SYNTHESIS OF ZnS-KAOLIN AS AN APPLICATION OF PHOTOREDUCTION OF CO_2

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A thesis submitted in fulfillment
Of the requirement for the award of Degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

JANUARY 2012

SUPERVISOR'S DECLARATION

"I hereby declare that I have read this thesis and in my opinion this thesis has
fulfilled the qualities and requirements for the award of Bachelor Degree
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ABSTRACT

Nowadays, due to the industrialization or urban process cause the high concentration of carbon dioxide (CO_2) in environment. CO_2 is a trace gases and is the largest factors contribute to the world's greenhouse gas emissions. Early studies have shown that conventional treatment such as energy conservation, carbon capture and storage and using CO_2 as a raw material in a chemical process is efficient method but it have some drawbacks. Advanced oxidation technologies (AOTs) are innovative methods for pollutant treatment and are extremely useful in the case of substances resistant to conventional technologies. In this study, the oxidation process using heterogeneous catalyst assisted with UV light will be used to reduce the concentration of CO_2 in environment. Heterogeneous catalyst was prepared using Zinc Sulfide (ZnS) deposited on kaolin as an inert support for catalyst. ZnS-Kaolin catalyst was prepared by using two methods which are by impregnation and hydrothermal method. The results of these two methods was compared and investigated to know which catalyst will be giving a high performance in photo-reduction process. To investigate the performance of the catalyst, ZnS-Kaolin catalyst was characterized by using Brunauer-Emmett-Tellar (BET) method, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and X-Ray diffraction (XRD) to study the surface morphology and the characteristics of the catalyst.

ABSTRAK

Pada masa kini, proses perindustrian atau perancangan bandar boleh menyebabkan peningkatan kepekatan karbon dioksida (CO_2) dalam persekitaran dengan lebih tinggi. CO_2 adalah gas surih dan merupakan faktor terbesar menyumbang kepada pelepasan gas rumah hijau di dunia. Kajian awal telah menunjukkan bahawa rawatan konvensional seperti penjimatan tenaga, penangkapan dan penyimpanan karbon dan menggunakan CO_2 sebagai bahan mentah dalam proses kimia adalah kaedah yang berkesan tetapi ia mempunyai beberapa kelemahan. Teknologi pengoksidaan lanjutan (AOT_S) adalah kaedah yang inovatif untuk rawatan pencemar dan amat berguna dalam hal bahan-bahan yang tahan kepada teknologi konvensional. Dalam kajian ini, proses pengoksidaan yang menggunakan mangkin heterogen yang dibantu dengan cahaya UV akan digunakan untuk mengurangkan kepekatan CO_2 di persekitaran. Pemangkin heterogen telah disediakan dengan menggunakan Sulfida Zink (ZnS) dicampurkan dengan kaolin sebagai sokongan lengai untuk pemangkin. ZnS-kaolin pemangkin telah disediakan dengan menggunakan dua kaedah iaitu kaedah melahirkan dan kaedah hidroterma. Keputusan kedua-dua kaedah dibandingkan dan disiasat untuk mengetahui pemangkin yang terbaik yang akan memberi prestasi yang tinggi dalam proses pengurangan gas karbon dioksida. Untuk menyiasat prestasi pemangkin, ZnS-kaolin pemangkin akan dicirikan dengan menggunakan kaedah Brunauer-Emmett-Tellar (BET), Spektroskopi Fourier Transform Infrared (FTIR), Pengimbasan Mikroskop Elektron (SEM) dan pembelauan X-Ray (XRD) untuk mengkaji keadaan morfologi permukaan dan ciri-ciri mereka.

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LIST OF ABBREVIATION

CO	- Carbon Monoxide
NOx	- Nitrogen Oxides
HC	- Hydrocarbons
SO_2	- Sulfur Dioxide
PM	- Particulate Matter
CO_2	- Carbon Dioxide
FTIR	- Fourier Transform Infrared Spectroscopy
SEM	- Scanning Electron Microscope
XRD	- X-Ray Diffraction
BET	- Brunauer, Emmet, Teller
CdS	- Cadmium Sulfide
ZnS	- Zinc Sulfide
TiO_2	- Titanium Oxide
ZnO	- Zinc Oxide
VB	- Valence Band
CB	- Conduction Band
Fe_2O_3	- Iron Oxide
ZB	- Zinc Blende
WZ	- Wurtzite
UV	- Ultraviolet
S	- Sphalerite
0D	- 0 Dimensional
NCs	- Nanocrystals
Na2S	- Sodium Sulfide
SOH	- Surface Hydroxyl
MMT	- Montmorillonite

LIST OF SYMBOLS

$^{\circ}$	- degree
$^{\circ}C$	- degree celcius
Å	- Amstrong
atm	- atmospheric
cm^{-1}	- per centi meter
cm^3/g	- centimetre cube per gram
e^-	- Negative electron
eV	- Electron volt
g	- gram
g/cm^3	- gram per centimetre cube
h	- hour
h^+	- Positive electron
kV	- kilo Volt
mA	- mili ampere
min	- minute
mL	- mililitre
m^2/g	- meter square per gram
nm	- nanometer
rpm	- Revolutions per minute
s	- second
V	- Voltage
W	- Watt
μm	- micro meter
λ	- wavelength

CHAPTER 1

INTRODUCTION

1.1   Environmental Impact Assessment

Nowadays, with accelerating urban and industrial growth, the quantities of harmful waste products have been released into the atmosphere. The rate of discharge is beyond the limits of natural cleansing ability and "buffering capacity" of the atmosphere (Elson, 1992). A number of human based activities have been responsible for these emissions. Amongst the most significant have been operation of fossil fuel fired power stations, petroleum refineries, petrochemical operations, iron and steel mills, hazardous wastes incineration plant, major highways or freeways and airports. In a number of less developed countries controlled burning of forests has been responsible for much air pollution. In addition, the construction of many of these facilities causes deterioration of air quality (Canter, 1995).

Air pollution in Malaysia falls into three main categories which are air pollution due to exhaust gas from mobile emission sources such as motor vehicles, principally in urban areas, haze caused by the weather and by forest fires in neighbouring Indonesia and pollution caused by industrial activities (Canter, 1995)

Of these three problems, air pollution from mobile emission sources is of greatest concern. In 1997, there were roughly 8.5 million registered motor vehicles in Malaysia, climbing at the rate of 10 percent or more every year. According to 1997 figures, the estimated quantities of air pollutants released by these vehicles were 1.9 million tons of carbon monoxide (CO), 224,000 tons of nitrogen oxides (NOx), 101,000 tons of hydrocarbons (HC), 36,000 tons of sulfur dioxide (SO_2) and 16,000 tons of particulate matter.

Mean values for the years 1993 to 1997 show that the amount of air pollutants from mobile emission sources accounts for 81 percent of all air pollution occurring in Malaysia. The problem will clearly become even more critical as the number of motor vehicles keeps on increasing. As a result of these forms of pollution, Kuala Lumpur and its outskirts, which have heavy motor vehicle traffic, are exposed to high levels of NOx and SO_2 and of particulate matter (PM). Air pollution due to particulate matter, although still below the environmental standard at present is growing more severe as time goes on (Canter, 1995).

Another problem is black smoke from diesel motor vehicles, the subject of numerous complaints from the public. In response, the government has launched a campaign to crack down on vehicles that violate the regulations. In regard to lead pollution, the government in 1991 introduced incentives to use unleaded gasoline and since 1996 it has been obligatory for gasoline-fueled vehicles to have catalytic converters. These policies have been successful in reducing the level of lead in the atmosphere year by year (Canter, 1995).

Haze is another major problem in Malaysia. There were minor haze incidents in 1993 and 1994, years that recorded low rainfall, but haze on an unprecedented scale occurred from the summer of 1997 due to the huge forest fires that blazed in Sumatra and Kalimantan in Indonesia (Canter, 1995).

As well as affecting health and causing an increase in respiratory complaints, the 1997 haze incident had major economic costs, impacting on transportation services, tourism and the fishing industry among others. The disaster prompted the government to subsequently ban all open burning within Malaysia. Air pollution caused by industrial activities is still low in Malaysia. Including industrial fuels and industrial processes, the industrial sector contributes only 7 to 8 percent of total air pollution in the country (Canter, 1995).

1.2   Research Background

Carbon Dioxide (CO_2) is a greenhouse gas representing the largest contribution of human activities. Since CO_2 is rather an inert and stable compound, the reduction of CO_2 is difficult. The reduction of CO_2 using photo-catalyst is one of the most promising methods because CO_2 can be reduced by the UV radiation at room temperatures and atmospheric pressure.

The Climate Change mandated a return of CO_2 emission levels to those of 1990. Although the remediation of CO_2 can be physically stored or chemically transformed but by storage can overcomes the problem only temporarily. To solve the CO_2 problem permanently, it requires transforming CO_2 into other useful or non-toxic compounds. By upgrading CO_2 to reusable hydrocarbon resources can give beneficial to humans and the environment (Anpo, 1992).

The study of photo catalytic reactions was initiated in 1970's. The concept and the term ''heterogeneous photocatalysis'' were introduced and developed in Lyon to describe the partial oxidation of alkanes and olefinic hydrocarbons. The reactions took place at ambient temperature in the presence of the catalyst under UV irradiation. Heterogeneous photocatalysis is defined by as "a catalytic process during which one or more reaction steps occur by means of electron–hole pair's photo generated on the surface of semiconducting materials illuminated by light of suitable energy." This pathway differs from the usual thermal reaction sequence and leads to reaction product selectivities different from those for the thermal or catalyzed reactions (Palmisano and Sclafani, 1997).

Semiconductors such as metal oxides or metal sulphides possess typical physico-chemical properties that make them very photosensitive materials (Anpo *et al.,* 1995). By the absorption of photons with energy equals to or higher than their band-gap energy, electrons are excited from valence to conduction bands. Along with electrons, positive holes are generated as well. Semiconductors have been widely applied in photonics and optoelectronics and also in photo-catalysis (Palmisano and Sclafani, 1997).

By using the catalyst as photo-catalysts, it will generated electrons and holes take part in reduction or oxidation reactions with electron acceptors or donors on the surface of semiconductors (Adachi, 1994). The properties of nano-sized semiconductors strongly depend on their size if compared to other nano-particles. The catalyst with the high specific surface area is results in high chemical reactivity. The decrease of their size also leads to an increase of the band-gap energy that is known as a quantum size effect (Yamashita *et al*., 1998). This effect can be simply observed by a blue-shift of the luminescent and absorption spectra of nano-sized semiconductors. The prepared of nanoparticles tend to agglomerate and therefore to stabilized the catalyst by using various polymers and surfactants or are fixed on solid platforms (Palmisano, 1997).

The aim of this study will be focused on the development of catalyst deposited on low cost materials for photo-reduction process of carbon dioxide (CO_2). In this study, kaolin will be chosen as a support due to the extraordinary properties and abundantly available in Malaysia. The catalysts weree prepared by two different methods which are by hydrothermal method and impregnation method. The catalyst was attached on the support (kaolin) as a way to prevent or reduce Zn^{2+} ion leached out into the solution when photo-reduction process is occurred. Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) and Textural Characterization (BET method) were used to measure or characterize the prepared catalysts.

1.3   Problem Statement

The concentration of atmospheric carbon dioxide (CO_2) has been gradually increasing resulting mainly from human activities and industrial development at the beginning of the twentieth century. CO_2 is the most prominent and effective greenhouse gas contributing to global warming if compare with another chemicals such as methane, nitric acid and hydrochlorofluorocarbons. Thus, it is required not only to reduce CO_2 emission from carbon burning industries but also to utilize CO_2 as a natural carbon source to produce hydrocarbons. Converting CO_2 to organic compounds by artificial photo-chemicals technologies for example photo-catalytic technology accompanied by nanotechnology has been attracting more attention from investigators and is considered

one of the most promising technologies in the future (Ching *et al.*, 2007). Photo-catalytic technology is an emerging process applied to reduce of environmental pollutants. It uses semiconductors materials such as CdS, ZnS, TiO_2, ZnO as a photo-catalysts to enhance the reactions (Shin, 1998).

1.4   Objectives

Based on the research background and problem statement described in the previous section, the following are the objectives of this research:

a) To prepare a ZnS-kaolin as a catalyst for the photo-reduction of CO_2.
b) To characterize the prepared catalyst for their physical and chemical properties.

1.4   Scope Of Study

In order to handle the above mentioned objectives, the following scopes were drawn:

a) Developing the ZnS-kaolin catalyst as an application for photo-reduction of CO_2 by using two methods which are by hydrothermal and impregnation method.
b) Kaolin as an inert support for ZnS nanostructures that used for their long term stabilization because they tended to agglomerate in the aqueous dispersion as demonstrates by UV spectra.
c) The prepared catalyst will be characterized by using FTIR, SEM, BET method and XRD.

1.5   Benefits And Significant Of Research

The prepared catalyst deposited on low cost material will be economically in application for photo-reduction of CO_2. By using kaolin as a support, it will be more efficient due to the high surface area with their small particle size. Their surface area, pore structure and chemical composition are widely tunable by changing the synthetic conditions and the precursor solutions used. Kaolin also capable of removing pollutants from the environment and thereby controls the spread of the pollutants in soil, water and air. For the reforming reaction, kaolin also interesting as catalyst or support due to their low cost and particular properties and structures (Hao *et al.*, 2003). Meanwhile, ZnS will be used as catalyst in this research due to their band gap and types. ZnS is a semiconductor with high band gap in range 3.7 eV. It appears to be very promising material for photo-catalysis due to the rapid generation of electron-hole pairs by photo-excitation and highly negative reduction potentials of excited electrons.

CHAPTER 2

LITERATURE REVIEW

2.1   Catalyst Development

Catalyst plays a key role in industry, as well as everyday life. A catalyst's main function is to increase the rate of a reaction without being consumed. Catalyst's increase productivity and efficiency, which translates into increase in profit, which is why finding more catalysts is such an important topic today. Solid catalysts are composed of metals or metal oxides that form supports onto oxides and create metal particles with high surface areas. The goal is to form small metal particles with high surface areas, since reactions take place on the surface, so the more surface area, the more the reaction can take place (Navada, 1999).

2.2   Photo-Catalytic CO_2 Reduction

The CO_2 reduction process is thermodynamically uphill as illustrated by its standard free energy of formation ($\Delta G° = -394.359$ kJ/mol) (Indrakanti, 2009). Economical CO_2 fixation is possible only if renewable energy, such as solar energy is used as the energy source. Equally difficult is the reduction or splitting of water to yield hydrogen and hence requires similar combination of activation steps. The most ideal and desirable process would then be the simultaneous reduction of CO_2 and water to yield hydrocarbons which essentially works out to artificial photosynthesis. The utilization of solar energy via chemical storage can be achieved by photo catalytic or photo-electrochemical activation of light-sensitive catalytic surfaces. When comparing the two systems, photo-catalytic system is simpler and easy to construct. Photo-catalytic process

occurs via the direct absorption of photons with energy greater than or equal to the band gap of the photo catalyst to generate electron-hole pairs. The initial excitation and electron energy transfer to the adsorbed reactants on the photo catalyst make chemical reactions in the photo catalytic process possible (Koci, 2010).

2.2.1 CO_2 Conversion

There are two conceptual routes to produce renewable carbon containing fuels using solar energy that are the direct photo reduction of CO_2 using water as a reductant and the photolysis of water to generate hydrogen and further reaction of this hydrogen with CO_2 forming C_1–C_2 fuels (Indrakanti, 2009).

CO_2 is the most oxidized form of carbon and therefore the only chemical transformation at normal energies that would be possible is to reduce it. A wide range of CO_2 conversion techniques are under investigation (Aulice and Viswanathan, 2004) which includes themochemical conversion, radiochemical method, photochemical conversion, bio-chemical conversion, electro-chemical conversion, bio-photochemical conversion and electro-photochemical conversion.

Thermochemical conversion

$$CO_2 \longrightarrow CO + \tfrac{1}{2} O_2 \tag{1}$$

Radiochemical method:

$$CO_2 \longrightarrow HCOOH + HCHO \tag{2}$$

Photo-chemical conversion:

$$CO_2 \longrightarrow CO + HCHO + HCOOH \tag{3}$$

Bio-chemical conversion:

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad (4)$$
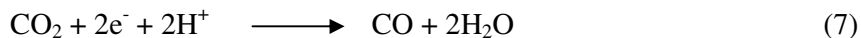
The bacteria Methanobacterium thermoautotrophicum can be immobilized in a fixed bed or on hollow fibres and feeding stoichiometric ratios for the reaction attains 80% of the theoretical yield.

Electro-chemical conversion:

$$CO_2 + xe^- + xH^+ \longrightarrow CO + HCOOH + (COOH)_2 \qquad (5)$$
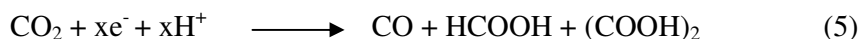
Bio-photochemical conversion:

The "bio" part of the energy consists in catalysis and information content of an enzyme.

$$CO_2 + \text{oxoglutaric acid} \longrightarrow \text{isocitric acid} \qquad (6)$$

Electro-photochemical conversion:

$$CO_2 + 2e^- + 2H^+ \longrightarrow CO + 2H_2O \qquad (7)$$

Conventional catalytic reduction of CO_2 to chemicals (formic acid, methanol and methane) with external hydrogen is feasible but hydrogen has to be produced via renewable resources to render it viable and sustainable (Nam *et al*.,1999).

From the reaction shows at above, it is clear that CO_2 photo reduction is not a single-step reaction.Upon transfer of one electron, the structure changes from linear to bend which results in irreversible reduction (Aulice and Viswanathan, 2004). Additionally, single electron transfer to CO_2 is highly endergonic because of the negative adiabatic electron affinity of CO_2. The initial step in the photo catalytic reduction of CO_2 is the generation of electron-hole pairs upon absorption of photons of energy greater than or equal to the band gap of the photo catalyst. The time scale of this

electron-hole recombination is two to three orders of magnitude faster than other electron transfer processes. Therefore, any process which inhibits electron-hole recombination would greatly increase the efficiency and improve the rates of CO_2 photo reduction. The kinetics of CO_2 photo reduction are also dependent upon many other factors such as incident light intensity, fraction of the incident light absorbed by the photo catalyst and the specific surface area of the photo catalyst absorbing the light (Konho, 1999).

2.3   Reduction of CO_2 Emissions

The reduction of CO_2 emissions can be achieved by three approaches that are use of carbon-based energy sources use of alternative or carbon-free energy sources and use of a post treatment carbon-capture technology (carbon capture refers to the removal of CO_2 from industrial flue gas by a gas separation is process prior to release to the atmosphere) (Usubharatana *et al*., 2006).

2.3.1   Sequestration (Storage)

Carbon sequestration or storage is the isolation of carbon dioxide (CO_2) from the earth's atmosphere. Sequestration can play a significant role in preventing continued CO_2 buildup in the atmosphere. Geological sequestration involves storing CO_2 underground in rock formations that can retain large quantities of CO_2 for long periods of time. The CO_2 would be held in small pore spaces inherent in rocks. It is possible that CO_2 injection into coal seams and mature oil fields could assist in the extraction of coal bed methane or oil that would otherwise be left in the ground which could help offset the costs of sequestration (Usubharatana *et al*, 2006).

2.3.2   Other Carbon Capture Technologies

Currently, technologies such as gas absorption into chemical solvents, permeation through membranes, cryogenic distillation and gas adsorption onto a solid sorbent are available for the capture of CO_2 from flue gas. However these are not economically feasible (Usubharatana *et al*, 2006).

2.4   Principles And Elementary Steps of the Photo-catalytic Reactions

The band gap is characteristic for the electronic structure of a semiconductor and is defined as the energy interval (ΔEg) between the valence band (VB) and the conduction band (CB). VB is defined as the highest energy band in which all energy levels are occupied by electrons whereas CB is the lowest energy band without electrons. According to the band gap model as shown in Figure 2.1, VB electrons are transferred to the CB when the semiconductor is illuminated with photons having an energy content equal to or higher than the band gap, creating electron–hole pairs (1) (Demeestere *et al.*, 2007). After migration to the semiconductor surface (2), electron–hole pairs may induce redox reactions with adsorbates having suitable redox potentials (3). From a thermodynamic point of view, VB holes can oxidize adsorbed compounds if the redox potential of the VB is more positive than that of the adsorbates. Similarly, CB electrons can reduce adsorbed species if they have a more negative redox potential than the adsorbates. In the absence of suitable adsorbates, electron–hole pair recombination occurs with release of thermal energy or light (4).
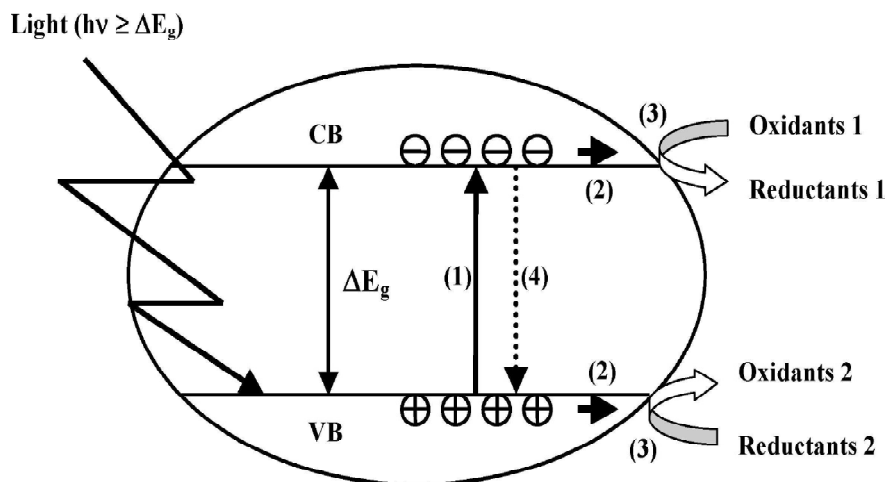

Figure 2.1: Schematic representation of the "band gap model." (1) Photo induce electron-hole pair creation; (2) charge migration to the surface; (3) redox reactions; (4) recombination. VB and CB represent valence band and conduction band respectively.

The rate of a photo catalytic reaction especially depends on the type of the photo-catalytic semiconductor and on the light radiation that it used in its initiation.

4.3 X-Ray Diffraction (XRD)

Figure 4.4 (a) and (b), Figure 4.5 (c) and (d) and Figure 4.6 (e) and (f) illustrates XRD patterns of the six series of nanocomposites for pure ZnS, ZnS deposited on Kaolin and ZnS deposited Kaolin with HTAC.
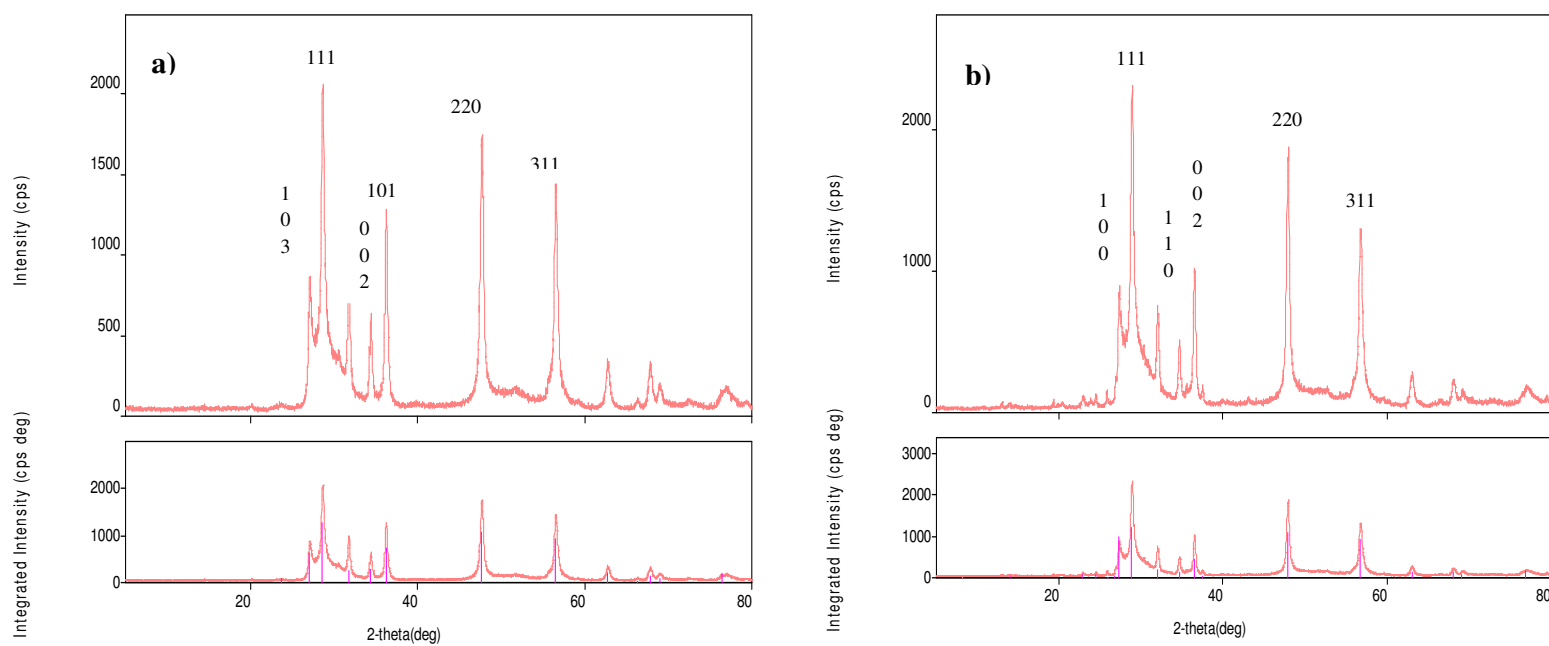

Figure 4.4: XRD patterns of (a) ZnS preparation by impregnation method and (b) ZnS preparation by hydrothermal method