Photocatalyst for Solar Generation of Hydrogen via Cu/TiO_2 Catalyst

by

Nisha Sreetharan

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2009

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Name of Main Supervisor)

DR CHONG FAI KAIT
Senior Lecturer
Fundamental & Applied Sciences Department
Universiti Teknologi PETRONAS, PERAK

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NISHA SREETHARAN

ABSTRACT

Photocatalyst process has drawn the attention of many researches at present time as it has tremendous potential in near future. To be more specific, semiconductor mediated photocatalysis has been a subject of vigorous academic research for the past 30 years as its application towards the environmental sector is crucial. As far as this project is concern, the main aim is to produce hydrogen via Photocatalysis using visible light with the aid of suitably supported semiconductor in a water-glycerol system. Cu is incorporated onto titanium dioxide (TiO_2) for the reduction of water (H_2O) in the presence of sacrificial agents. CuO component which dominates in the anatase phase of Cu/TiO_2, acts as the water reduction site which promotes charge separation. The catalyst is prepared using wet impregnation method and studies were conducted on the effect of various amounts of CuO content and calcinations temperature with respect to hydrogen production. Apart from that, several techniques are used to characterize the properties of the prepared catalyst which includes TPR, SEM, XRD and TGA. Since the oxidation of water by holes is a slow process, hole scavengers or sacrificial agents are introduced to expedite the process. The sacrificial agents reacts irreversibly with the photogenerated holes suppressing the recombination of photogenerated electrons and holes on the semiconductor surface leading to higher photocatalytic H_2O reduction to H_2.

ACKNOWLEDGEMENT

I would like to thank numerous individuals for their tremendous support in performing this project. Deepest gratitude goes to my Final Year Project (I and II) supervisor, Dr. Chong Fai Kait for her tremendous support and technical guidance throughout the experimental process and preparation of this report.

I would also like to thank all the lecturers of Chemical Engineering Program of UTP, who have been very helpful and resourceful while guiding me. My deepest gratitude is also dedicated to the postgraduate student, Ms.Leong Siew Yoong for her guidance and assistance, through which without, this study might not have come up to the completion level.

I would like to also extent my gratefulness to all the technicians at Block 3, 4 and 5 for their kindness in assisting me to operate the laboratory equipments throughout the project and as well all my friends who have directly or indirectly aided me in completing this project.

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CHAPTER 1

PROJECT BACKGROUND

1.1 BACKGROUND OF THE STUDY

Hydrogen has been receiving much attention as the potential fuel at the present era. The question in the production method of this promising fuel is yet another field which has drawn much attention in research. Major development in the hydrogen production province is experienced when Fujishima et al., 1972 discovered the photocatalytic splitting of water using TiO_2 electrodes. Hydrogen production via photocatalytic activity is much opted due to the fact that hydrogen is produced in a lower cost with lesser environmental impact.

1.2 PROBLEM IDENTIFICATION AND SIGNIFICANCE

Solar hydrogen production using water-glycerol system is the main intention of this project. With the aid of a semiconductor incorporated with impurities an enhanced performance in hydrogen evolution can be observed in the photocatalytic reaction. Though producing hydrogen through solar power has been in place widely, the efficiency of it is low due to the cause of UV composition which is less than 5% in sunlight. TiO_2 has a wide band gap of 3.2 eV which hinders the absorption of visible light (higher than 500 nm) but is compatible for UV light of 388 nm. This system can be improved to absorb light in the visible range if the band gap of TiO_2 is narrowed. Titania, the commonly used semiconductor has been opted for this project due to its high stability and low cost in conjunction with copper. The band gap of TiO_2 has proven to be lowered by incorporating copper on TiO_2 based on the studied conducted by Slamet et al., 2005.

1.3 OBJECTIVE AND SCOPE OF STUDY

The main aim of the project is to produce hydrogen via visible light using the photocatalytic activity with copper loaded TiO_2 catalyst, in the presence of sacrificial agent. With variety of techniques available in order to shift the titania band gap, the scope is narrowed towards metal incorporation on titania in order to shift the band gap of titania to the absorption of visible light range. The objective of the project is to develop Cu/TiO_2 photocatalyst for hydrogen production from water-glycerol system.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Hydrogen has been considered as one of the most promising fuels near future. As far as researches are concern, hydrogen production has received much attention at present time as it do not exist alone in nature but must be "made" typically by isolating hydrogen from a hydrogen-containing substance or feedstock. As a matter of fact, hydrogen has the potential to reshape the entire energy industry due to the reason that it almost does not produce local air pollutants or greenhouse effect when it is either combusted or consumed in fuel cell. Various modes have been opted in producing hydrogen. One of them is via renewable energy. Solar and wind power are two major sources of renewable energy where hydrogen is produced in a clean life cycle. However at present, renewable energy contributes approximately 5% to the commercial hydrogen evolution, due to its high cost of operation. The second option is evolving hydrogen through photovoltaic water electrolysis process. This method is even more competitive as the cost decreases with the advancement in the technology. Nevertheless, this approach may invite serious life cycle environmental impact due to the consideration of using smaller band gap semiconductor material. Solid oxide fuel cell is another increased level of interest by producing hydrogen with the aid of methanol. Though hydrogen is produced at lower pressure, at the bulk level production, it requires higher compression to apply the technology to where most of the customers are located. Higher compression results in higher cost. Alternatively, photocatalytic water splitting using semiconductor especially TiO_2, has been recognized as the most promising technique of producing hydrogen. The reason behind this preferred method is that the process used for hydrogen evolution is clean, environmental friendly, utilizes solar energy and most of all low cost.

The study of photocatalysis goes way back approximately 30 decades where it was first initiated in 1970. Huge development has taken its way up to present time on enhancing and developing new methods on this activity. Photocatalyst is defined as acceleration of a photoreaction in the presence of a catalyst (Cornills et al., 2003). This activity has taken into serious consideration as it has the potential for the development of the hydrogen production technology as it has the ability of producing hydrogen from water molecules under UV light and/or visible light with the aid of sacrificial agents. Photocatalytic process functions based on simple principle where light energy is converted into electricity on the exposure of a semiconductor to light. The photocatalysis activity is initiated by the absorption of a photon with energy equal to or greater than the band gap of the semiconductor used, migrating the electron form the valence band to the conduction band. The separation of electron and hole can be enhanced further if electron donors (sacrificial reagents or hole scavenger) are added, the hole splits water molecules into oxygen gas and hydrogen ions while the electrons reduces the hydrogen ions to hydrogen gas as shown in Figure A1 (Appendix A).

As photocatalyst has drawn the attention of many researchers, rapid development has been noticed in the application of photocatalyst as well. With respect to the discovering of water splitting using TiO_2 by Fujishima et al., 1972, the application of photocatalyst commercially in the industry has doubled. Some of the applications are removing trace metals, destruction of organics removing inorganic compounds, water disinfections, and degradation of natural organic matter, seawater treatment, hydrogen evolution and water splitting.

2.2 TITANIUM DIOXIDE (TIO_2) AS SEMICONDUCTOR

Semiconductors at presents a widely being used as photocatalyst due to the fact that it possesses the ideal band gap between the conduction and valence band in the band gap energy diagram. Band gap is referred to the energy difference between the valence and conduction band while band gap energy is the minimum energy of light required to make the material electrically conductive for electrons to be excited enough to get moving. Some of the commonly used semiconductors are TiO2, ZnO, MgO, WO3, Fe2O3, CdS. The most apt semiconductor should at least meet the following properties in order to provide a better photocatalytic activity;

- Photo activity
- Biological and chemical inertness
- Stability towards photo-corrosion
- Suitability towards visible or near UV light
- Low cost
- Lack of toxicity

Compared with other photocatalyst, titania (TiO_2) has proven to be one of the most ideal as it is stable, environmental friendly, low cost, non-corrosive and abundant availability. TiO_2 has a wide band gap of 3.2 eV which hinders the absorption of visible light (higher than 500 nm) but is compatible for UV light of 388 nm or below. Huge number of research is on going, in order to shift the band gap of Titania towards the visible light region. Visible light water splitting necessitates suitable semiconductor band gap where it should be in the range of $1.23 \text{ eV} < E_g < 3.0 \text{ eV}$. Vast exploration on the field of enhancing hydrogen production through photocatalyst are experienced with relation to the modification that can be made on the semiconductor, whereby in this case is TiO_2.

2.2.1 Noble Metal Loading

TiO_2 photocatalysis has been proven to be further enhanced with the use of noble metals which includes Pt, Au, Pd, Rh, Ni, Cu and Ag. The photo excited electrons can be transferred from CB to metal particles deposited on the surface of TiO_2, while photo generated VB holes remain on the TiO_2. This is due to the fact that the Fermi levels of these noble metal particles are lower than that of TiO_2. This method reduces the possibility of electron-hole recombination which results in efficient and stronger photocatalytic reactions. However, there are limitations to this method where it takes the chances that the recombination cannot completely be eliminated and there are possibility of backward reaction of H_2 and O_2 to form water. This setback can be resolved by adding electrons donors or carbonates salts.

2.2.2 Metal Ion Doping

Transition metal doping and rare metal ion doping have been extensively being studied for the improvement of the photocatalytic reactions. Based on the studies conducted by Choi et al, it is found doping of metal ions could expand the photo response of TiO_2 into visible spectrum. As the metal ions are incorporated into the TiO_2 lattice impurity energy levels in the band gap of TiO_2 are formed.

2.2.3 Anion Doping

Anion doping is rather a recent method investigated in enhancing hydrogen production. Anion doping in TiO_2 crystalline has the possibility of shifting its photo response into visible spectrum. Anions are less likely to form recombination centers which indirectly enhance the photocatalytic activity.

2.2.4 Metal Ion Implantation

Metal ion implantation has reported to be an effective method to modify semiconductor electronic structures to improve visible light response. The TiO_2 which is bombarded with high-energy transitional metal ions modifies the TiO_2 electronic structures and shifts its photo-response to the visible region.

2.3 HOLE SCAVENGER OR ELECTRON DONOR

The water splitting reaction from TiO_2 photocatalyst tends to get tedious with the rapid recombination of photo-generated conduction band (CB) and valence band (VB). The addition of sacrificial agent or electron donors reacts irreversibly with the photo-generated VB holes and enhances the photocatalytic electron/hole separation giving higher quantum efficiency. In order to sustain the hydrogen production, continual addition of electron donors are essential. Electron donors are basically oxidized by the VB holes whereby CB electrons reduce protons to hydrogen molecules. Glycerol oxidation has been proven to form large number of products as shown in Figure A2 (Appendix A). During photocatalysis, these are some of the possible products which may be produced when oxidation of glycerol occurs. Most glycerol oxidation has complex reaction pathway with large number of products with possibility of forming other products with further oxidation process.

Glycerol is one of the most low cost hole scavenger which exist in large quantity form the palm oil industry and its non hazardous to human and as do not give severe impact to the environment. Glycerol is being added into the reaction in order to act as a hole scavenger. As said earlier, the water splitting reaction from TiO_2 photocatalyst tends to get tedious with the rapid recombination of photo-generated conduction band (CB) and valence band (VB). The addition of sacrificial agent or electron donors reacts irreversibly with the photo-generated VB holes and enhances the photocatalytic electron/hole separation giving higher quantum efficiency.

2.4 COPPER

Metal loading is one of the techniques which has been successfully experimented and produced promising results. Nobel metals such as Pt, Au, Ni, Cu, Ag, Pd and Rh are some of the metals which have been reported to be very effective for the enhancement of hydrogen production via photocatalyst. Of all the stated metals, copper incorporated TiO_2

photocatalyst has been receiving much attention at present time. Though Cu is being used as the noble metal, upon conduction of experiment and with respect to the XPS characterization, CuO component dominates in the anatase phase of Cu/TiO_2. It is proven by Wu and Lee.,2002, that at optimal loading of Cu, hydrogen production rate was enhanced as much as 10 times higher.

Basically in hydrogen production via photocatalytic activity, CuO acts as a water reduction site and as well helps the charge separation. J.Bandara et al., 2005, claims that CuO/ TiO_2 is generally found to be very stable with prolonged use and the stability of the catalyst could be understood on the basis of rapid electron transfer as in Figure A3 (Appendix A). Electrons (e^+) and holes (h^+) are produced in the valance and conduction band as light greater than the band gap energy of TiO_2 is being absorbed. The holes from the valence band are consumed by the sacrificial electron donors leaving electrons in the conduction band simultaneously. The electrons rapidly transfers from the conduction band (CB) of TiO_2 to the conduction band of CuO since the CB of CuO is situated below the CB of TiO_2 in competence with the electron transfer to O_2.

2.5 CATALYST PREPARATION AND PRETREATMENT

2.5.1 Wet Impregnation

Wet impregnation method is opted for the project. Impregnation is generally is divided into two sub-method which are wet impregnation and incipient wetness impregnation. Impregnation is basically contacting the precursor of the active phase with the solid support whereby the succeeding step is to remove the imbibed solvent by drying. The main purpose of the usage of this method is due to the fact that it is the most versatile technique which can be controlled to give good dispersion and known loading of reagents or support.

In the case of wet impregnation, excess of solution is used where within a given time period, the solid is separated while the solution is removed by drying. As far as the precipitation and sol-gel method is concern, it is yet another common method selected for catalyst preparation. However, precipitation method has a disadvantage. Precipitation method has numerous factors which affects the properties of the precipitated catalyst.

2.5.2 Effect of Calcination Temperature

In general, calcination is defined as a process that involves heating without the formation of a liquid phase which is carried out in air at temperature higher than those used in the catalytic reaction or regeneration. Several processes occur during calcinations which are loss of chemically bonded H_2O or CO_2, modification of the nature or surface of the phase present, generation of the active phase and stabilization of mechanical properties (Campanati et al., 2003).

Calcination temperature is one of the factors which has a significant influence on the catalytic performance due to different extent of solid solution formation in the catalyst. J.Bandara et al., 2005, claims that as the as the calcination temperature increases, the H_2 gas produced increases as well. The H_2 evolution increases from a temperature of 80^0C and then gradually starts to decrease as it reaches about 400^0C.

2.5.3 Effect of Aging Period

Yet another factor that affects the properties of a catalyst is the aging process. The prepared catalyst is generally aged for a certain period if time at specific temperature in order to encourage the interaction between metallic species and the support which indirectly aids in enhancing the catalyst activity.

With reference to the study conducted by M. Campanati and friends, ageing is generally performed at room temperature and pressure for extended time (Campanati et al., 2003). According to the study, at low temperature which is below 40^0C, the reaction between the precipitating precursor ions and the support is generally restricted to the surface of the support. However, at higher temperature which is about 100^0C, the reaction between the support material and the precipitating agent is not restricted to the formation of an interface structure and as a result mixed bulk structure are also formed.

CHAPTER 3

METHODOLOGY

All the chemicals used in this research were obtained from commercial sources as analytical grade and is being used without any further purification. This research is basically divided into three phases as listed below:-

i. Catalyst Preparation and Pretreatment
ii. Catalyst Characterization
iii. Catalyst Performance Based on Reaction Studies

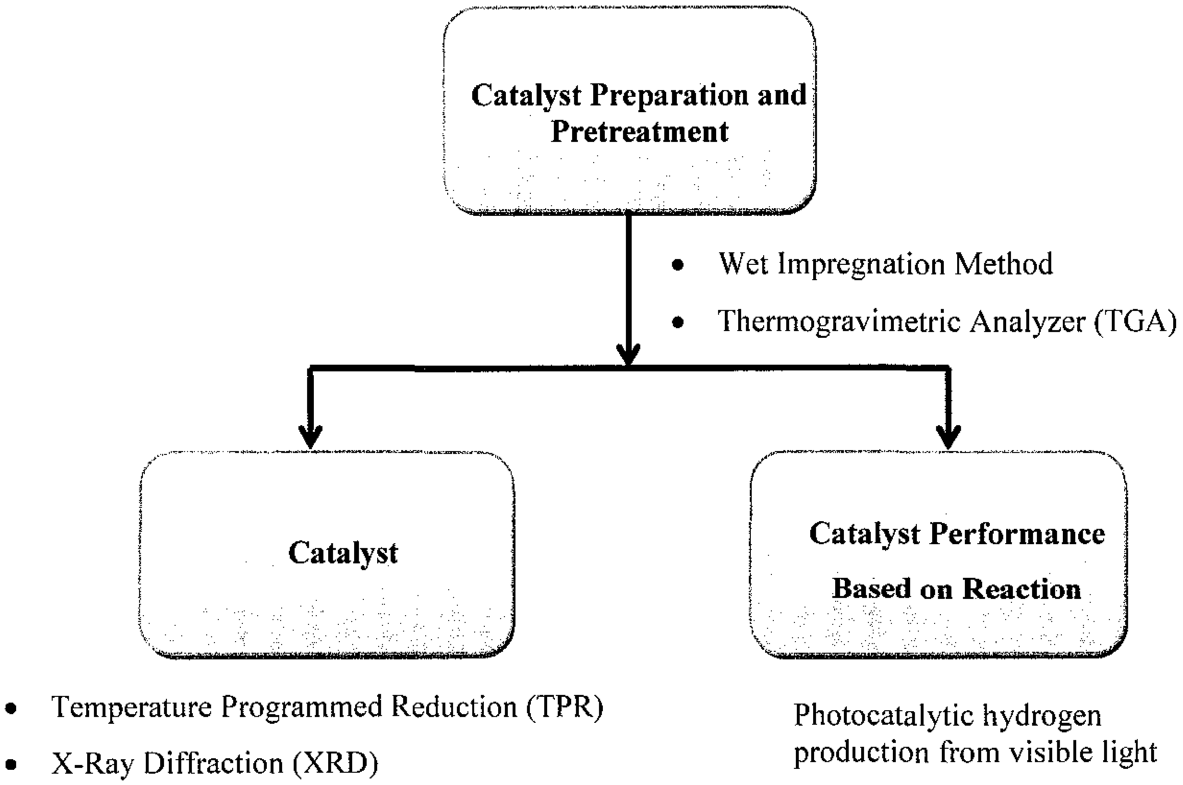

Figure 3.1: Overall Project Methodology

3.1 CATALYST PREPARATION

As far as this project is concern, various preparation methods and techniques have been researched beforehand commencing the preparation of the desired catalyst. The method opted for this Cu/TiO_2 catalyst is wet impregnation. Wet impregnation is given the priority as it is certainly an extremely versatile technique which can be controlled to give good dispersion and a known loading of reagents or supports. As for this project, sixteen samples have been prepared with variation of copper loading, aging period and calcination temperatures. For every copper loading of the four loading amount suggested, two samples each are prepared with two different aging periods. A summary of the preparation is given in Table 3.1.

Figure B2 (Appendix B) provides the flow diagram for the catalyst preparation. Appropriate amount of $Cu(NO_3)_2.3H_20$ was dissolved into specific amount of distillate water. The solution was then added to the TiO_2 slurry and is being mixed. The total amount of distillate water used to prepare the copper solution of $Cu(NO_3)_2.3H_2O$ and TiO_2 slurry was 150ml. Mixture was stirred until the copper is fully dispersed within the titania slurry. It formed a light bluish color slurry substance due to the color from the copper as shown in Figure B3 (Appendix B).

The mixture was then left for either a day or three, depending on the aging period. Once the aging period has completed, the slurry was dried in a water bath at 80^0C, as shown in Figure B4 (Appendix B). It took about five to six hours before the slurry mixture turns into numerous pieces of chunks and then proceeded to further drying in the oven at 120^0C for an overnight period. The dried chunks of the Cu/TiO_2 are shown in Figure B5 (Appendix B). The chunk was then crushed into powder form and sent for characterization.

Table 3.1: Summary of the amounts of $Cu(NO_3)_2.3H_2O$, titania and water used for the preparation of the catalyst.

Content	**Copper loading (wt %)-Aging Days**			
	3wt%-1&3 Days	***7wt%-1&3 Days***	***10wt%-1&3 Days***	***15wt%-1&3 Days***
Amount of Catalyst (g)	20	20	20	20
Mass of Cu(NO3)2.3H2O (g)	2.2805	5.3159	7.6017	11.4030
Mass of TiO2 (g)	19.4	18.6	18	17
Mass of Cu (g)	0.6	1.4	2	3
Volume of Distillate Water (ml)	150	150	150	150

3.2 CALCINATION TEMPERATURE

Calcination (also referred to as calcining) is a thermal treatment process applied to ores and other solid materials in order to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials. Calcination is to be distinguished from roasting, in which more complex gas-solid reactions take place between the furnace atmosphere and the solids, as calcination takes place in the absence of air.

The calcination temperatures of this project are 200^0C and 300^0C. A furnace was used to carry out the calcination process. A dry run process was conducted on the furnace whereby the temperature was increased to 800^0C and left for a day. The temperature is then lowered to 50^0C and left over night. This was done in order to clean the furnace as it will be free from external factors which may give and impact on the catalyst.

Calcination was done on the 16 samples prepared at 200^0C and 300^0C. The temperature of the furnace was increased gradually for every 10 minutes with the temperature increment of 10^0C. The temperature was then sustained at 200^0C and 300^0C for an hour before removing the samples from the furnace.

3.3 PHOTOCATALYTIC REACTION

The main aim of the photocatalytic reaction is to analyze the performance of the catalyst for hydrogen production. A multiport reactor was used for this process together with a halogen lamp (500 Watt), which provides the visible light source. 0.1g of catalyst was added to 6 ml glycerol, 8 ml distill water and 2 ml NaOH. The equipment set up is as shown in Figure B6 (Appendix B). The gas produced was monitored with time intervals of 10 minutes for 1 hour reaction time period.

3.4 CATALYST CHARACTERIZATIONS

Catalyst is a fast moving field of study at the present technological advancement world. Apart from the preparedness of the catalyst and its active performance capability, numerous techniques are now in place as in to characterize the activation and the reactivity of these heterogeneous catalysts.

3.4.1 Temperature Programmed Reduction (TPR)

In particular, temperature-programmed reduction (TPR) has proved a powerful tool to analyze the reduction kinetics of oxidic catalyst precursors. This technique consists of heating the catalyst with a linear temperature ramp in a flow of hydrogen while monitoring the hydrogen consumption. In this way, Fingerprint profiles are obtained which allow one to study the influence of the support and of promoters on the reducibility. Furthermore, the amount of reducible species in the catalyst and their degree of reduction can be derived from the integrated hydrogen consumption, and lumped kinetic parameters can be estimated if an adequate model of the reduction process exists. (S.Besselmann et al., 2001). The pretreatment and analysis conditions are given in Table 3.2 below:-

Table 3.2: Pretreatment and Analysis Conditions of TPR

Pretreatment Condition	**Analysis Condition**
40-110 °C hold 10 min	40-400 °C hold 30 min
Ramp 10°C/min	Ramp 10°C/min
Flow rate 20 ml/min under N_2 flowing	Flow rate 20 ml/min reduction under 5%H_2/N_2 flowing

3.4.2 X-Ray Diffraction (XRD)

X-Ray diffraction (XRD) is used to investigate the bulk phases present in the sample and to determine the ageing-induced solid-solid phase transformations. X-rays are energetic enough to penetrate into the material and their wavelengths are of the same order of magnitude as interatomic distances in solids. Thus, a collimated beam of X-rays is diffracted by the crystalline phase in the sample according to Bragg's Law as shown below;

$$n\lambda = 2d\sin\theta$$

Where;

λ = Wave length of the X-rays
θ = Is the incoming diffraction angle
n = Is the order of the diffraction
d = Distance between two atomic planes in the crystalline phase

3.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5% O_2 in N_2 or He) to slow down oxidation.

3.5 CATALYST PERFORMANCE

The catalyst performance is measured by the photocatalytic reaction. The prepared catalyst is exposed to the halogen lamp with the addition of catalyst, NaOH, distillation water and as well glycerol. Halogen light tends to irradiate light on the visible light range. The lamp uses 500W of power and it is placed about 30cm from the multiport single reactor and the intensity of light is 250W/m^2.

When photocatalyst titanium dioxide (TiO_2) absorbs illuminated light source (halogen lamp), it will produce pairs of electrons and holes. The electron in the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promoted the electron to the conduction band of titanium dioxide therefore creating the negative-electron (e-)in the conduction band and positive-hole (h+) pair in this valence band. The electron breaks apart the water molecule to form hydrogen gas and hydroxyl radical.

As this reaction occurs, the glycerol plays a role in reacting irreversibly with the photo-generated VB holes and enhances the photocatalytic electron/hole separation, whereby it directly oxides to produce large number of products. Most glycerol oxidation has complex reaction pathway with large number of products which has the possibility of forming other products with further oxidation process.

CHAPTER 4

RESULTS AND DISCUSSION

As mentioned earlier, the production of hydrogen via visible light photocatalyst has begun to receive reorganization widely at present. Copper incorporated titania is a peak research at the moment due to its high stability in rapid electron transfer and stability for prolonged use. Various researches have been conducted to explore further on enhancing the performance of this catalyst in order to improve the hydrogen production via visible light. By incorporating impurities in the case of this project is copper, huge difference is proven to be noticed in the band gap of TiO_2 and as well the hydrogen evolution. TiO_2 has the band gap of 3.2 eV whereby hinders the absorption of visible light (higher than 500 nm) but is compatible for UV light of 388 nm.

Upon carrying out this project for about six weeks, some observation has been spotted in the first phase of the project which is the catalyst preparation phase. All the catalyst was prepared via the wet impregnation method, whereby excess of solution is used where within a given time period, the solid is separated while the solution is removed by drying. Various copper loading is being used and the aging period has been varied as well. As the samples are yet to be sent for characterization, only visual characterization can be noted on the prepared samples. One clear observation is that, the bluish color of the samples tends to become much darker as the copper loading is increased from 3%wt, 7%wt, 10% and 15%wt. This might be due to the fact that the $Cu(NO_3)_2.3H_2O$ which is in blue color initially and as the amount used is increased, the color gradually blends through the samples.

Apart from the copper loading as one of the variable parameter, ageing period is yet another variable which is being said to be one of the influences to the performance of the catalyst. Based on a study conducted by M.Campanati and co-researches, 2003, ageing process is normally being performed at room temperature and pressure for extended time. The main aim of ageing is to promote interaction between the metallic species and support which indirectly contributes to the enhancement of the catalytic activity. Based on this research, for every loading, a one day and three days ageing period were chosen.

4.1 CATALYST CHARACTERIZATION

4.1.2 Temperature Programmed Reduction (TPR)

The main aim of TPR is to determine the reduction behavior of Cu/TiO_2 catalyst and also to reveal if the reducibility depends on the loading or not. Reduction profiles of Cu/TiO_2 for different copper loadings are shown in Figure C1 to C4.

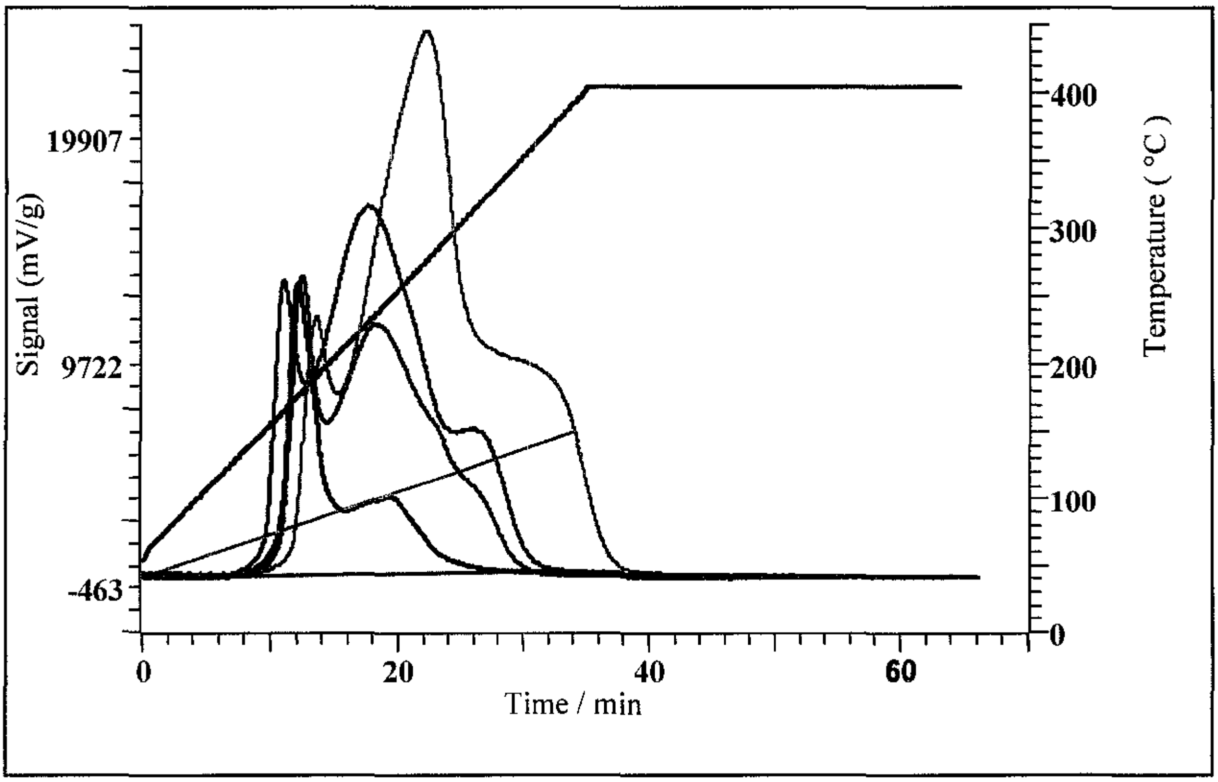

Figure 4.1: TPR Profile for Samples Calcined at 300^{0}C for 3 Days Aging Period

Based on Figure 4.1, the TPR show the presence of a few peaks within the range of 40^0C to 410^0C. The peak area attributed to the reduction of dispersed copper oxide which would reach the maximum with the copper oxide loading amount, while the area of the peak attributed to the reduction of crystalline CuO would increase with the copper oxide loading amount. (Haiyang et al., 2006). The area below the peaks gives the amount of hydrogen consumed while the presents of several reduction peaks explains that there are several types of copper species which exists in the wet impregnation samples.

From Table 4.1, it can be concluded that as the copper loading increases, the amount of hydrogen consumed also increases. This is simply due to the fact that as the copper loading increases, the higher amount of hydrogen is needed in order to reduce the copper species.

Table 4.1: Summary of TPR Analysis for Samples Calcined at 300^0C for 3 Days Aging Period

Samples	**Identification**	**Reduction temp,**	**Amount of H2 consumed, μmol/g**
3wt% Cu/TiO_2	Red Line	175, 246	395.69084
7wt% Cu/TiO_2	Blue Line	164, 221	867.05832
10wt% Cu/TiO_2	Purple Line	166,231,312	1321.21495
15wt% Cu/TiO_2	Pink Line	172,258, 356	1881.74352

4.1.3 X-Ray Diffraction (XRD)

The XRD test is conducted to determine the components present in the catalyst and as well to determine the active phase located on Cu/TiO_2 catalyst. From the analysis, TiO2 and CuO are noted to be present in the samples. The major phase of TiO_2 is noted to be in anatase and rutile phase. As far as the photocatalytic reaction is concern, the most active phase of TiO_2 is the anatase phase, (Tseng et al., 2001). The presents of the anatase and rutile phase explains a limitation of this study. One major factor could be during the catalyst preparation phase. The technical flaws during the preparation of catalyst may have contributed to the presence of the extra phase.

Based on Figure 4.2, copper peak is being detected basically on all the samples of the 10% copper loading. Two unknown peaks are noted for the calcination temperature of 200^0C, which exist between 10 theta to 15 theta. No copper peak was observed for the 3% Cu loading which as a matter of fact is due to the small Cu clusters. Further details of the XRD results for all samples are shown in Appendix C.

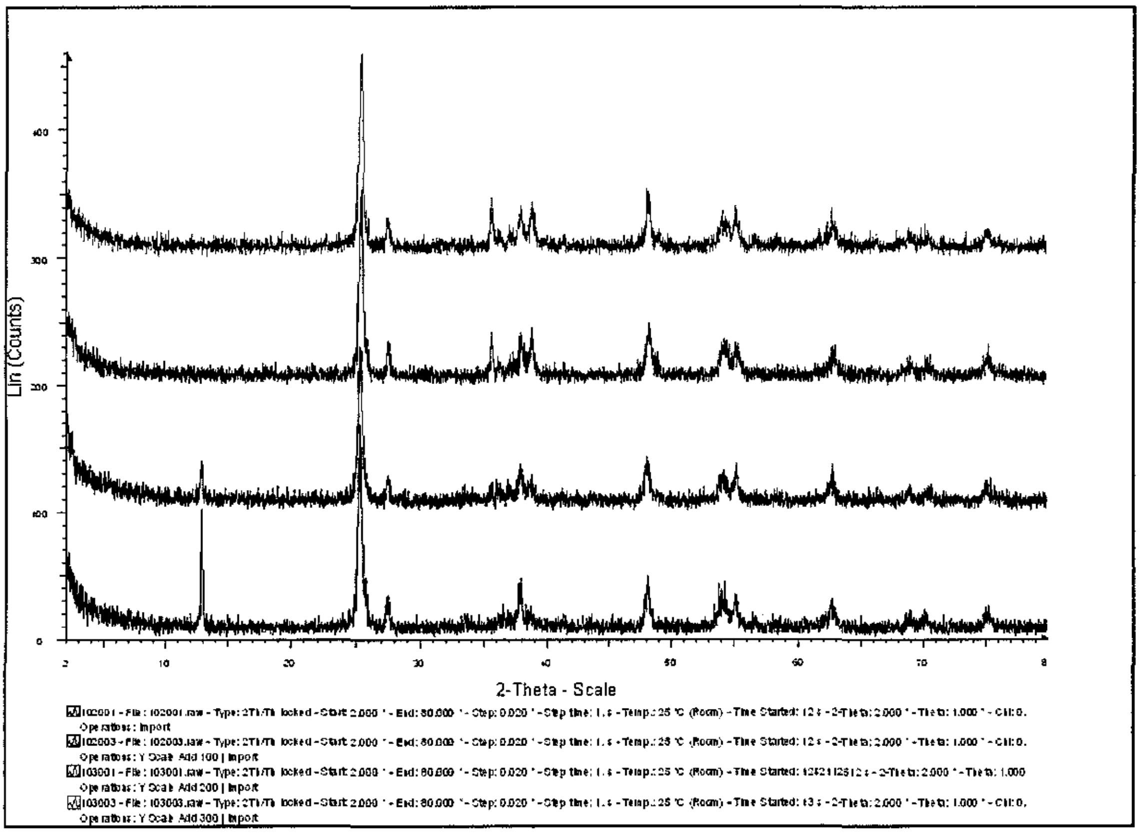

Figure 4.2: XRD Results for 10% of Copper Loading

4.2 CATALYST PERFORMANCE

With reference to the photocatalytic reaction carried out, gas was produced by the samples. The results of the gas productions are shown in Table 4.2 and 4.3.

Table 4.2: Volume of Gas Collected for Cu/TiO_2 Calcined at 300^0C

Catalyst	**Volume of Gas Produced (ml)**	
	1 day aging	**3 days aging**
3wt%	2.7	3.3
7wt%	2.8	3.9
10wt%	2.9	4.0
15wt%	2.8	3.7

Table 4.3: Volume of Gas Collected for Cu/TiO_2 Calcined at 200^0C

Catalyst	**Volume of Gas Produced (ml)**	
	1 day aging	**3 days aging**
3wt%	1.9	2.9
7wt%	2.4	3.2
10wt%	2.8	3.5
15wt%	2.8	3.4

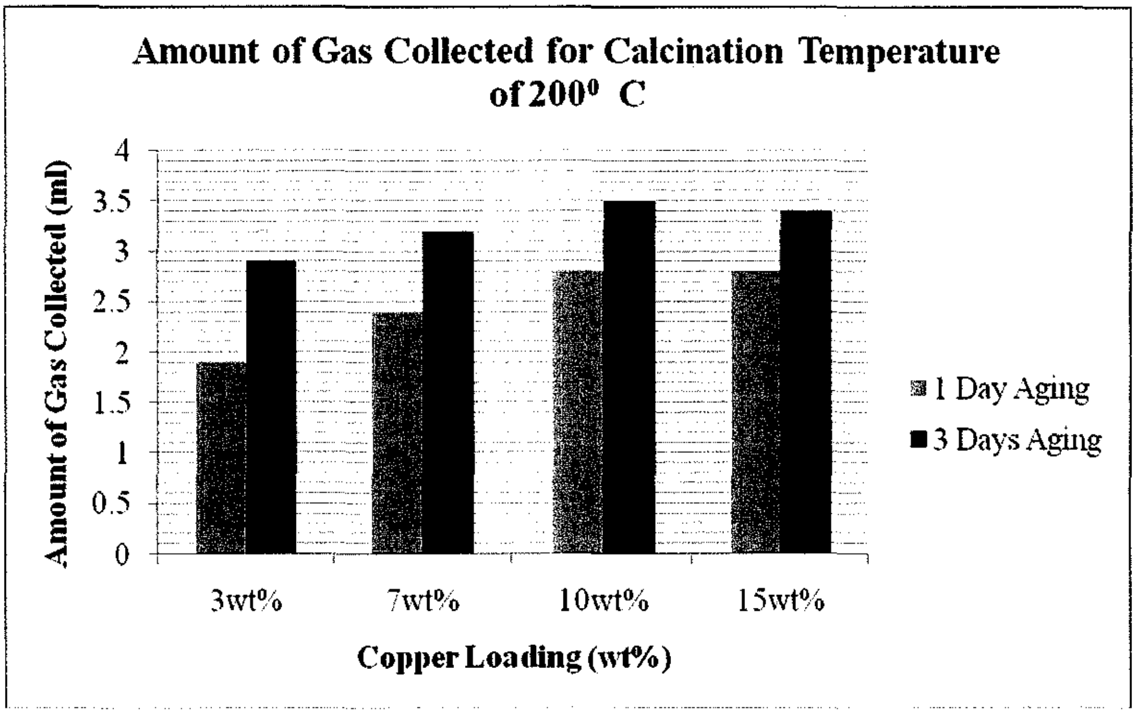

Figure 4.3: Graph of Amount of Gas Collected for Calcination Temperature of 200^0 C

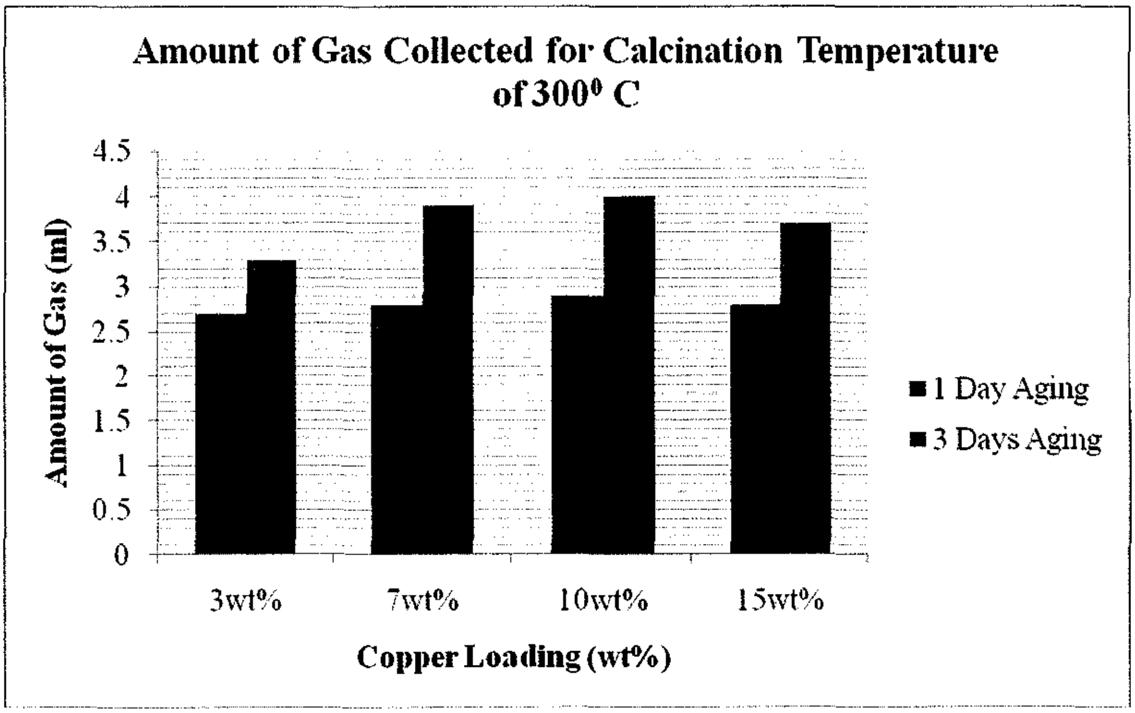

Figure 4.4: Graph of Amount of Gas Collected for Calcination Temperature of 300^0 C

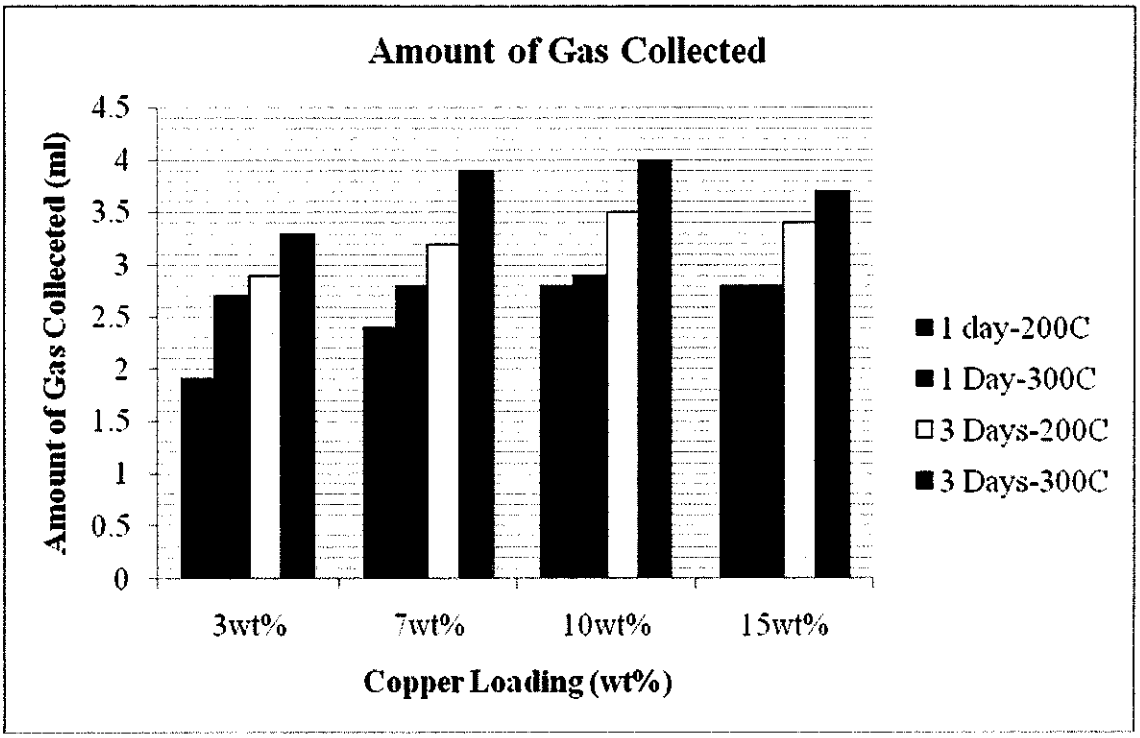

Figure 4.5: Summary of Amount of Gas Collected

Based on the Table 4.2 and 4.3 and Figure 4.3 and 4.4, for calcination temperature of 200^0C and aging period of 1 day, copper loading of 10wt% and 15wt% produces the equal volume of gas while for 3 days aging, copper loading of 10wt% produces the highest volume of gas. As for the calcination temperature of 300^0C, 10wt% performs much better than the rest of the copper loading for 1day aging period while for 3 days aging period, yet again 10wt% produces highest volume of gas.

On the whole from Figure 4.5, copper loading of 10wt% performs much better compared to the rest of the loadings at calcination temperature of 200^0C for 1 and 3 days aging period. However, for the 1 day aging at calcination temperature of 200^0C, 10wt% and 15wt% has the equivalent amount of gas produced. On the other hand, 10wt% gives the best results in gas production at calcination temperature at 300^0C for both 1 and 3 days aging period.

With regards to the figures above, aging period contributes to the performance of the catalyst. The longer the aging period, the higher volume of gas is being produced. The longer the slurry is being aged; better interaction occurs between the copper and titania molecules (M.Campanati et al., 2003). This may be one of the factors which enhance the performance of the catalyst.

Apart from aging period, calcination temperature too is factor that gives effect to the catalyst performance. Based on the experiment conducted, its shows that higher volume of gas is collected at the calcination temperature of 300^{0}C compared to 200^{0}C. Thus, this explains that the ideal calcination temperature is 300^{0}C. In order to justify this findings, the prepared catalyst was sent for TGA to determine its decomposition temperature. The TGA results in Figure C10 (Appendix C) shows that the decomposition of $Cu(NO_3)_2.3H_2O$ is identified around 250^{0}C. Thus, a calcination temperature which is slightly higher (e.g.300^{0}C) is suggested.

In several studies, it has been observed that increasing the calcination temperature of the impregnated catalyst much above 500-600^{0}C usually results in decreased in catalytic activity (Seung Kon Ryu et al., 2004). As $Cu(NO_3)_2{\cdot}3H_2O$ is being used in this project, the approximates temperature of calcination is between 200-310^{0}C as this is its thermal decomposition temperature with respect to (Seung Kon Ryu et al., 2004). Refer to Table 4.4 for detailed thermal decomposition of $Cu(NO_3)_2{\cdot}3H_2O$.

Table 4.4: Thermal Decomposition Temperature of $Cu(NO_3)_2{\cdot}3H_2O$ *(Retrieved from Seung Kon Ryu et al., 2004)*

Temp. (°C)	40-80	80-110	116-152	120-150	167-205	199-217	200-250	247-260	263-310
D.D.Perlmutter [18] (reduced Pressure)			Melting to $Cu(NO_3)_2$			$Cu_2(OH)_3NO_3$			CuO
D.Dollimore [19]	$3Cu(NO_3)_2\,Cu(OH)_2$				182~312 CuO				
B.V.Lvov [20]					$Cu_2(OH)_3NO_3$			CuO	
I.V.Morozov [21] (reduced P=1Pa)	$Cu(NO_3)_2{\cdot}2.5\,H_2O$ $Cu(NO_3)_2H_2O$	Melting to $Cu(NO_3)_2$		Sublimation			CuO		

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

Copper coated TiO_2 has proven to decrease the band gap of TiO_2 and produce improved results in hydrogen production, (J.Bandara et al., 2005). As far as this project is concern, glycerol is also being used as hole scavenger and wet impregnation is chosen as the catalyst preparation method. Besides that, a few characterization techniques are opted to study the behavior of the prepared catalyst which includes TPR, XRD and TGA. The success of this kind of study has already been experienced with the fact that it is conducted in UV light. Studies' using visible light on Cu/TiO_2 for hydrogen evolution is still in the developing era but there are several researches that have succeeded. If the studies on this particular field have the capability of proving extreme results, in time to come this method would be the most preferred way of producing hydrogen as it is low in cost and environmental friendly.

As far as this project is concern, the conclusion of the progress is up to catalyst preparation and pretreatment, catalyst performance based on photocatalytic reaction studies and catalyst characterization. The Cu/TiO_2 samples are prepared through the wet impregnation method. Copper loadings of 3wt%, 7wt%, 10wt% and 15wt% were loaded on to titania with two different calcination temperature and two different aging period. The effect of copper loading, calcination temperature and aging period is investigated in this report. A few characterization techniques (XRD, TGA, and TPR) are utilized in order to study the properties of the prepared catalyst. Based on the results obtained during the photocatalytic reaction studies, it can be concluded that:

i. As the amount of copper increases, the amount of gas collected in the reaction studies increases as well. The best performance is noted to be from the copper loading of 10wt%.

ii. Apart from that, the calcination temperature affects the performance of the catalyst as well. It is noted that, higher volume of gas is being collected from the samples that is calcined at 300^0C compared to the samples calcined at 200^0C.

iii. Aging period too contributes to the catalyst performance. Higher volume of gas is obtained from samples which are aged for 3 days compared to the 1 day aged samples. This applies for both the calcination temperature (200^0C and 300^0C).

iv. One of the characterization studies which have been included in this report is the TPR studies. The aim of TPR is to analyze the information of the reducibility of the oxide's surface as well as heterogeneity of the reduced surface. The TPR of this study shows that as the copper loading increases, the amount of hydrogen consumed increases as well. The presence of several peaks explains that there are number of copper species that exists.

v. As for the XRD analysis, TiO_2 is noted to be present in form of anatase and rutile phase. While CuO is present only on the Cu loading of 10%. This is due to the facts that lower Cu loading as smaller cluster of Cu which cannot be detected. The presence of two different phase of TiO_2 leads to the fact of technical errors which might have occurred during the catalyst preparation step.

vi. The TGA results justifies the reason for choosing the calcination temperature of 200^0C and 300^0C. $Cu(NO_3)_2 \cdot 3H_2O$ is being noted to start its decomposition at about 250^0C. Thus, a slightly higher temperature of calcination is suggested.

5.1 Recommendation

Based on the study conducted, a few suggestions have been proposed in order to enhance the performance of the experimental results further:-

i. The comparison parameter should be increased in order to obtain a detailed analysis on the catalyst performance. Various methods of catalyst preparation (precipitation, sol gel method) and longer aging period are two of the parameters which can be considered.

ii. A gas chromatography analysis and mass spectrometer is suggested to be carried out right after the reaction studies is done in order to identify the composition of hydrogen produced.

iii. Reaction studies should also be carried out using various types of lights such UV lamp and as well under solar irradiation in order to investigate the catalyst performance between both types of lights in order to make a wider comparison.

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APPENDIX A

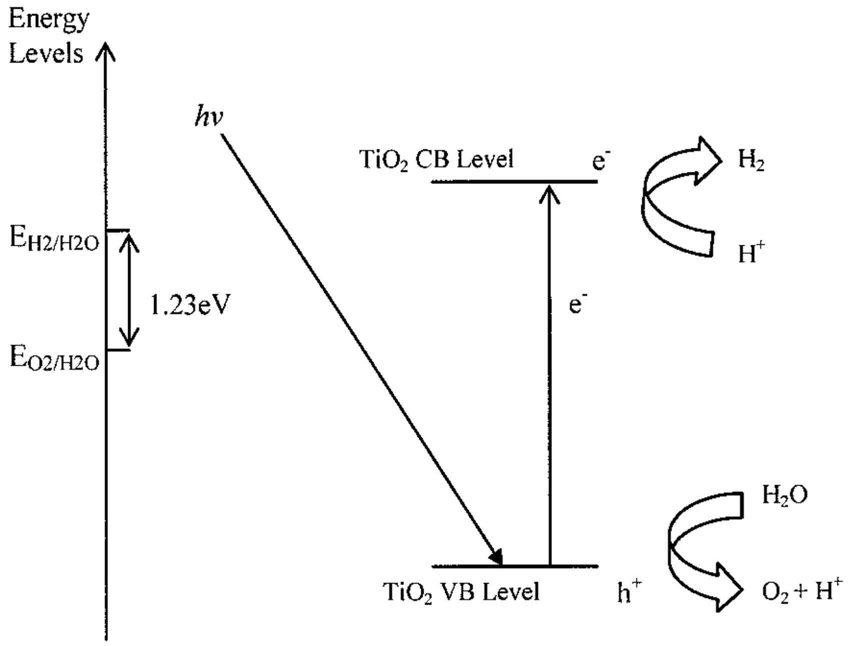

Figure A1: Mechanism of TiO_2 photocatalytic water-splitting for hydrogen production (Meng Ni et al., 2007)

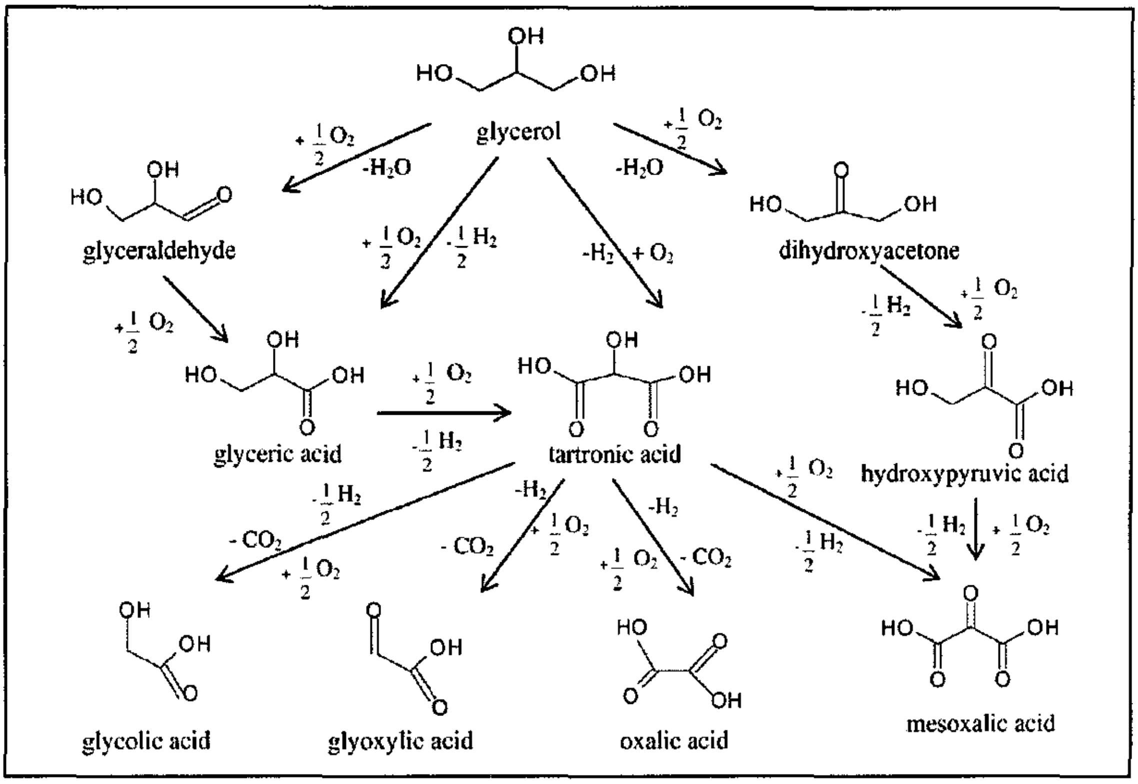

Figure A2: Reaction network of the glycerol oxidation (Demirel-Gulen et al., 2005)

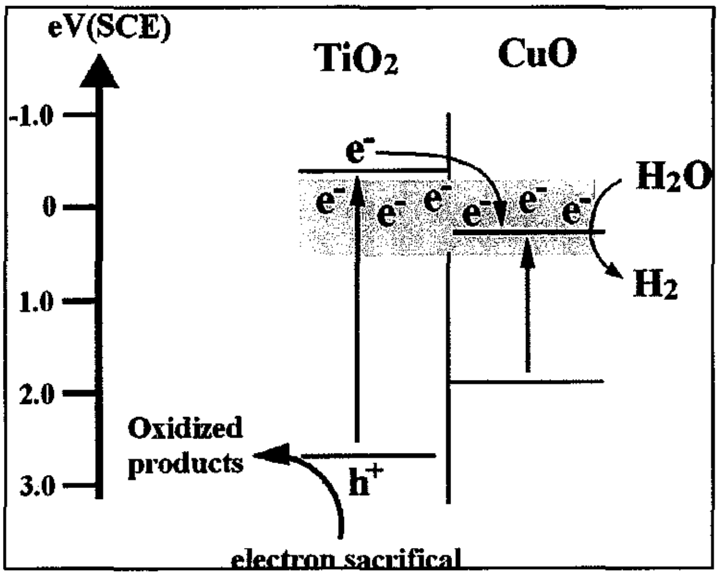

Figure A3: Schematic diagram of the electron transfer and the energy band positions TiO_2 and CuO (J.Bandara et al., 2005)

APPENDIX B

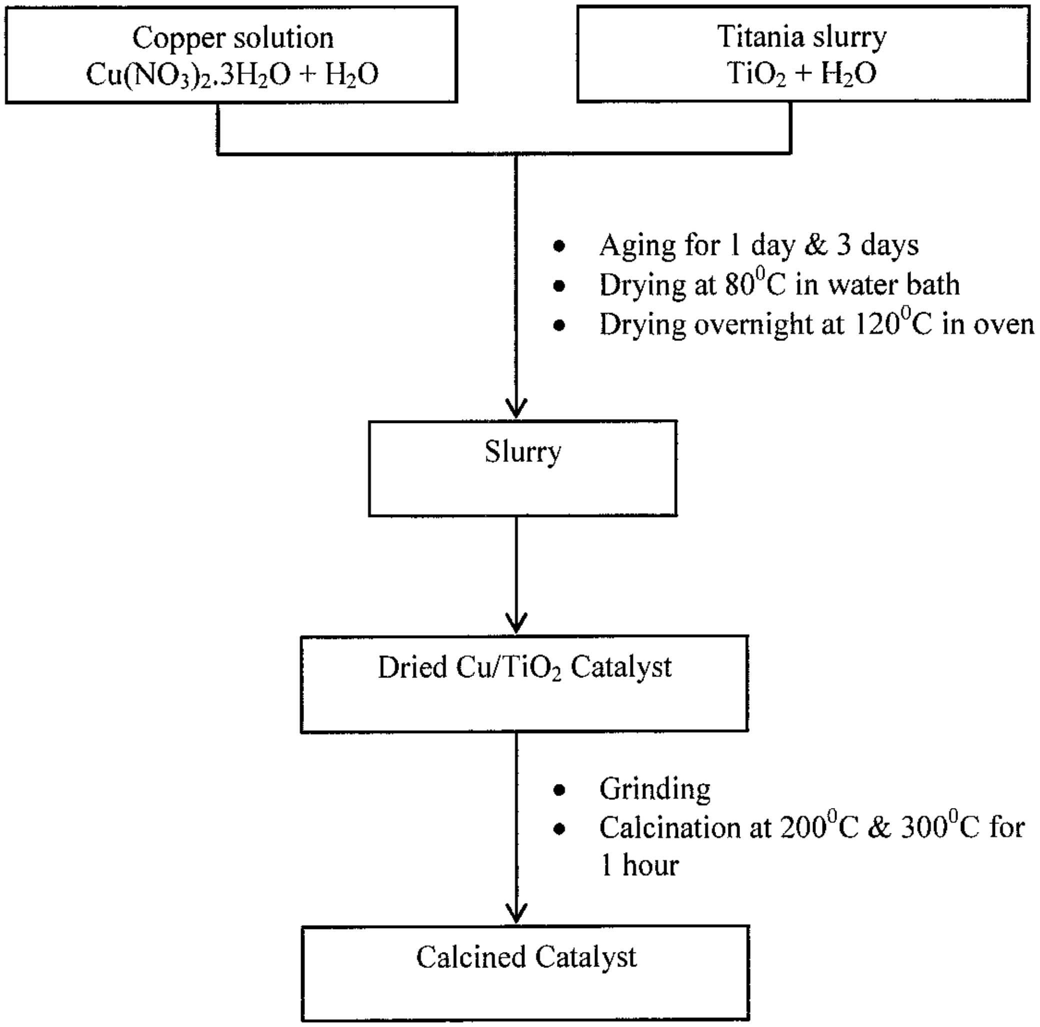

Figure B2: Summary of Cu/TiO_2 catalyst preparation

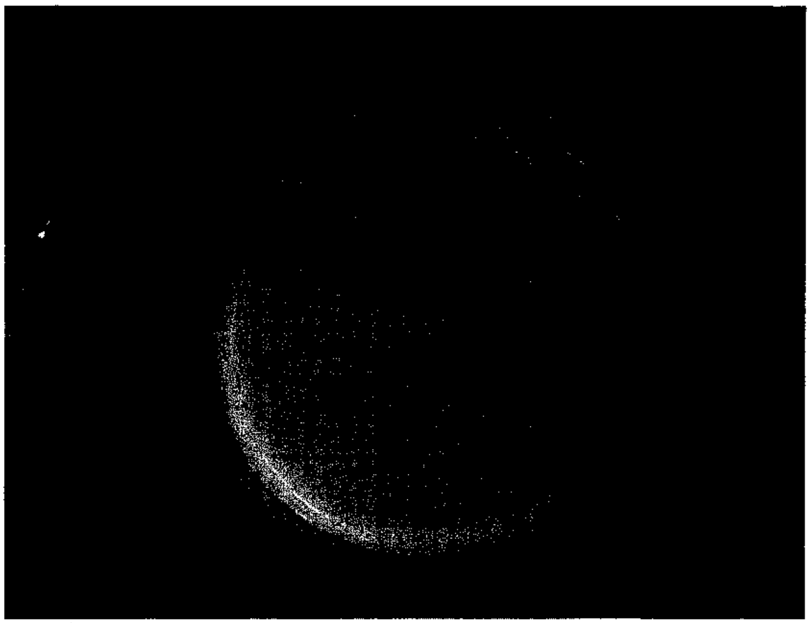

Figure B3: The light bluish slurry of $Cu(NO_3)_2.3H_2O$ and titania mixture

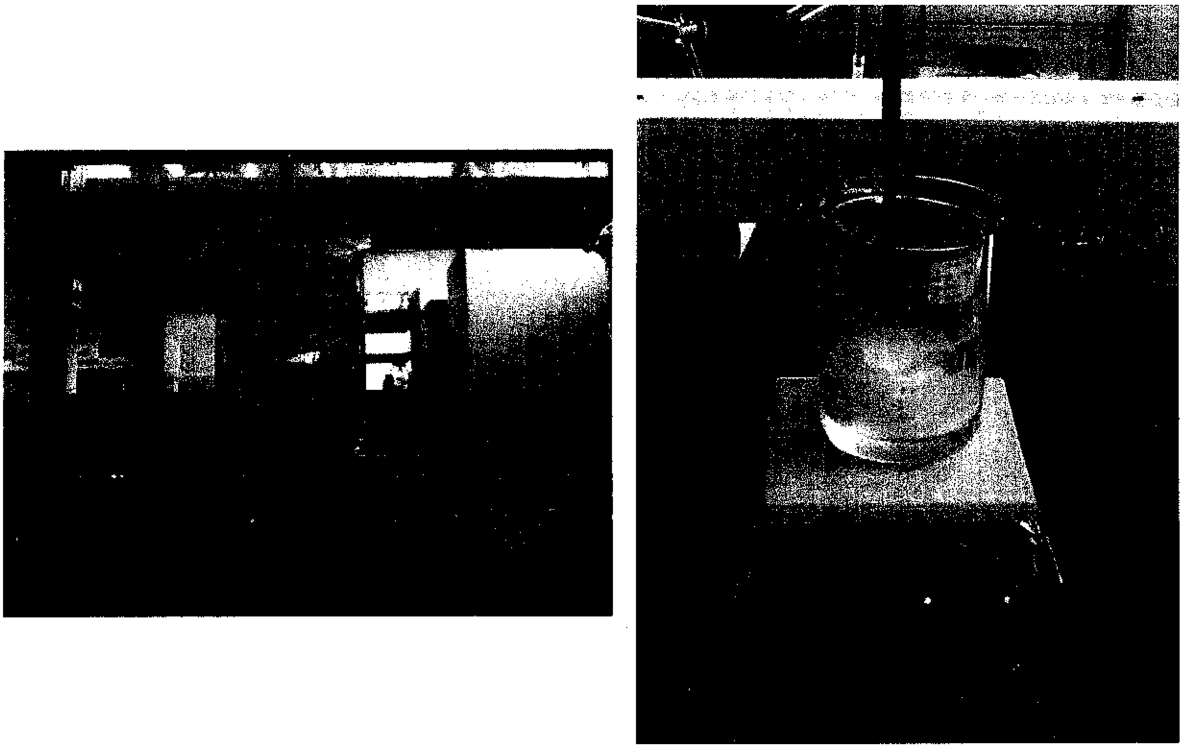

Figure B4: Water bath at 80^0C

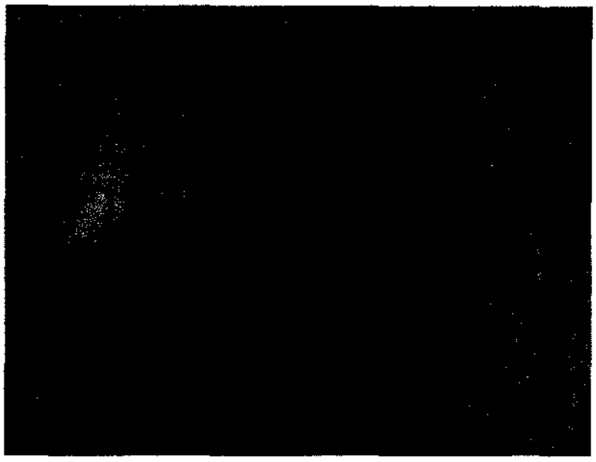

Figure B5: Dried chunks of the Cu/TiO$_2$

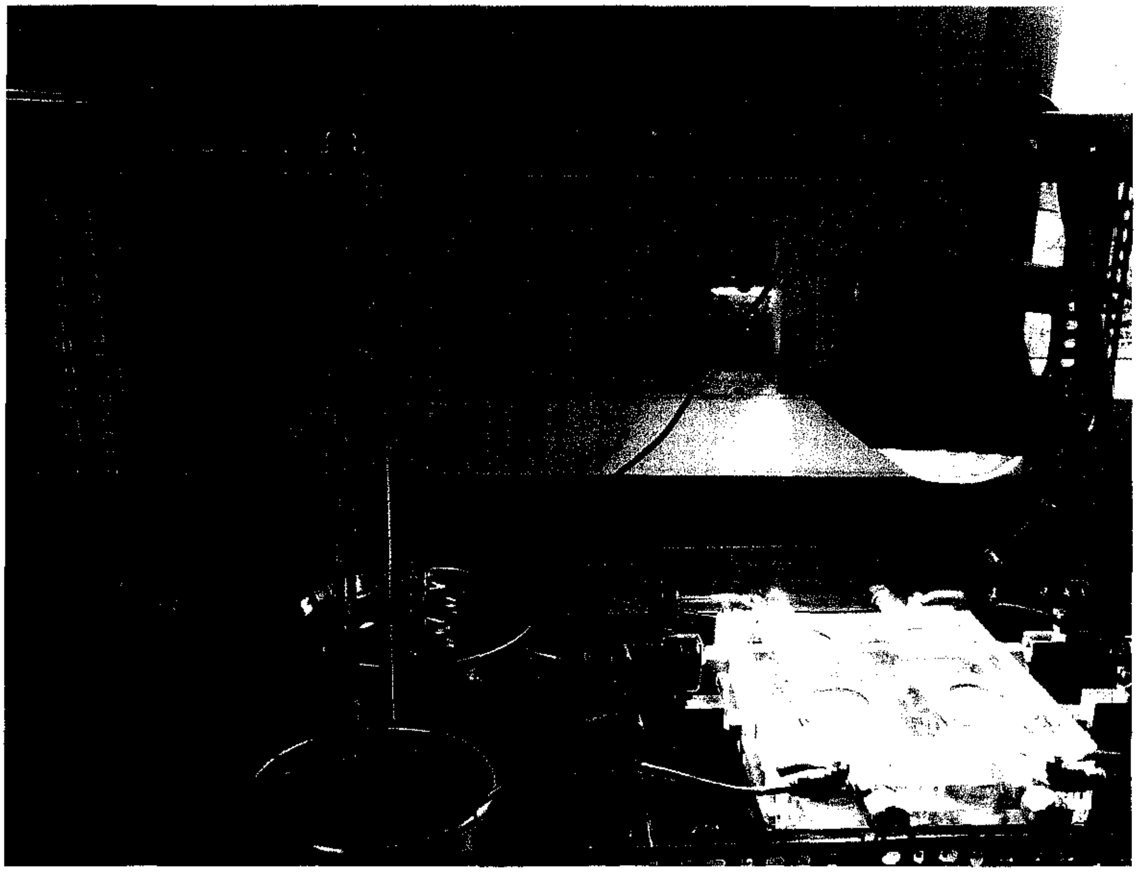

Figure B6: Photocatalytic Reaction Equipment

APPENDIX C

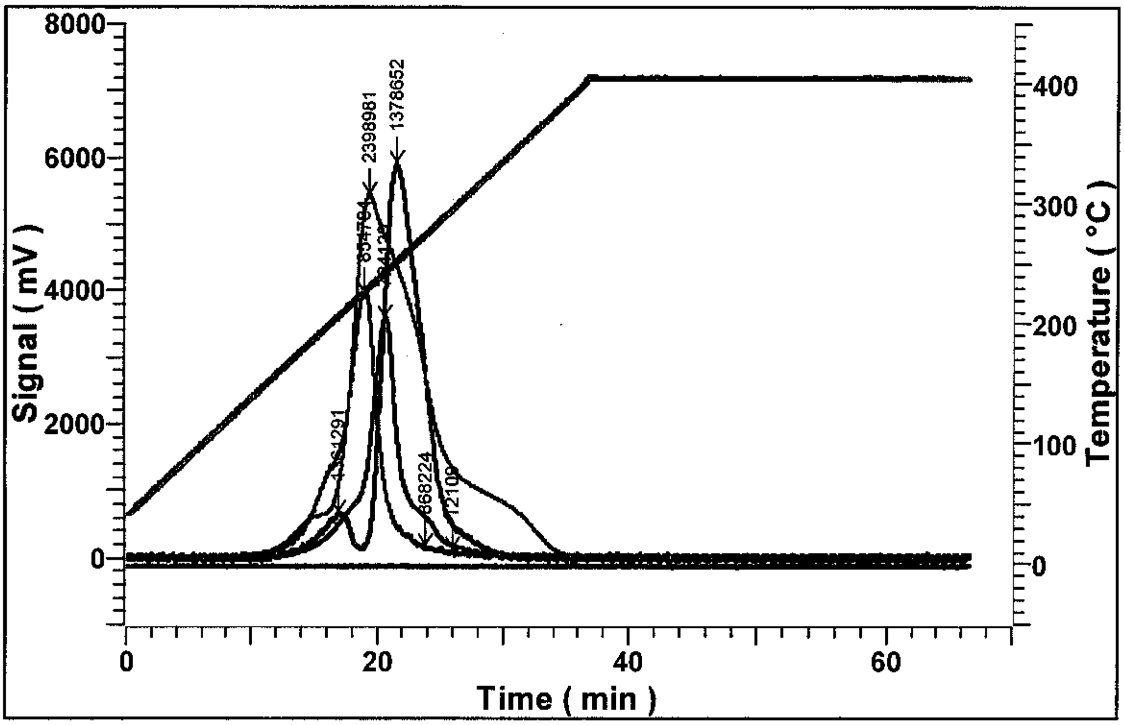

Figure C1: TPR Profile for Samples Calcined at 200^{0}C for 1 Day Aging Period

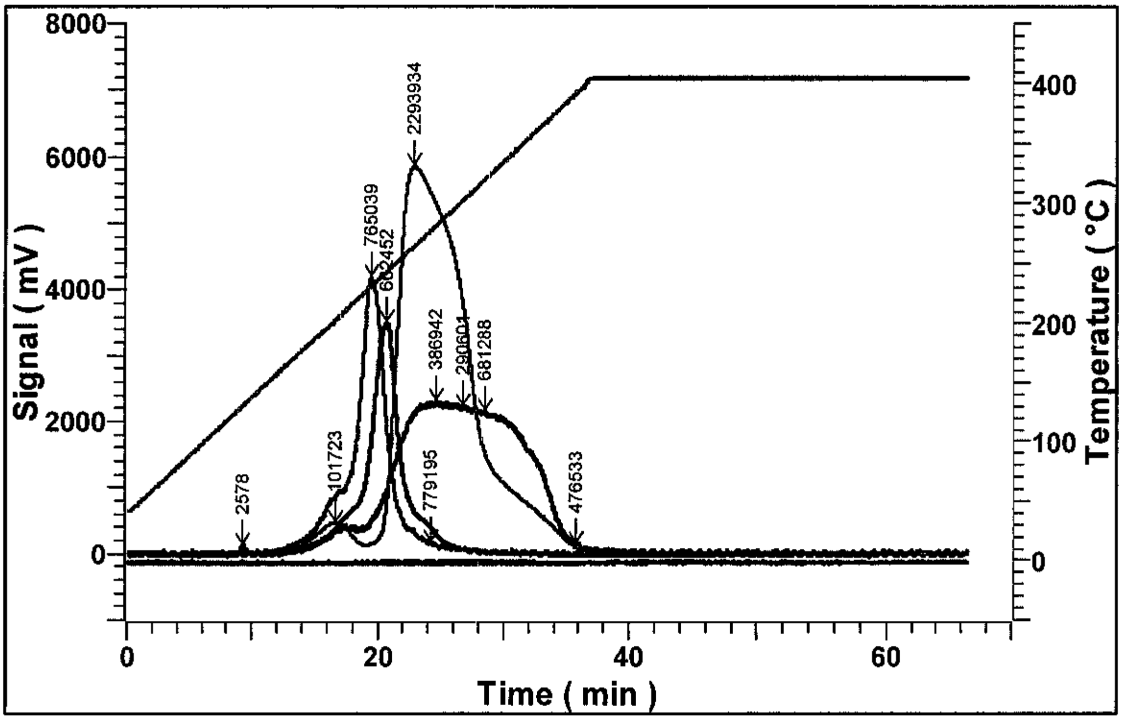

Figure C2: TPR Profile for Samples Calcined at 200^{0}C for 3 Days Aging Period

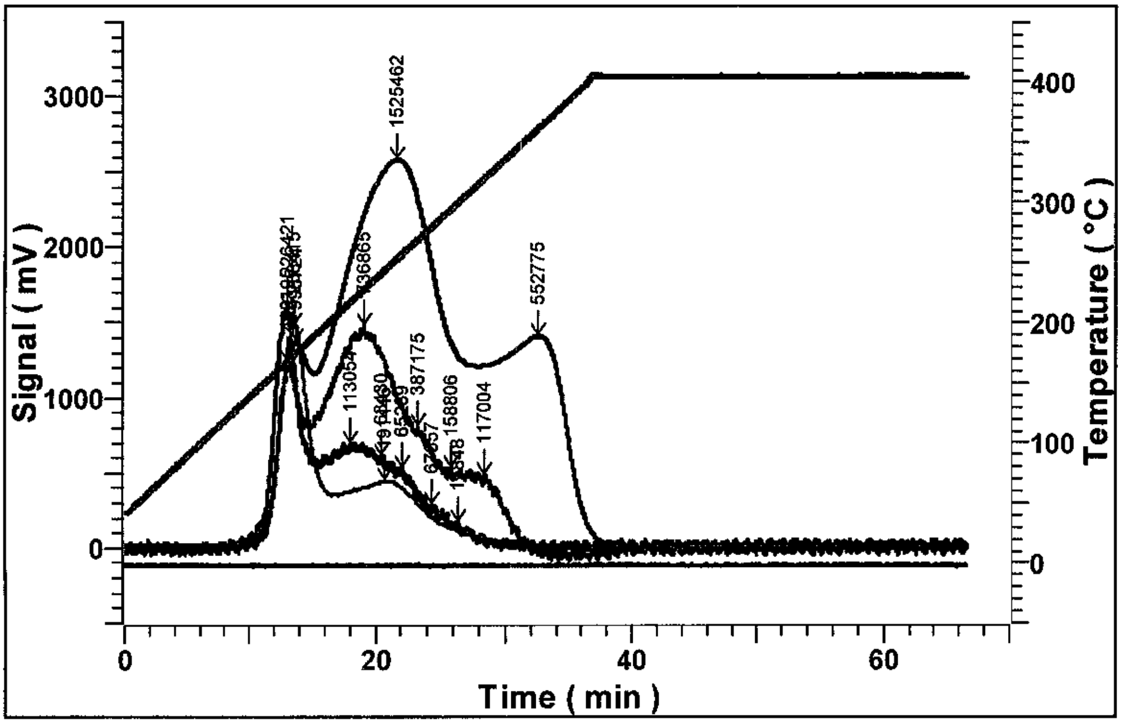

Figure C3: TPR Profile for Samples Calcined at 300^0C for 1 Day Aging Period

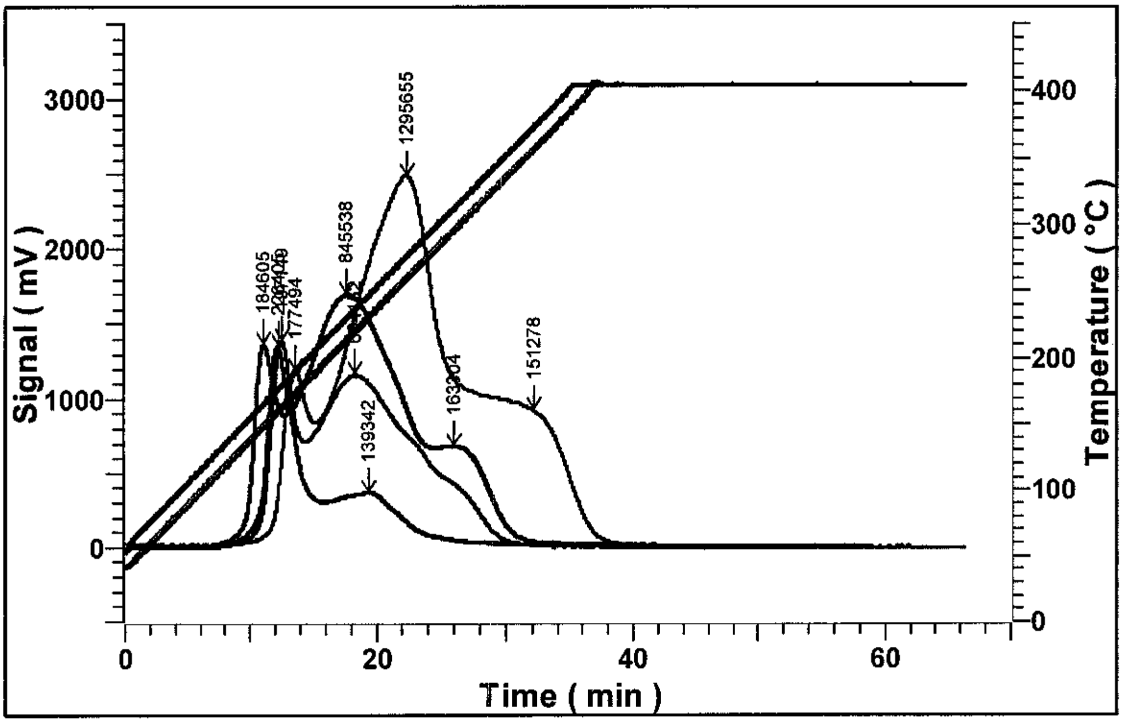

Figure C4: TPR Profile for Samples Calcined at 300^0C for 3 Days Aging Period

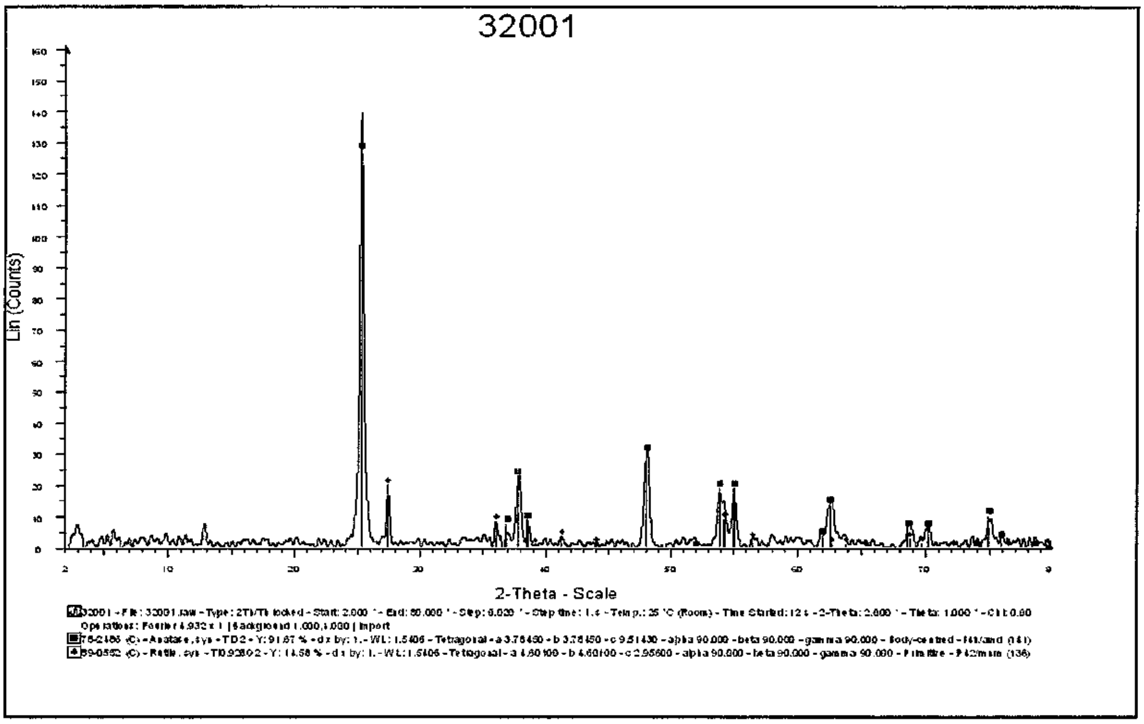

Figure C5: XRD Results for 3%Cu Calcined at 200^0C for 1 Day Aging Period

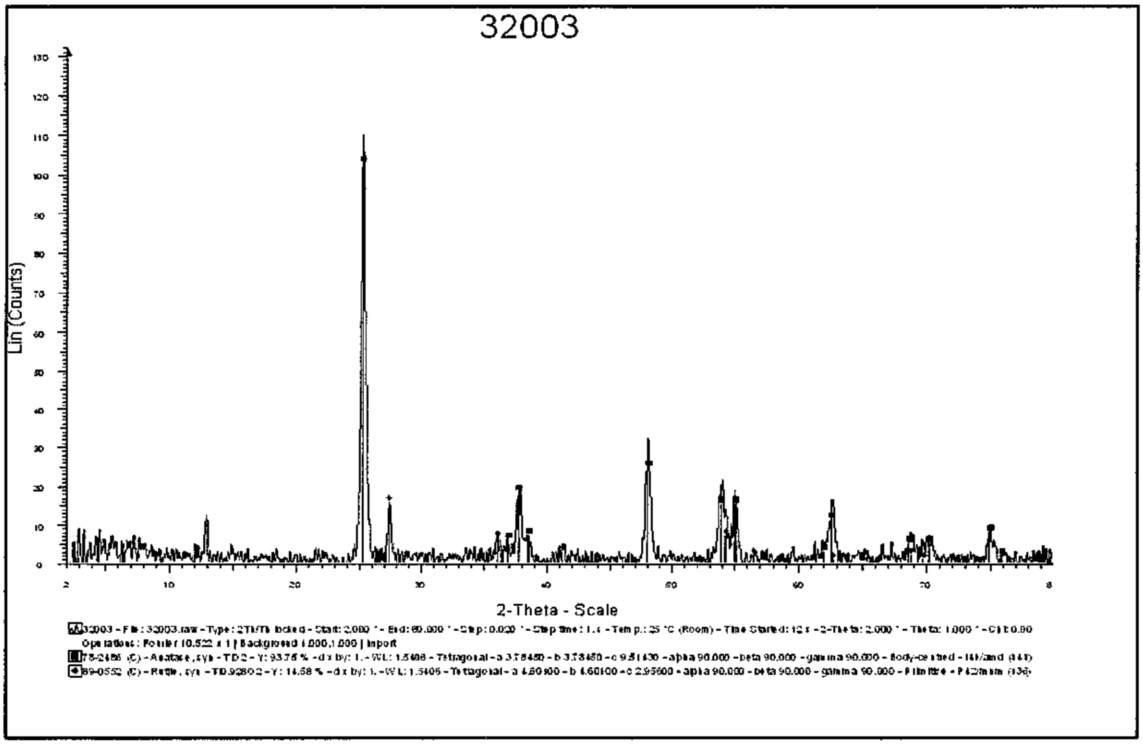

Figure C6: XRD Results for 3%Cu Calcined at 200^0C for 3 Days Aging Period

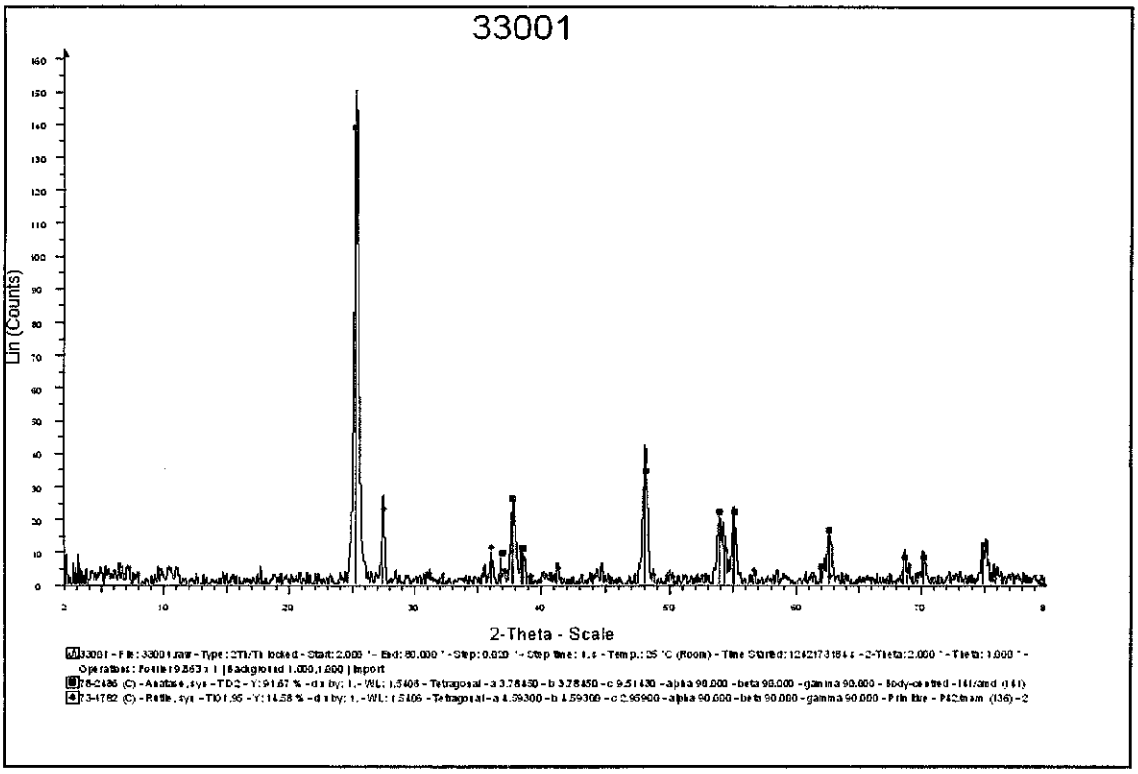

Figure C7: XRD Results for 3%Cu Calcined at 300^{0}C for 1 Day Aging Period

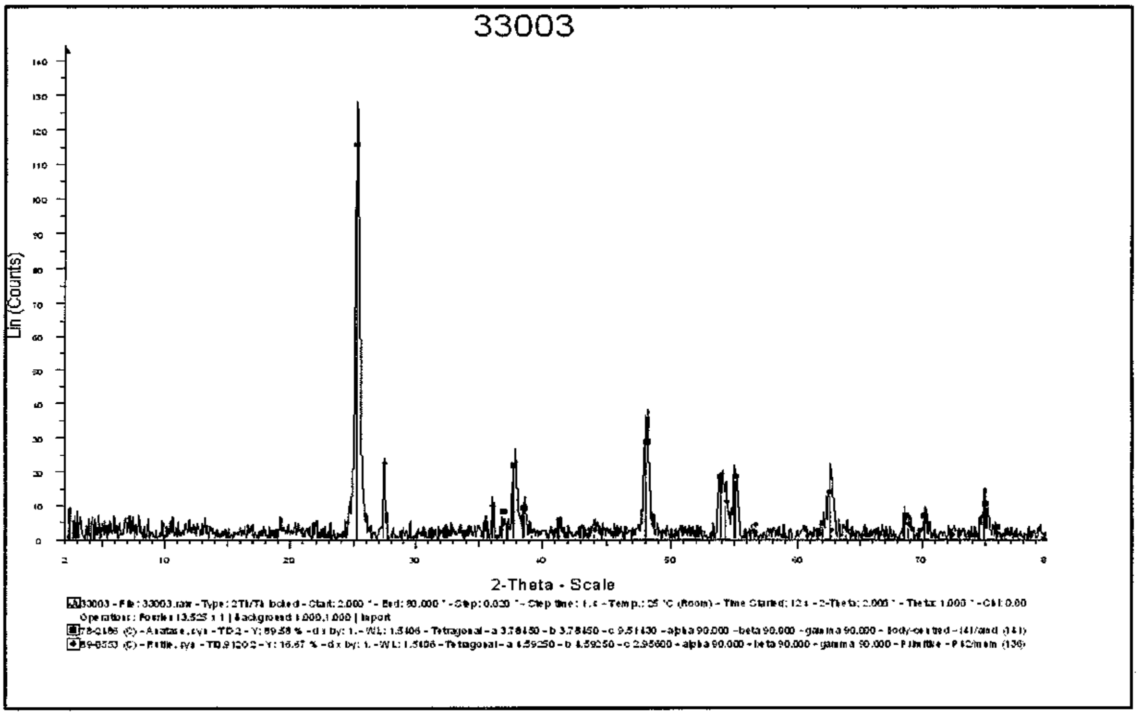

Figure C8: XRD Results for 3%Cu Calcined at 300^{0}C for 3 Days Aging Period

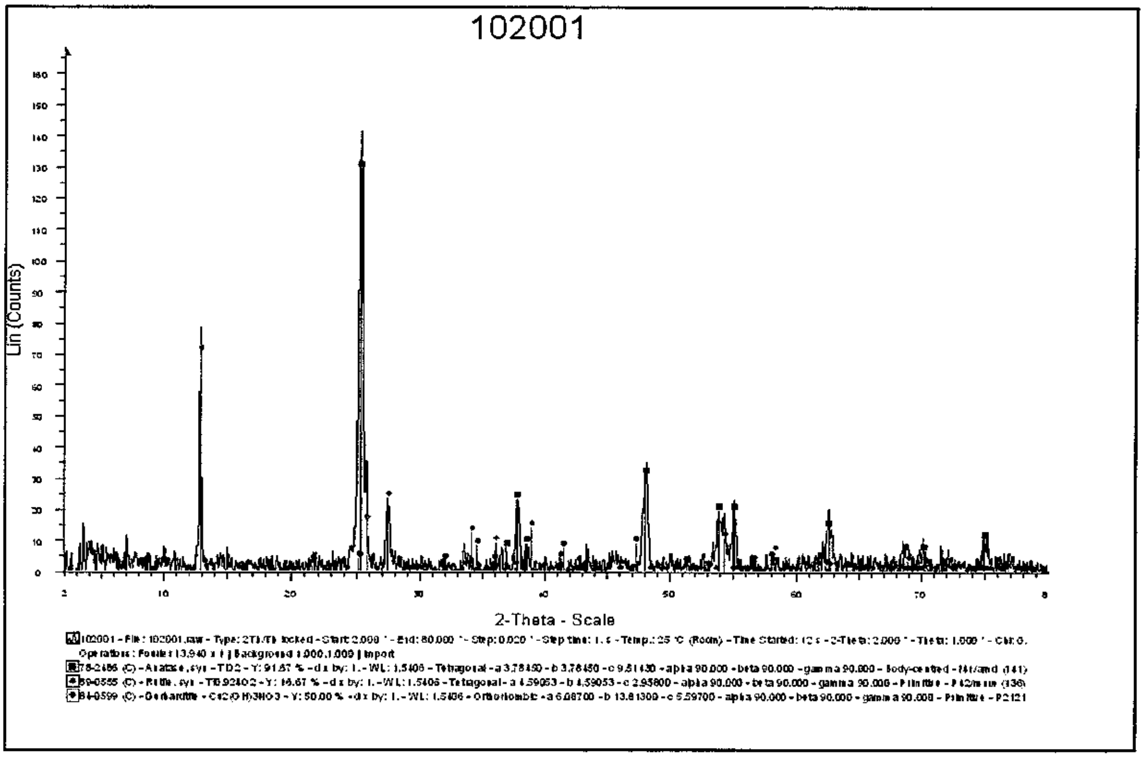

Figure C6: XRD Results for 10%Cu Calcined at 200^{0}C for 1 Day Aging Period

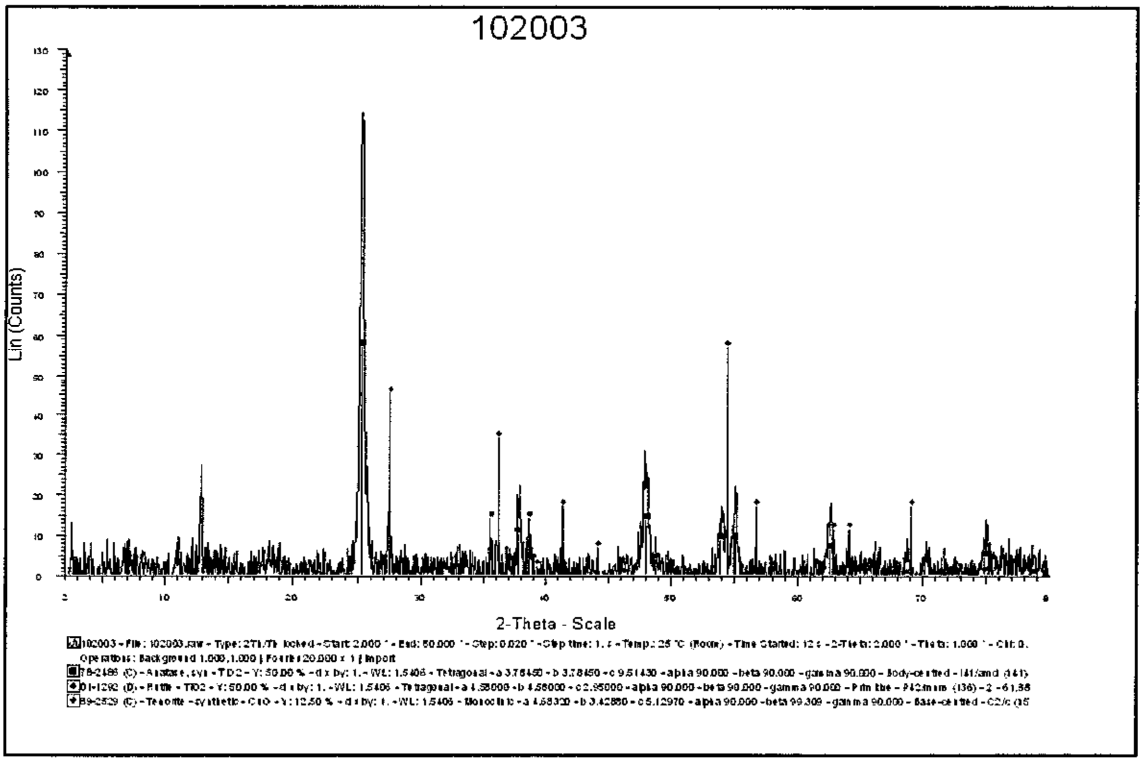

Figure C7: XRD Results for 10%Cu Calcined at 200^{0}C for 3 Days Aging Period

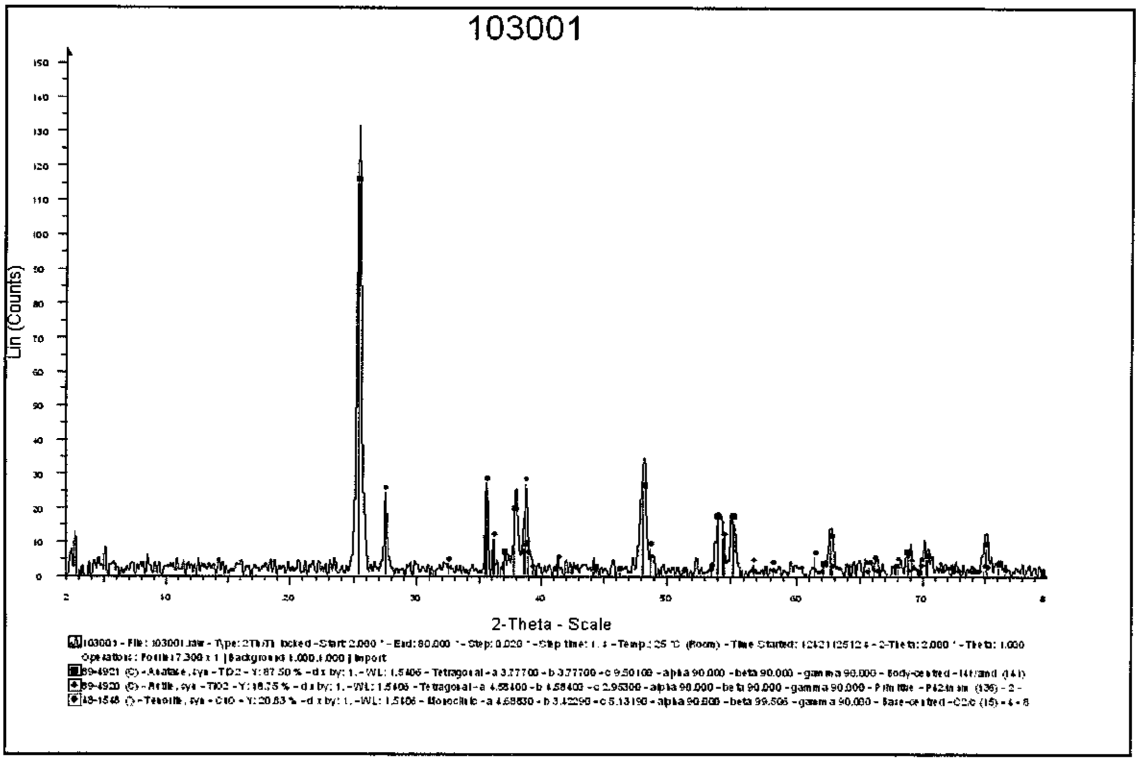

Figure C8: XRD Results for 10%Cu Calcined at 300^0C for 1 Day Aging Period

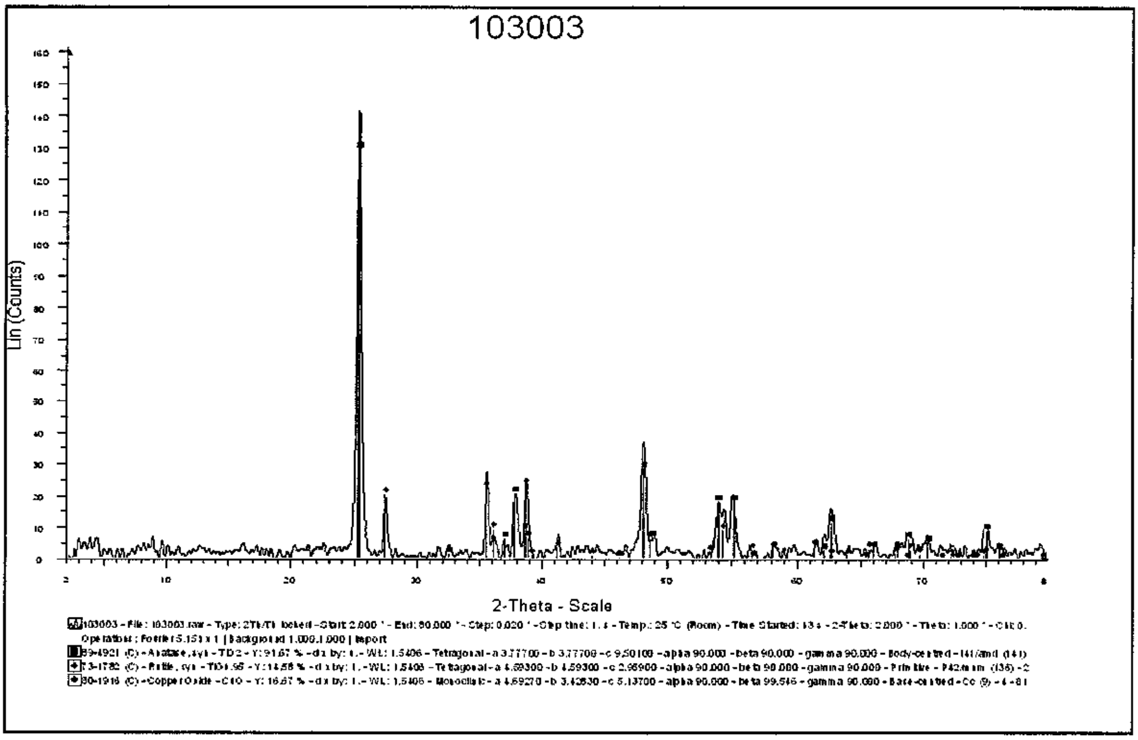

Figure C9: XRD Results for 10%Cu Calcined at 300^0C for 3 Days Aging Period

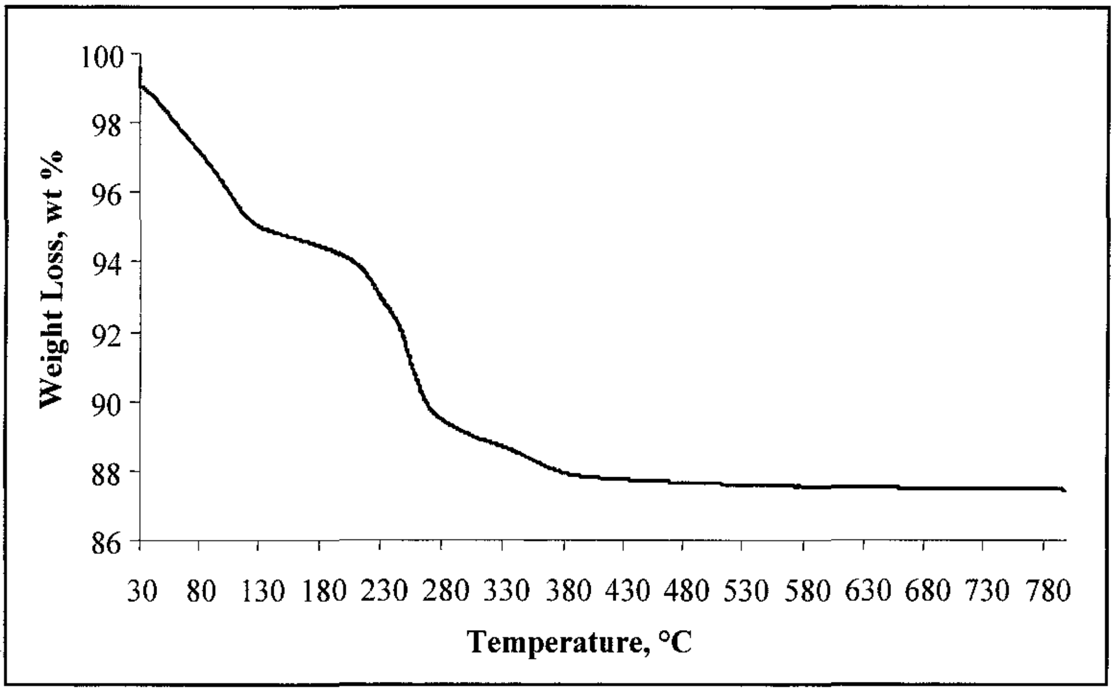

Figure C10: TGA Results