. Nickel nitrate hexahydrate [Ni(NO₃)₃ · 6H₂O, Merck, 97% pure] copper nitrate [Cu(NO₃)₂·3H₂O, Merck, purity 99.5%], ammonium metavanadate [NH₄VO₃, Sigma Aldrich], manganese(II) nitrate hydrate [Mn(NO₃)₂ · 6H₂O] Sigma Aldrich], and Chromium (III) nitrate nanohydrate [Cr(NO₃)₃ · 9H₂O, Sigma Aldrich] were used as a source for nickel, copper, vanadium, manganese, and chromium respectively. Metal precursor solution was prepared by adding measured amount of respective metal precursor equal in to the distilled water equal to the incipient volume of support. For bimetallic catalysts, respective metals precursors were added together. Required amount of support material was added in to the already prepared metal precursor solution and the mixture was stirred for 2 hrs to distribute the precursor solution uniformly in the support. The wet material was dried in desiccator overnight and followed by in an oven at 373K for 6hr. The dried material was calcinated at 723K for 6 hrs. The prepared catalysts were represented as xMTi, (M=Ni,Cu, Mn, Cr, Co) where x denotes the wt% of metal incorporated. The bimetallic catalysts were denoted as xM1yM2Ti (M1=Ni and M2=Cu, V), where x and y represents atomic ratio of first (M1) and second (M2) metal.

3.2 Catalyst characterization

3.2.1 BET surface area measurement and pore size distribution

The BET surface area was determined from N₂ adsorption-desorption measurement at 77K using Micromeritics ASAP 2020 physisorption analyzer. Prior to physisorption studies, all the samples were degassed under vacuum (5×10^{-6} mm of Hg) at 423 K for 3 h. The BET surface area was determined from the N₂ adsorption data with relative pressure ranging from 0.03-0.3 using multi-point BET equation. The pore distribution (PSD) was calculated based on the desorption isotherm data using Barret-Joyner-Halenda (BJH) method and the average pore size was considered as the maximum of the PSD curve. The volume of the adsorbed liquid nitrogen at P/P⁰ = 1.0 ca. was considered as the average pore volume of the samples.

3.2.2 X ray Diffraction

The X ray diffraction pattern of pure support and supported metal catalysts were obtained by a Philip X-ray diffractometer using a Cu K α radiation ($\lambda=1.54$ A \AA), 15 kV and 30mA current at 2 Θ interval of 5 to 90⁰ with a scanning speed of 1⁰/min.

3.2.3 Temperature Programmed Reduction

. The TPR studies of Titania supported metal catalysts were performed using Micromeritics AutoChem II 2920 chemisorption analyzer. All the samples were degassed at 473K for 1 hr in flowing pure argon at 20ml/min. The samples were cooled down to 323K and a gas mixture of 10 vol % H₂-Ar was introduced. The sample was heated to 1073K using thermal conductivity detector (TCD)

3.2.4 UV-Vis-NIR Spectrometer:

The UV-Vis spectra of pure supports and supported metal catalysts were obtained by PerkinElmer LAMBDA™ 1050 UV/Vis/NIR spectrometer equipped with reflectance accessory (Harrick Scientific) to determine the band gap energy of material. All the spectra were acquired in the reflectance mode and in the wavelength range of 200 to 800 nm using BaSO₄ as background. The band gap energy calculation is given below.

3.1 Calculation of Band Gap Energy

$$\text{Band Gap Energy (E)} = h \cdot c / \lambda$$

H	C	λ	E	eV
6.62X10 ⁻³⁴	3.0X10 ⁸	410.57X10 ⁻⁹	4.84156E-17	3.025964

3.2.5 FTIR analysis

The FTIR spectra of fresh catalyst and spent catalyst were obtained in a BRUKER TENSOR 37 spectrometer in transmission mode. All the samples were diluted with spectroscopic grade KBr powder and a transparent pellet was made in a hydraulic press. All the spectra were collected in the wavenumber region 400-4000 cm⁻¹ using KBr as background and 128 no of scan with a spectral resolution of 4 cm⁻¹.

4.3 Experimental setup and procedure for Photocatalytic H₂ Production System

The photo catalytic H₂ production activity tests were performed out in a batch reactor as shown in Fig.4.1. The batch reactor consists of a vertical cylindrical glass reactor of volume 1 liter. External illumination source comprises of Phillips Halogen lamps (2) of each 150W for the irradiation of the catalyst. The glass reactor is connected with a reflux condenser and the sampling port. The evolution of the H₂ during the experiment was collected in a gas burette. The whole experimental set up was covered with a wooden box. The batch reactor was charged with a measured amount of catalyst and feed solution containing certain percentage of sacrificing agent. In this particular study glucose was used as sacrificing agent and 1 to 5 wt% of glucose in water was used as a feed solution. The whole mixture was stirred continuously using magnetic stirrer at a speed of 1200 rpm. The evolution of the H₂ during the experiment evolved gas was mixture was collected in a gas burette and the gas mixture was analyzed offline Gas chromatography (GC)

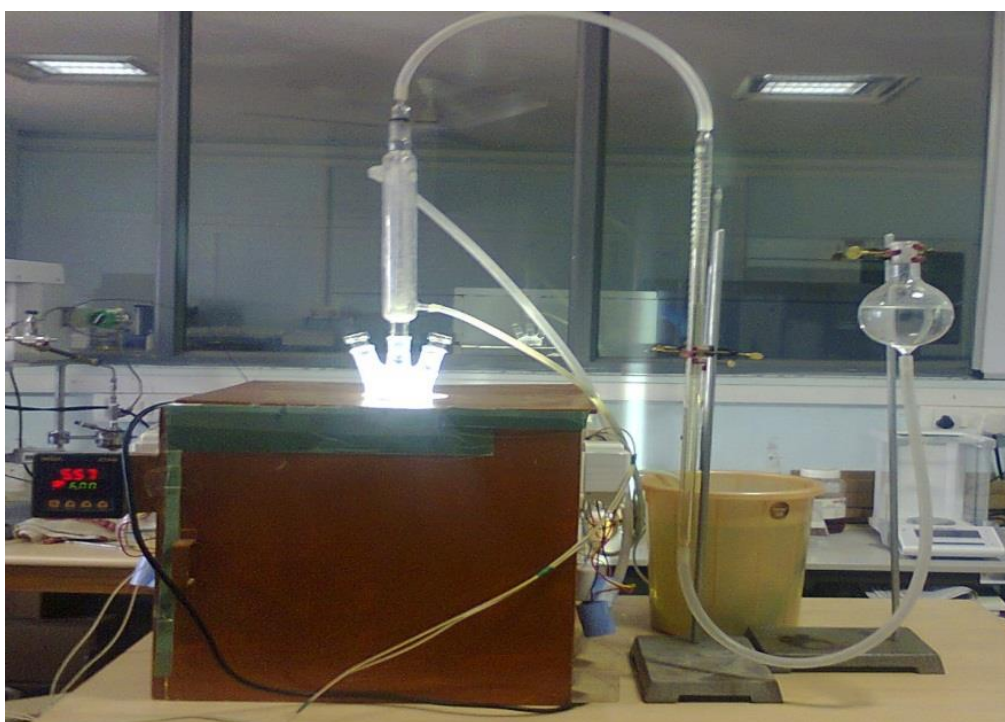


Fig.3.1 Image of photo-reactor

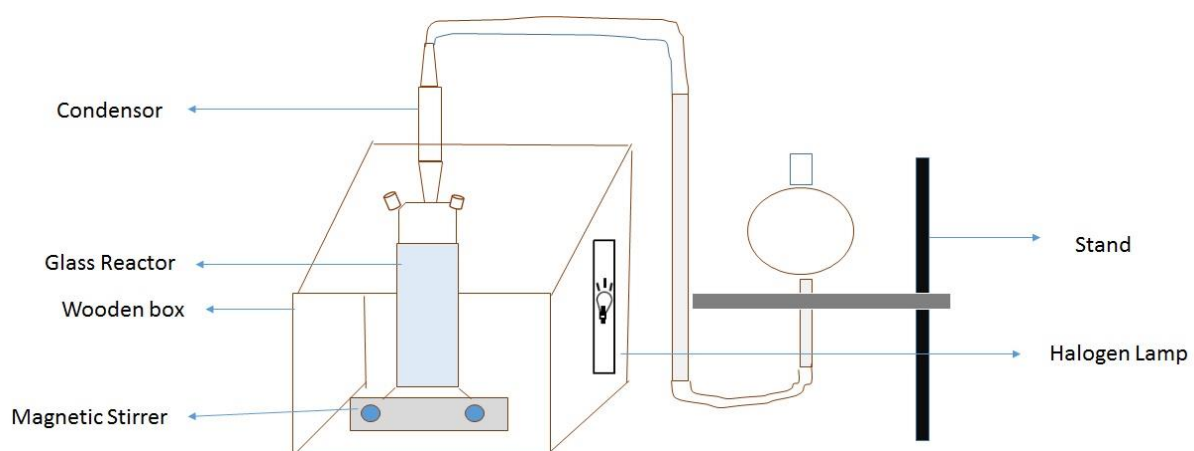


Fig 3.2 Schematic of Photo reactor

3.5 Analysis of the product

The gas samples was analyzed using a gas chromatograph equipped with TCD (Shimadzu chromatograph, Model: 2014ATF using nitrogen as a carrier gas.

Chapter 4

Results and Discussion

4.1 BET surface area measurement and pore size distribution

The N₂ adsorption-desorption isotherm of synthesized mesoporous titania along with pore size distribution as insert is shown in Fig 4.1. This isotherm pattern exhibited type IV-like hysteresis loop, based on the IUPAC classification and confirmed the mesoporous of the material. The surface area of mesoporous titania was 81 m²/g, which was comparatively large as compare to that of commercially available photocatalyst TiO₂ (Degussa P25). The average pore size of the mesoporous titania obtained was 5.6 nm. The surface area of other samples were determined and tabulated in Table 4.1. It was observed that the surface area of catalysts was not affected due to the impregnation of metal.

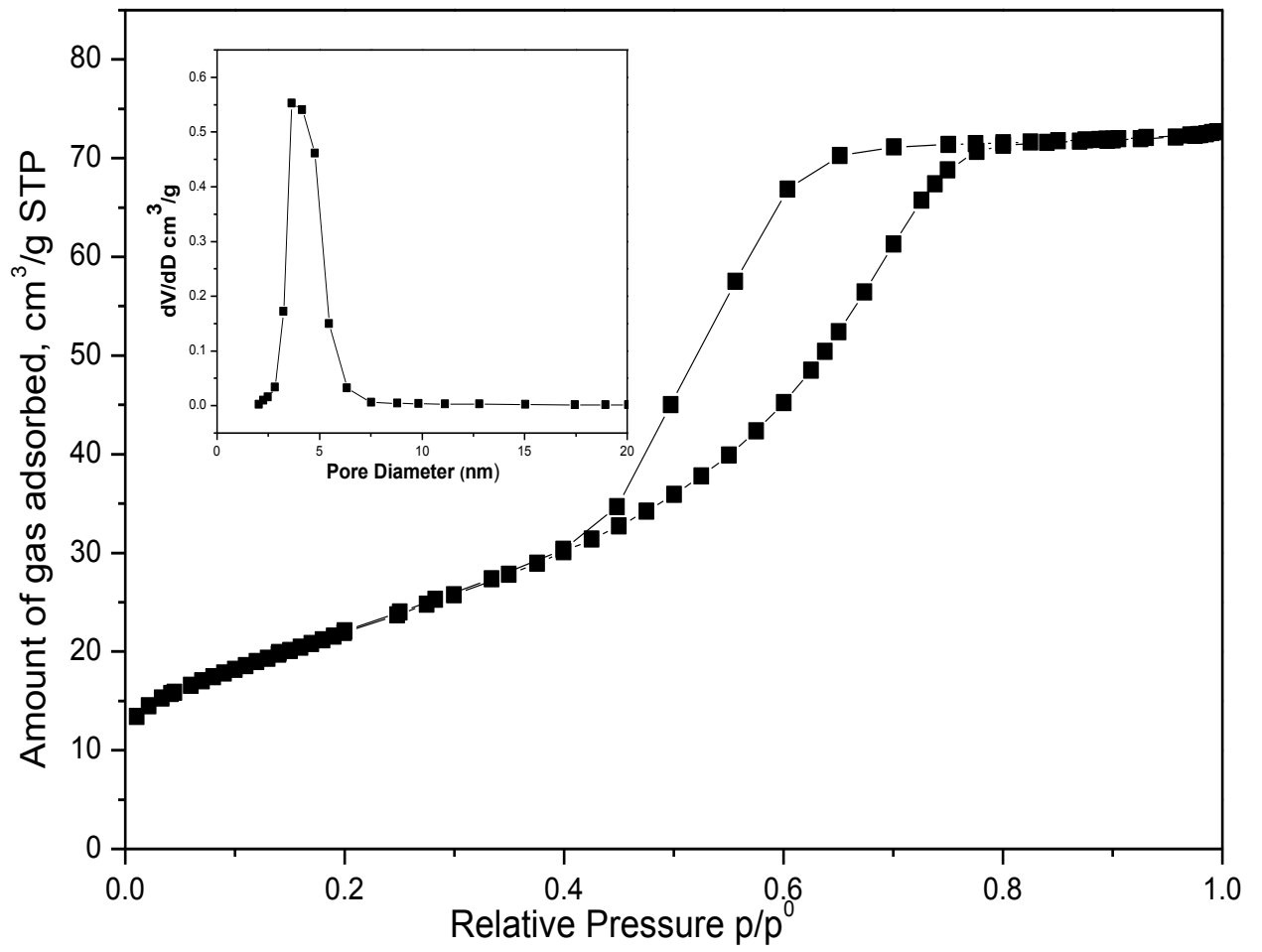


Fig4.1 Nitrogen Adsorption– desorption isotherm and pore size distribution of synthesized mesoporous titania

Table 4.1 BET surface area of the synthesized catalysts

Sample	Calcination Temperature (K)	Metal Loading (wt%)	BET Surface area (m ² /g)
P25	-		54
meso Ti	723		81
3NiTi	723	3	51
3CuTi	723	3	43
3CrTi	723	3	45
3VTi	723	3	49
1Ni1CuTi	723	3	51
1Ni2CuTi	723	3	49
2Ni1CuTi	723	3	46

4.2 X ray Diffraction

The XRD patterns of pure supports and supported metal catalysts are shown in Fig 4.2. XRD pattern of P25 revealed both the characteristics peaks of anatase (25.3°) and rutile phase (37.1°). Only peaks characteristics of anatase phase was observed for mesoporous titania. Thus the mesoporous titania possesses only the anatase phase. The XRD pattern of supported metal catalyst revealed only the features of titania support.

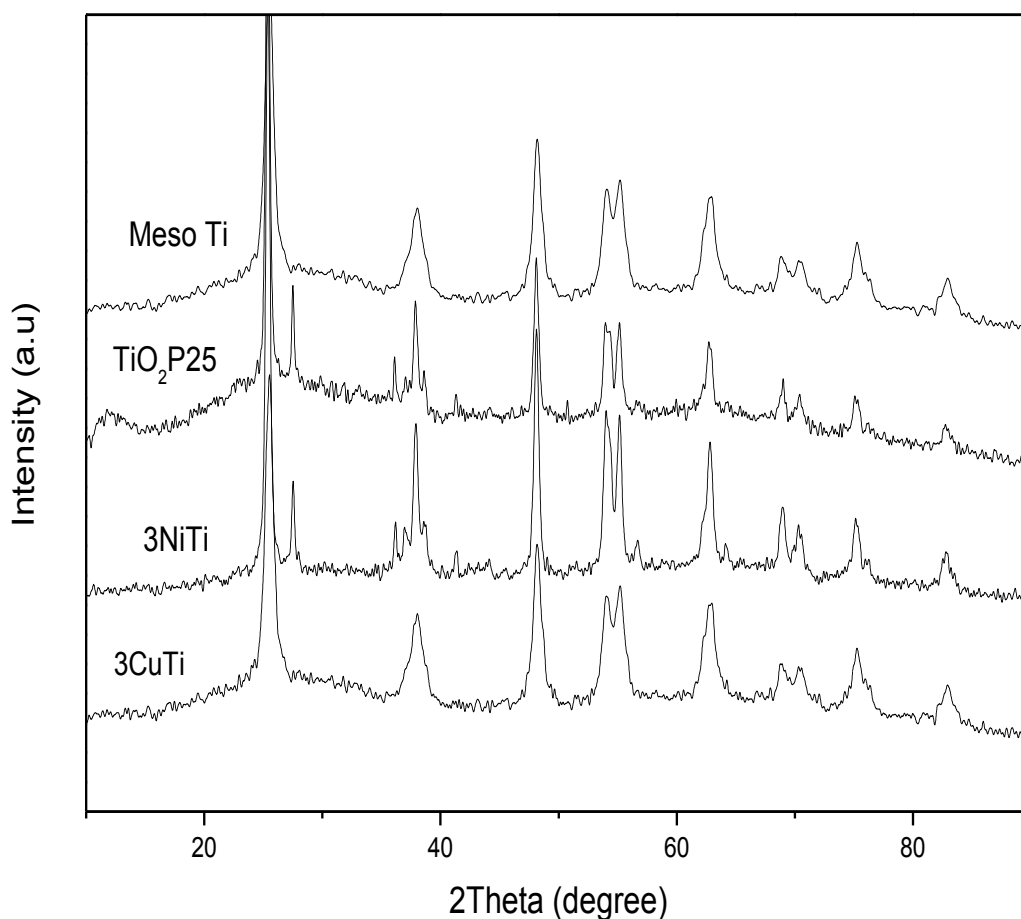


Fig 4.2 XRD pattern of the Titania supports (commercial (P25) and synthesized mesoporous titania) and supported P25 nickel and copper catalysts of 3 wt %.

4.3 Temperature Programmed Reduction

The copper and nickel impregnated bimetallic catalysts of varying atomic ratio were characterized by TPR and the results are shown in Fig 4.3. The reduction temperature corresponding to the maximum hydrogen consumption was considered as T_{max} . TPR profile of bimetallic catalysts revealed three peaks at T_{max} at 395, 460 and 614-628K depending on the bimetallic catalyst composition. The peak appeared at T_{max} of 395K was due to the reduction of copper oxide to metallic copper. The peaks appeared at 460 and 614-628 K were attributed to the reduction of bulk nickel oxide and dispersed nickel oxide respectively. The reduction of dispersed nickel oxide occurred at relatively lower temperature as the copper content in the bimetallic catalysts decreased. The shift in reduction temperature with decrease in copper content might be due to less interaction of copper with nickel which is expected to be higher for higher loading of copper due to formation of alloy. However, more detailed studies are required to describe the phenomena with more clarity.

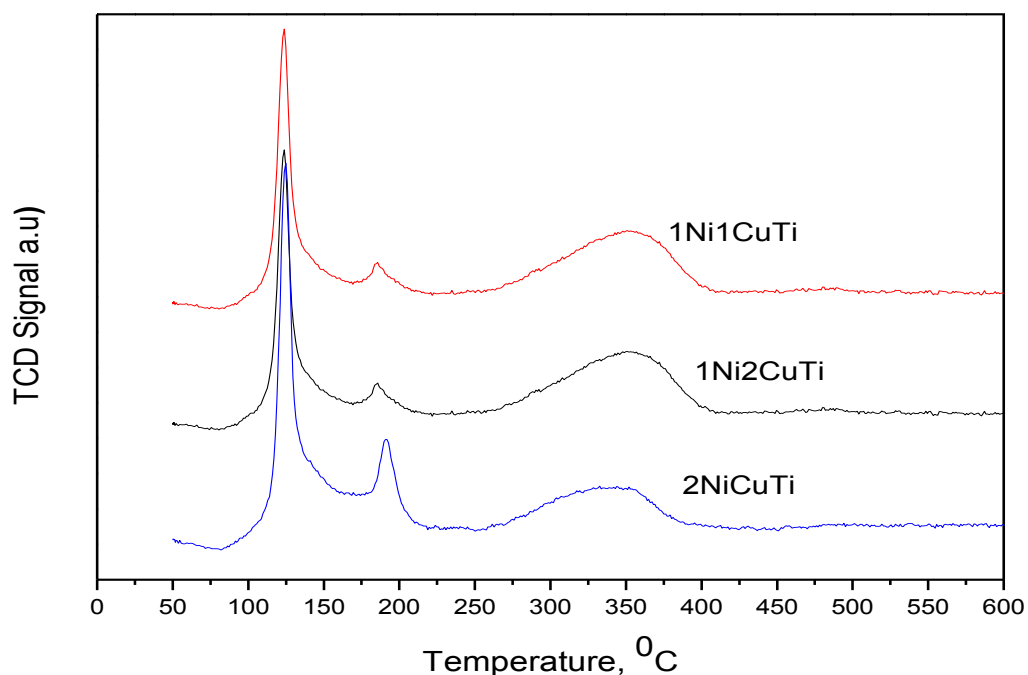


Fig 4.3 TPR results of bimetallic catalyst

4.4 UV-Vis-NIR Spectrometer

The results of absorption onset wavelength and their corresponding wavelength band gap energy of all the photo catalysts obtained from the UV-Vis- spectra are tabulated in the table 4.2. The band gap energy obtained for P25 was ~ 3.225 calculated at a wavelength of 385.13nm. From Fig 4.4, the absorption band of mTi shifted towards the visible region at 434.5nm and corresponding calculated band gas energy was 2.8 The band gap energy was decreased further due to the impregnation of metals on commercially available TiO_2 whereas no further decrease in band gap energy was observed in case of mTi supported metal catalysts. It was because of change in the textural and structural properties due to doping [L. Kokporika et al 2013].

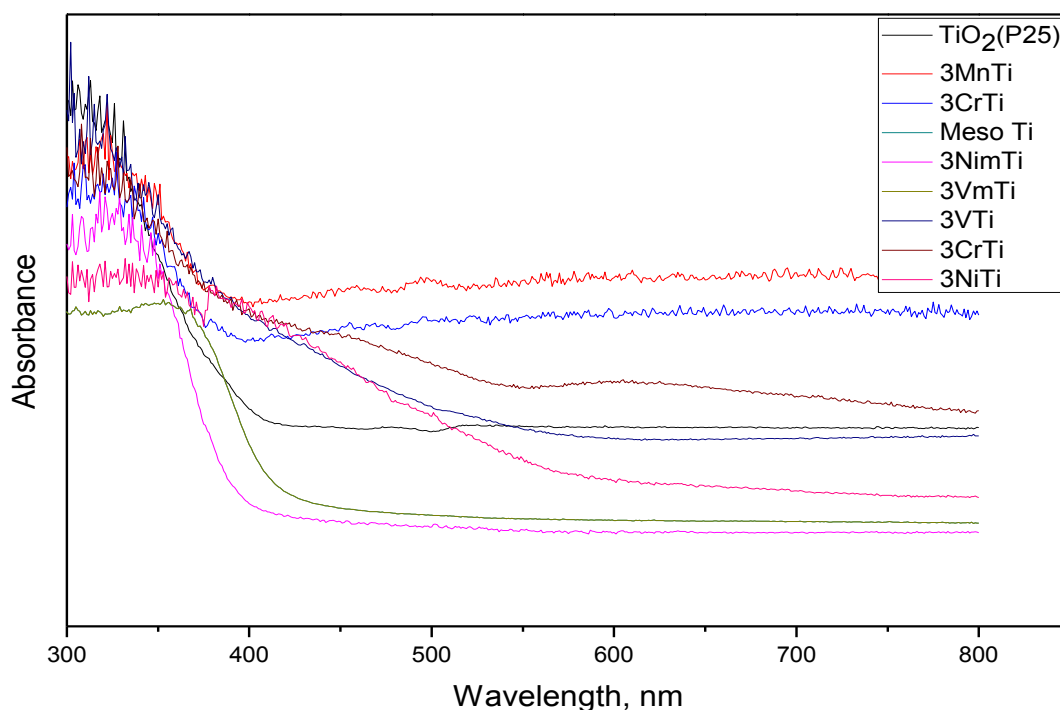


Fig 4.4 UV-Vis-NIR absorption spectra for supports (TiO₂(P25) and Meso Ti) and catalysts 3NiTi, 3CuTi, 3CrTi, 3MnTi, 3VTi, 3NimTi, 3VmTi.

Table 4.2 Band gap energy of different catalysts and supports

Photocatalyst	Calcination Temperature (K)	Absorption Wavelength (nm)	Band gap energy (ev)
TiO ₂ (P25)	-	385.13	3.2
3VTi	723	421.6	2.9
3NiTi	723	413.1	3.0
3CuTi	723	391.6	3.1
3CrTi	723	403.4	3.0
3MnTi	723	398.6	3.1
1Ni1CuTi	723	398.2	3.1
1Ni2CuTi	723	389.4	3.1
2Ni1CuTi	723	393.6	3.1
meso Ti	723	434.4	2.8
3NimTi	723	447.3	2.8
3VmTi	723	451.8	2.8

4.5 Photocatalytic H₂ generation

4.5.1 Effect of different concentrations of glucose in Photocatalytic H₂ generation

The photo catalytic conversion of biomass derived compound glucose to hydrogen was carried out in a batch reactor using pure titania (P25) as catalysts. In this particular study aqueous solution glucose of 1 to 5 wt % was used as sacrificing agent. The cumulative volume of hydrogen rich gas mixture evolved was collected and noted with time as shown in Fig 4.5. The cumulative volume of gas evolved increase with increase in time till a certain time and no further gas was evolved. The volume of gas evolved at a particular temperature depends on the concentration of glucose and was highest for 5 wt% of glucose concentration. Thus, the subsequent photocatalytic conversion of aqueous solution of glucose was performed with 5wt % concentration.

4.5.2 Effect of Various metals on Photocatalytic H₂ generation

Different types of metals are used in performing the photocatalytic conversion of oxygenated compounds like Ni, Cu, Cr, V and Mn. The catalysts were prepared using wet impregnation method with catalyst loading of 3 wt%. The reaction studies were carried out in a batch reactor with glucose and water system and halogen lights (2) each of 150 W were used to perform the reaction. It is observed from the reaction that the Ni and V gave a better result when compared to other metals and P25. The results of the reaction study were plotted and shown in Fig 4.8 Transition metals as Cu and Ni on the TiO₂ surface which is the most widely used semiconductor due its low cost, abundance, stability and low toxicity. These metals not only improve the optical properties of the TiO₂ to absorb visible light, but their

presence on the TiO₂ particles also reduces the electron hole recombination and therefore facilitates charge transfer to species in contact with the TiO₂ surface.

4.5.3 Effect of catalyst weight on Photocatalytic H₂ generation

The photo catalytic hydrogen production reaction was studied using different amount of catalyst to see the effect of catalyst loading. The reaction system was glucose 5wt% in 1 liter of water and 2 halogen lights each of 150 W were used as a light source. The activity results obtained was shown in Fig 4.6. It was observed with the increase in the amount of catalyst the amount of gas evolved was not much effected. The reason for the less activity of catalyst greater than 1g was the light source used was not able to illuminate the higher weights of catalyst.

4.5.4 Effect of supports on Photocatalytic H₂ generation

The photocatalytic H₂ generation using glucose as a sacrificing agents was studied using different types of catalysts shown in Fig 4.8. One of the supports was commercially available TiO₂ support and the other was synthesized support. The former support P25 showed less activity compared to that of later support which is synthesized mTi. Synthesized mTi has been studied recently due to its high surface area and relatively large porous structure. The large surface area and pore are beneficial for the absorption of reactant and desorption of products [J.Zhu et al., 2009] was the main reason to have higher production of H₂ when compared to TiO₂ (P25).

4.5.5 Effect of different metals on synthesized meso Ti

The effect of various metals Ni, V on synthesized mTi were studied and . the results were shown in Fig4.9. It was clearly noticed that metals supported on mTi were more active towards the production of hydrogen rich gas compare to pure mTi

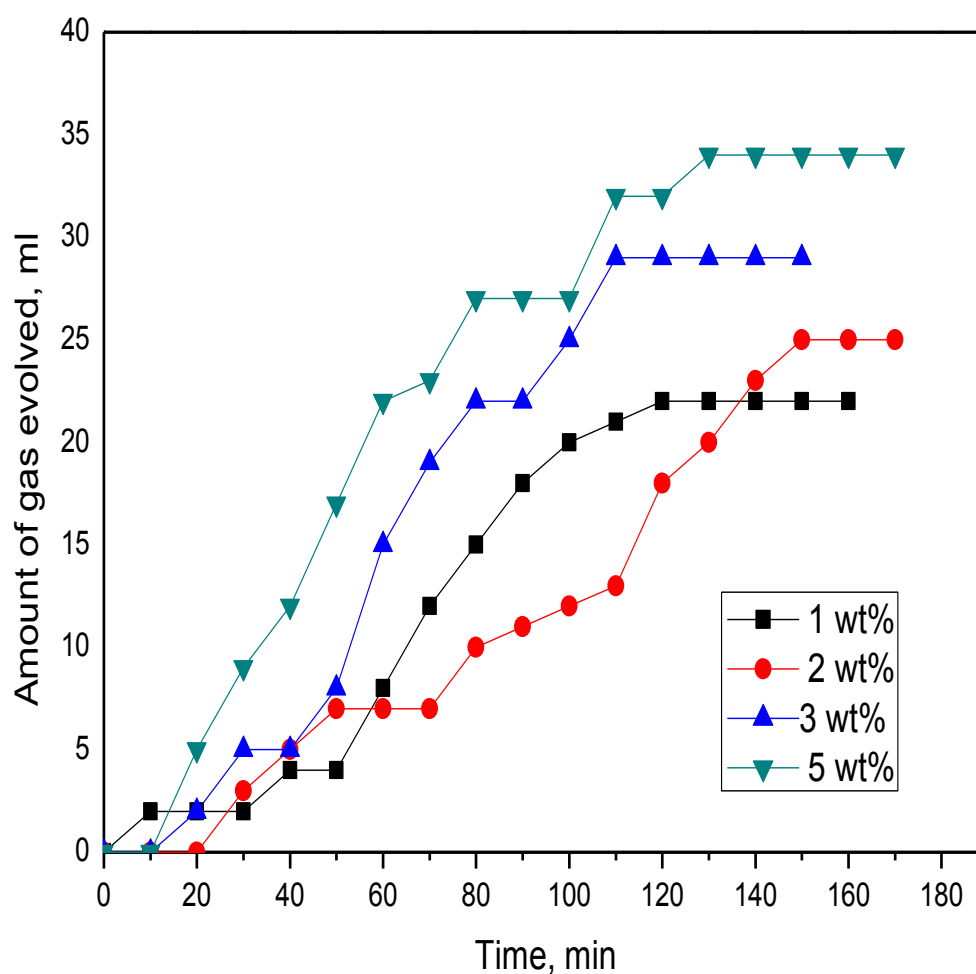


Fig 4.5 Different concentrations (weight %) of glucose on photo catalytic reaction. Conditions: Weight of catalyst= 0.5gP25, temperature=ambient, magnetic speed=1200 rpm, Halogen lamps (2 lamps each of 150W)

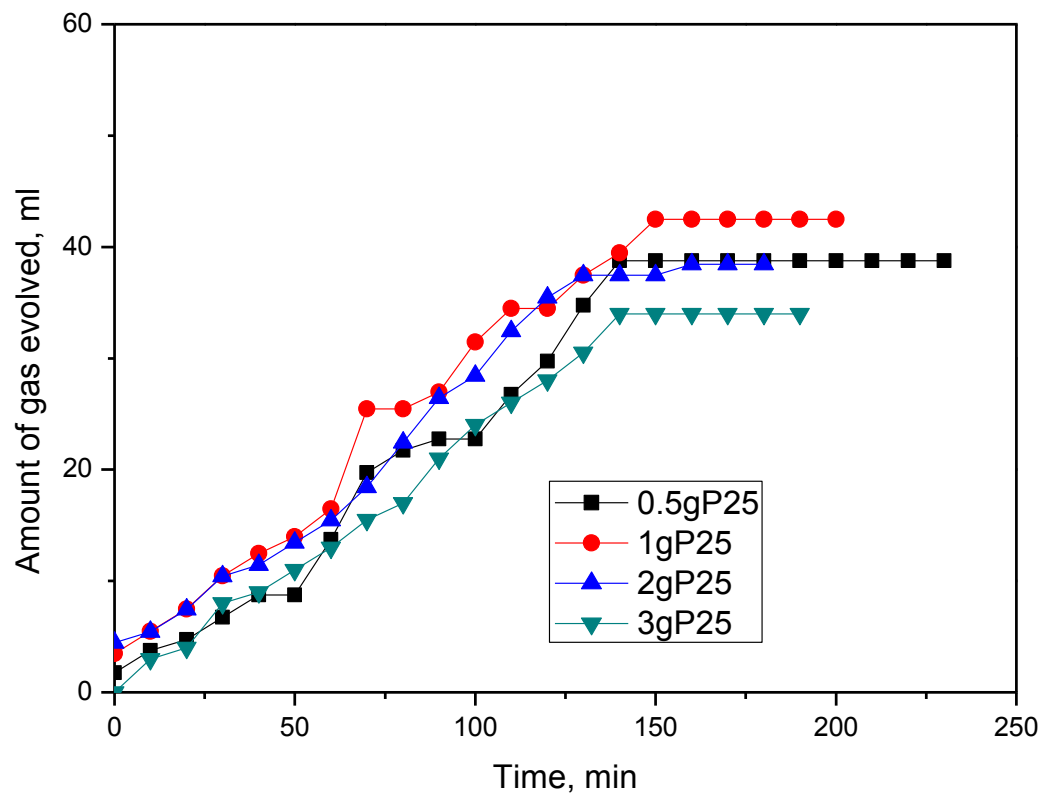


Fig 4.6 Different weights of catalyst on photo catalytic reaction. Ambient temperature, magnetic speed=1200 rpm, Halogen lamps (2 lamps each of 150W)

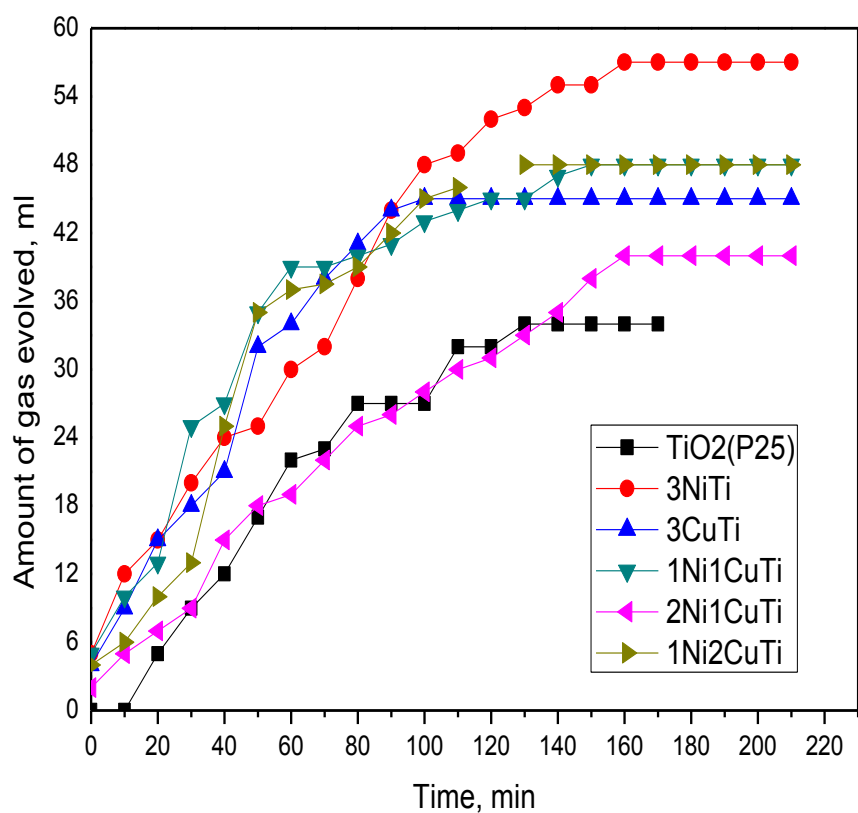


Fig 4.7 Effect of various mono and bimetallic catalysts on photo catalytic conversion of glucose. Conditions: catalyst weight=0.5g, catalyst loading is 3 wt%, glucose =5wt%, magnetic speed=1200 rpm, at ambient temp, halogen lamps 2 (each of 150W)

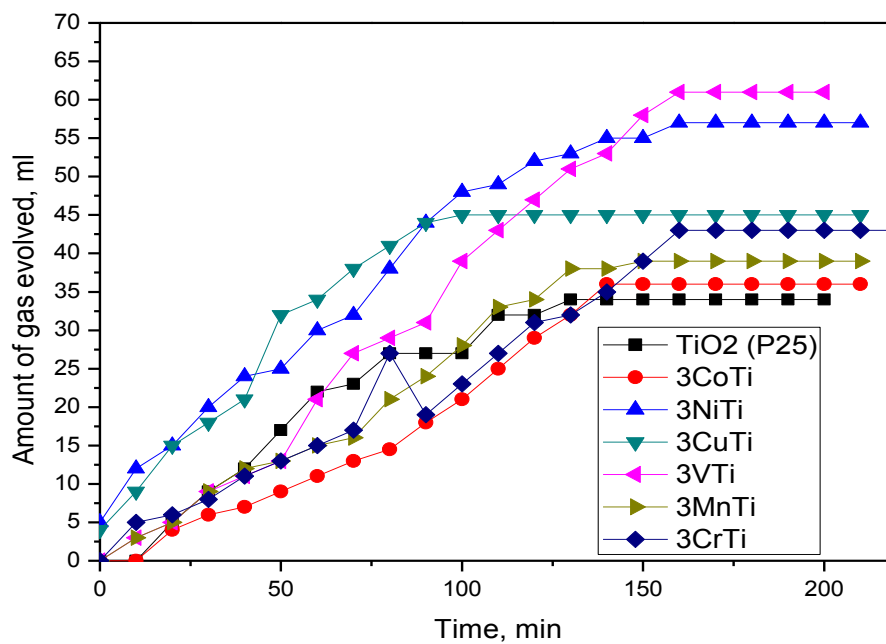


Fig 4.8 Effect of various metals on TiO₂ (P25) support on photo catalytic conversion of glucose. Conditions: catalyst weight=0.5g, catalyst loading=3 wt % glucose =5wt%, magnetic speed=1250 rpm, at ambient temperature, Halogen lamps 2 (each of 150W)

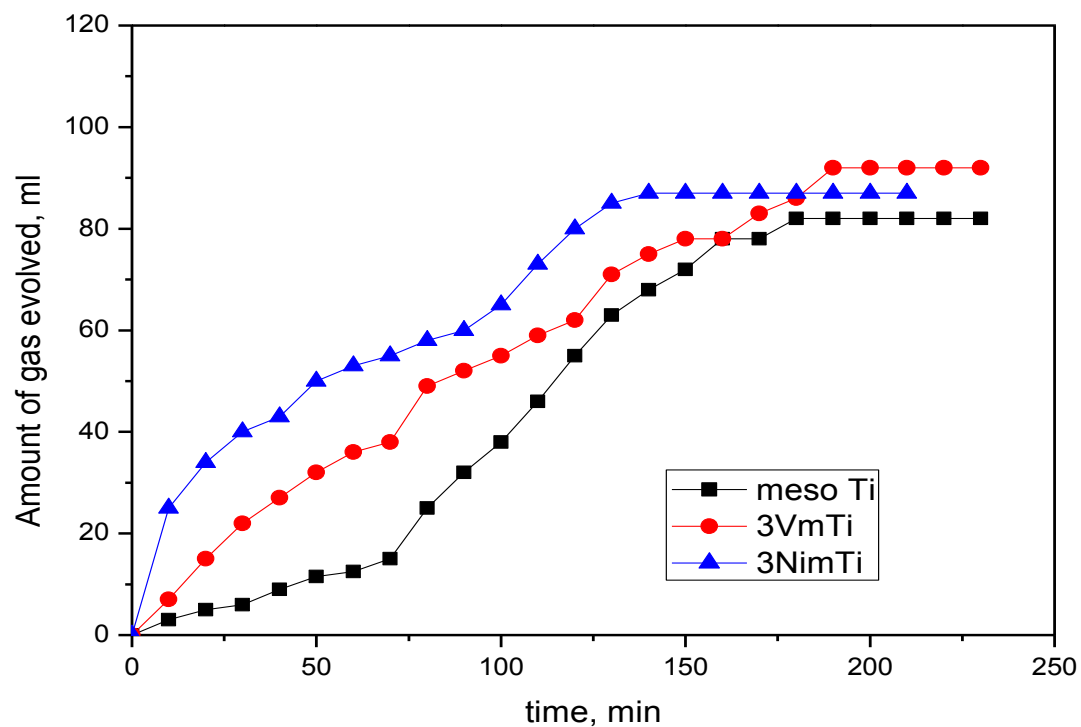


Fig 4.9 Effect of various metals on mesoporous titanium dioxide support on photo catalytic conversion of glucose. Conditions: catalyst weight=0.5g, glucose =5wt%, magnetic speed=1200 rpm, at room temperature, halogen lamps 2 (each of 150W)

4.5 FTIR Analysis

The FTIR spectra of synthesized catalyst and supports of both fresh and spent were characterized and shown in Fig 4.10, Fig 4.11 and Fig 4.12. The IR absorption bands of –OH- groups were found in supports TiO₂ (P25) and Meso Ti and catalysts 3VmTi in the region of 3400-4000 cm⁻¹. The characteristic bands of –OH- groups are at 3681 cm⁻¹, 3656 cm⁻¹, 3671 cm⁻¹, 3647 cm⁻¹ for 3VmTi, spent 3VmTi, Meso Ti, spent Meso Ti respectively. For commercial TiO₂ P25 the band of isolated hydroxyl groups is observed at 3698 cm⁻¹. According to the literature these hydroxyl groups are considered the most photoactive and are preferentially present on the surface of the TiO₂ structure and are usually associated with surface defects [E.Pulido et al., 2013]. Since the adsorbed water and the hydroxyl groups on TiO₂ are always present on all the catalysts, the absorption bands around 3620cm⁻¹ and 1621cm⁻¹ are ascribed to the stretching and deformation vibrations of hydroxyl group and water molecules, respectively. In the IR spectra of TiO₂, 3VmTi many similar characteristic bands are produced. The decrease of the absorption wavelength indicated that the active metal is bonded to the supports via –OH- groups.

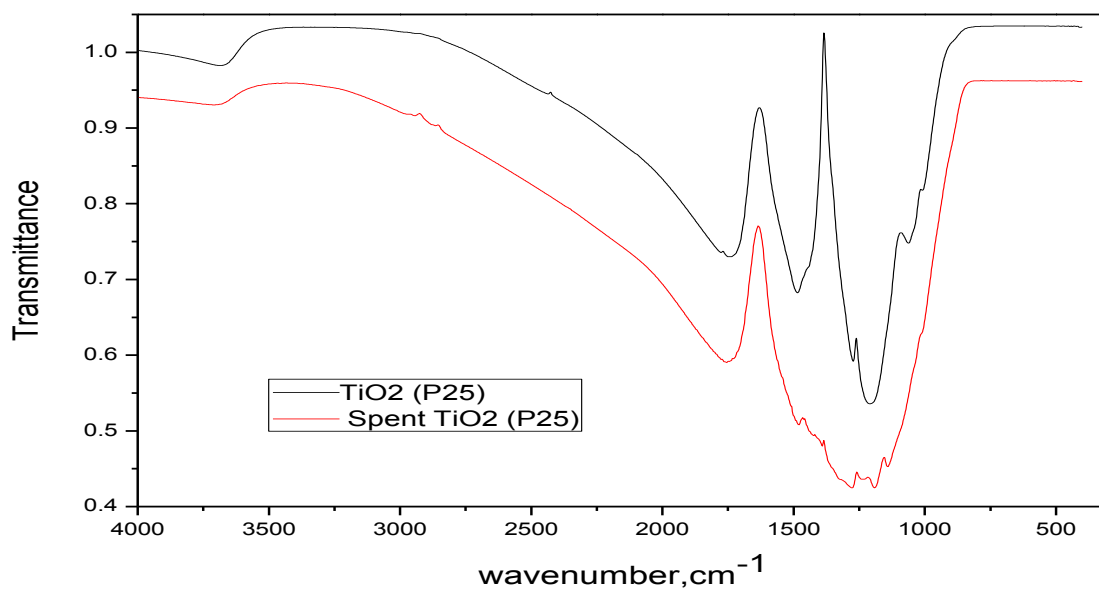


Fig 4.10 FTIR spectra of Fresh and Spent TiO_2 (P25) Support

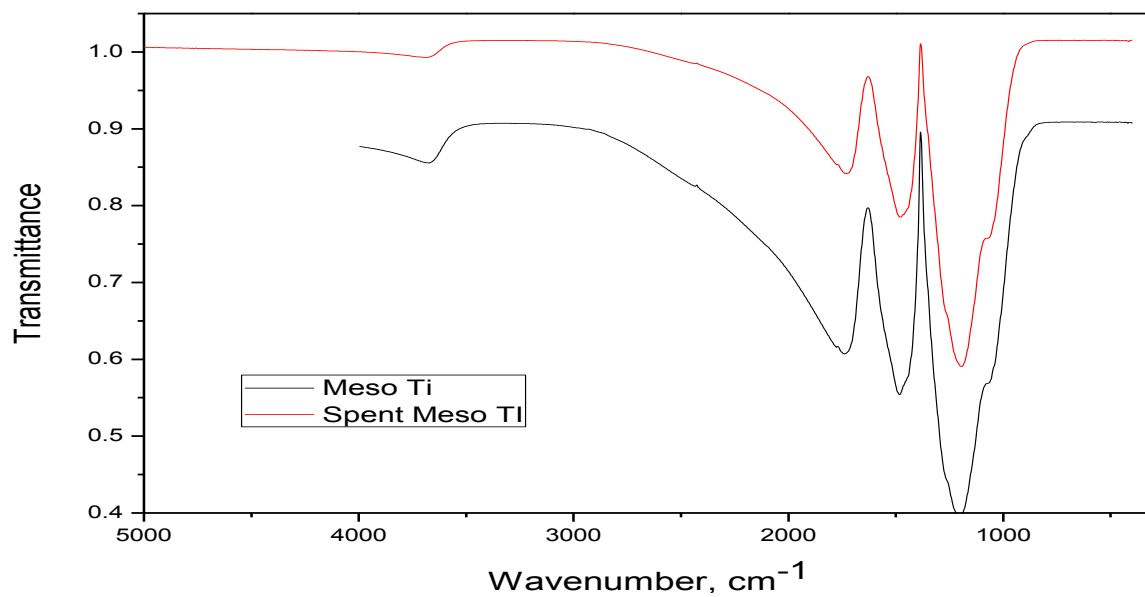


Fig 4.11 FTIR spectra of fresh and spent meso Ti support Calcined at 723K

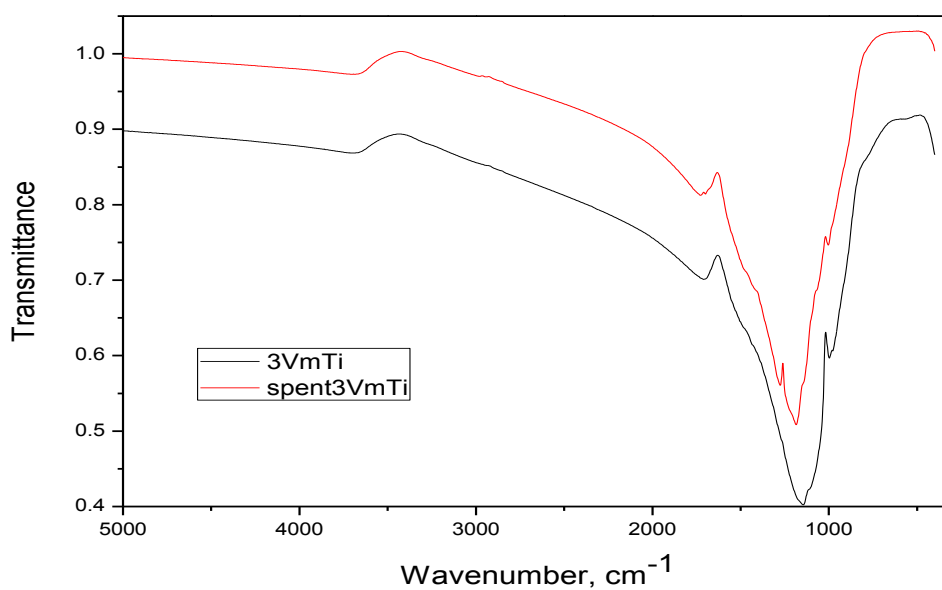


Fig 4.12 FTIR spectra of Fresh and Spent 3VmTi Catalyst calcined at 723K

4.6 Gas analysis chromatogram

The gas sample was analyzed by Gas Chromatography (GC). The chromatogram was shown as shown in Fig 4.13. In this chromatogram it was observed that the highest peak corresponds to hydrogen and second peak to nitrogen and then next peak was observed to be carbon dioxide.

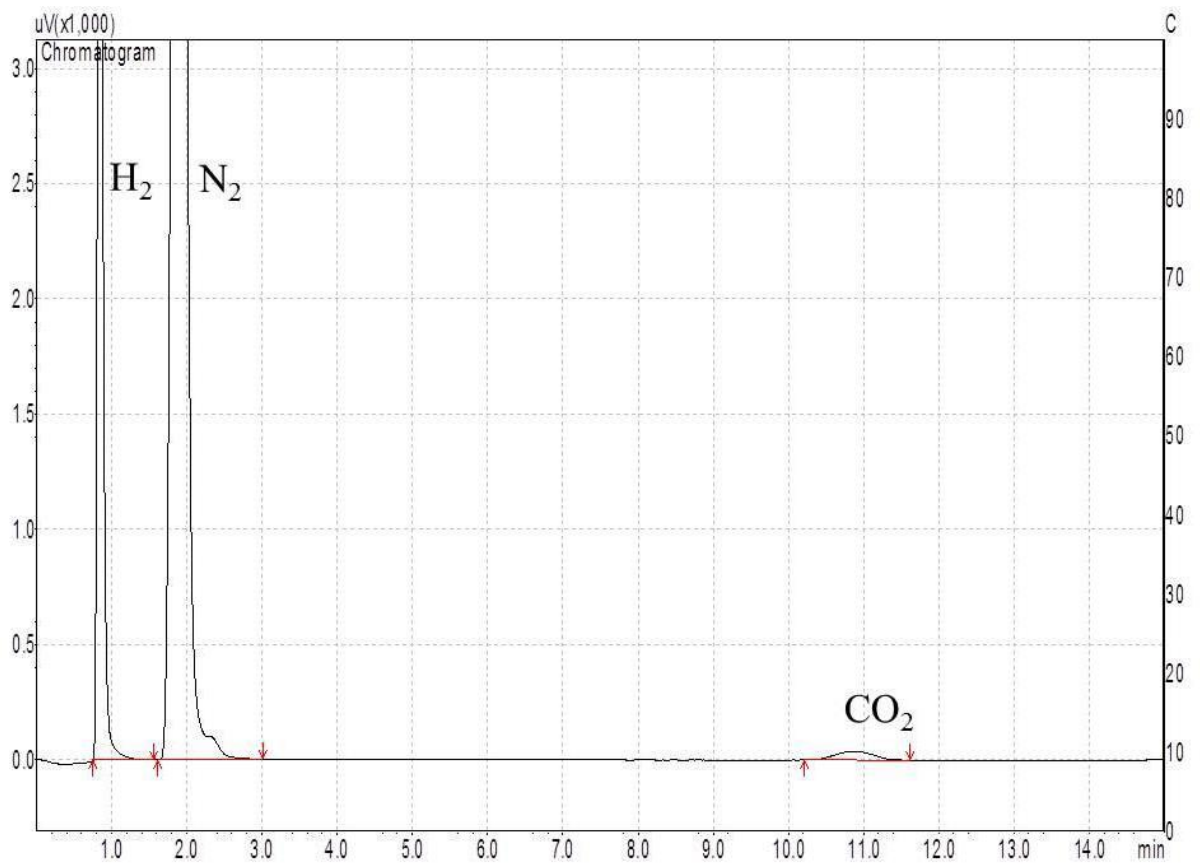


Fig 4.13 Gaseous product analysis by Gas Chromatogram

Conclusions

In the present work photocatalytic conversion of glucose over titania supported various metal catalysts was studied. Glucose was used as a sacrificing agent to improve the yield of hydrogen. These metals were loaded on P25 to see the effect on Photocatalytic hydrogen generation. The synthesized catalysts were characterized using BET, XRD, FTIR, TPR, UV-Vis-NIR. Among them Ni and V showed higher evolution of gas. Mesoporous titania support was synthesized and which showed higher BET surface area $\sim 81\text{m}^2/\text{g}$ than TiO_2 (P25) and also a better yield of gas. The band gap energies of all synthesized catalyst was calculated it was observed that synthesized meso Ti has less band gap energy to that of TiO_2 (P25). With the loading of metals on P25 the band gap decreased further. The effect of weight of catalyst was studied and noticed that with the increase in the weight there is not much change in the evolution of gas. Mono metallic and bimetallic catalysts were synthesized in which it was noticed the yield of monometallic catalysts was higher compared to bimetallic. Higher activity was found to be using synthesized mesoporous support because of its morphology.

Future Work

Photocatalysis is an emerging technology in production of clean H₂ and has a great scope in nearby future. In this present work, the photo catalytic reaction was studied with monometallic and bimetallic catalysts using oxygenated compound i.e., glucose. The study can be extended by using different types of sacrificing agents.

In the present work metal based catalysts were used. There is a scope for non-metallic doping, dye sensitizing and coupling of semi- conductors with mixed oxide supports like Cds-TiO₂, TiO₂-WO₃ etc.

Preparation of support as a Nano composite is a novel idea to increase the yield since the morphology of TiO₂ plays an important role and as it also exhibits a high surface area.

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