PHOTOCATALYTIC REDUCTION OF CO_2 USING ZnS PILLARING ON KAOLIN CATALYST

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ABSTRACT

Increasing of carbon dioxide (CO_2) concentration in atmosphere has gain major attention by the researchers. This is due to CO_2 ability to absorb heat from the UV light and emits the heat to atmosphere resulted in earth warming. In order to overcome this problem, the researchers come out with many solutions. Conventional method and also Advanced Oxidation Process (AOP) have been invented as a way to reduce the concentration of the predominant greenhouse gases especially CO_2. However, AOP has come out as the emerging technologies due to its practicality in reduction process in industry. This study will be focusing on one of the AOP which is photocatalytic reduction process of CO_2. In this process, a photocatalyst was needed. In this research, photocatalyst used was ZnS-Kaolin, a combination of semiconductor ZnS and phyllosilicate mineral, Kaolin. ZnS-Kaolin was prepared by using two methods which are hydrothermal method and simpler impregnation method. In this photocatalytic reduction process, the catalyst was dispersed in medium solution, NaOH aqueous and hence help to catalyze the process. The characteristics of the developed ZnS-Kaolin were observed by using Scanning Electron Microscope (SEM) and Thermal Gravimetric Analyzer (TGA). The effect of parameters such as irradiation time and dosage of ZnS-Kaolin used were observed and studied. This process was produced usable products such as methanol and was analyzed by using High Performance Liquid Chromatography (HPLC). Based on the results, from SEM analysis, it was found that raw Kaolin was constructed from hexagonal flakes structure. Meanwhile, both ZnS-Kaolin prepared from Hydrothermal and Impregnation methods are consists of leaf-like layers structure with ZnS nanoparticles deposited on Kaolin structure. From TGA analysis, it was found that ZnS-Kaolin prepared from Hydrothermal method has higher thermal resistance compared to ZnS-Kaolin prepared from Impregnation method. Meanwhile, for photoreduction process of CO_2, methanol production was observed to be

maximum by using ZnS-Kaolin prepared from Hydrothermal method at dosage of 0.75 g and at 2 hours irradiation time. In conclusion, ZnS-Kaolin prepared by using Hydrothermal method shows better performance in photoreduction process of CO_2 compared to ZnS-Kaolin prepared from Impregnation method.

ABSTRAK

Peningkatan kepekatan karbon dioksida (CO_2) di dalam atmosfera telah mendapat perhatian ramai penyelidik. Hal ini kerana CO_2 boleh menyerap haba daripada cahay UV dan memancar kembali haba tersebut ke dalam atmosfera dan menyebabkan pemanasan global. Bagi mengatasi masalah ini, para penyalidik telah mencipta pelbagai penyelesaian. Kaedah konvensional dan juga Advanced Oxidation Process (AOP) telah dicipta sebagai satu cara untuk mengurangkan kepekatan gas-gas rumah hijau terutamanya CO_2. Walaubagaimanapun, AOP muncul sebagai teknologi pilihan kerana bersifat praktikal dalam proses penurunan di industri. Kajian ini memfokuskan salah satu daripada AOP iaitu Proses Penurunan CO_2 yang menggunakn foto-pemangkin. Di dalam proses ini, foto-pemangkin diperlukan. Dalam kajian ini, foto-pemangkin yang digunakan ialah ZnS-Kaolin, iaitu kombinasi antara semikonduktor, ZnS dan mineral filo-silika, Kaolin. ZnS-Kaolin dihasilkan melalui 2 kaedah iaitu kaedah 'Hydrothermal' dan kaedah 'Impregnation'. Di dalam proses penurunan yang menggunakn foto-pemangkin, pemangkin digunakan di dalam medium cecair, NaOH dan seterusnya memangkinkan proses. Ciri-ciri pemangkin ZnS-Kaolin yang telah dihasilkan diperhati dan dianalisis dengan menggunakan 'Scanning Electron Microscope' (SEM) dan 'Thermal Gravimetric Analyzer' (TGA). Kesan-kesan seperti masa pancaran cahaya UV dan dos ZnS-Kaolin yang digunakan dianalisis dan dikaji. Proses ini menghasilkan produk yang berguna seperti metanol yang kemudiannya dianalisis dengan menggunakan 'High Liquid Performance Chromatography' (HPLC). Berdasarkan keputusan eksperimen, daripada analisis SEM, didapati bahawa Kaolin terdiri daripada struktur kepingan-kepingan yang berbentuk heksagon. Sementara, kedua-dua ZnS-Kaolin yang dihasilkan melalui kaedah 'Hydrothermal' dan 'Impregnation' terdiri daripada struktur lapisan-lapisan yang berbentuk seperti daun dengan zarah-zarah nano ZnS terlekat pada

struktur Kaolin. Seterusnya, berdasarkan analisis TGA, didapati bahawa ZnS-Kaolin yang dihasilkan melalui kaedah ‘Hydrothermal’ menunjukkan sifat rintangan haba yang tinggi jika dibandingkan dengan ZnS-Kaolin yang dihasilkan melalui kaedah ‘Impregnation’. Sementara itu, berdasarkan proses penurunan CO_2 dengan menggunakan foto-pemangkin, penghasilan metanol secara maksima diperhatikan berlaku apabila menggunakan ZnS-Kaolin yang dihasilkan melalui kaedah ‘Hydrothermal’ pada dos 0.75 g dan selepas 2 jam pancaran cahaya UV. Kesimpulannya, ZnS-Kaolin yang di hasilkan melalui kaedah ‘Hydrothermal’ menunjukkan kesan yang lebih baik dalam proses penurunan CO_2 jika dibandingkan dengan ZnS-Kaolin yang dihasilkan melalui kaedah ‘Impregnation’ .

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LIST OF ABBREVIATION

AOP	-Advanced Oxidation Process
CO	- Carbon Monoxide
NOx	- Nitrogen Oxides
CO_2	- Carbon Dioxide
FTIR	- Fourier Transform Infrared Spectroscopy
SEM	- Scanning Electron Microscope
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
Na_2S	- Sodium Sulfide
MMT	- Montmorillonite

LIST OF SYMBOLS

°C	- Degree Celcius
Å	- Angstrong
atm	- Atmospheric
cm^{-1}	- per centi meter
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
μmol/g	- micro mol per gram
λ	- lambda

CHAPTER 1

INTRODUCTION

1.1 Research Background

The global warming effect is believed to be associated with the increasing concentrations of greenhouse gases in the atmosphere, where the major contribution comes from carbon dioxide (CO_2) emissions from fossil fuel consumption (Zhang et. al., 2011). Currently, there is around 1 tera ton excess CO_2 in the atmosphere which is man-made and stemming mainly from the combustion of fossil fuels (Jensen et. al., 2011). Recent research has shown that once CO_2 has been emitted to the atmosphere, it will take centuries for natural removal. Clearly, the longer we delay deep reductions in CO_2, the greater the risk that total greenhouse gas emissions will exceed prudent limits for avoiding dangerous anthropogenic change (Moriarty and Honnery, 2009).

The concentration of CO_2 can be reduced by using several conventional methods such as activated carbon and air stripping by packed column (Zhao et. al., 2011). However, these conventional methods are only removes the CO_2 from air content without any conversion to useful products. Hence, advanced oxidation process (AOP) was proposed. AOPs are technologies based on the intermediary of hydroxyl or other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to inert end-products. AOP includes heterogeneous and homogeneous photocatalysis based on near ultraviolet (UV) or solar visible irradiation, electrolysis, ozonation, the Fenton's reagent, ultra-sound and wet air oxidation (Klavarioti et. al., 2008).

Reduction process of CO_2 is difficult since it is inert and stable compound. Conventional process requires high pressure and high temperature (Kozak et. al., 2010). Hence, photocatalytic reduction process by using photocatalyst is the most promising method since CO_2 can be reduced to useful compounds by irradiating it with UV light at room temperature and constant pressure (Lo et. al., 2007). Photocatalysis or photocatalytic reduction of CO_2 by UV light involves photocatalyst and UV irradiation. Photocatalytic reduction of CO_2 is not only reducing but also recycling the CO_2 into useful products such as CH_4, CH_3OH, CHOOH and C_2H_5OH. In the process, semiconductors like TiO_2 and ZnS were widely used (Li et. al., 2010).

Heterogeneous semiconductor photocatalysis using TiO_2 as the photocatalyst is an emerging technology with key advantages including operation at ambient condition as well as the fact that the catalyst itself is inexpensive, commercially available at various crystalline forms and particles characteristics, non-toxic and photochemically stable (Doll and Frimmel, 2004). When exposed to a UV light source with wavelength < 380 nm, an electron along with an electron vacancy, or hole (h^+) is produced within a TiO_2 particle (Turchi and Ollis, 1990).

In this study, ZnS-Kaolin (ZnS-K) has been proposed. Heterogenous ZnS-K photocatalyst is a combination of Kaolin, a kind of phyllosilicate mineral and ZnS semiconductor. Kaolin belongs to the kandites mineral group with the chemical composition of $Al_2Si_2O_5(OH)_4$ (Chong et. al., 2008). The combination combined the functions of the semiconductor and Kaolin together and exhibited synergetic effects (Miao et. al., 2008). The presence of catalyst supporter, Kaolin improved the activity of photocatalyst. The natural structure and adsorption ability of the clay materials can maintain large specific surface area, stability and consequently enhance the photocatalytic efficiency of the photocatalysts (Chong et. al., 2008). Kozak et. al., (2010) has proved that the yields of photocatalytic reduction of CO_2 by using heterogenous photocatalyst are higher than the yields by using raw semiconductor. ZnS which has wide band gap energy which is about 3.7 eV is very potential material since it can rapidly generates electron-hole pairs during illumination by UV light and has highly negative reduction potentials of excited electrons (Kozak et. al., 2010). Various sites on these particles act as reducing or oxidising centres, which will provide electrons to CO_2. When these semiconductor particles were illuminated by band gap irradiation, electron will be excited from valence to the conductance band. The photocatalytic process involves electrons (e^-) and holes (h^+) generated at these various sites with the aid of photonic energy (hv) from UV light (Kozak et. al., 2010).

Thus, in order to increase the efficiency of photocatalytic reduction process of CO_2, heterogeneous ZnS-K photocatalyst is strongly encouraged. In this study, the effect of operating temperature, irradiation time and percentage of ZnS loading on kaolin in photocatalytic reduction of CO_2 has been studied. ZnS-K was prepared with two different methods; hydrothermal and impregnation method. The performances of both catalysts were studied in photoreduction process. Two parameters that affect the reduction process that are effect of dosage of catalysts and irradiation time were studied.

1.2 Problem Statement

Earth is currently facing global warming due to human activities. Fossil fuel consumption is believed to be the major cause that contributes to this problem. The consumption of fossil fuel will emits high amount of greenhouse gases, predominantly carbon dioxide (CO_2). Global warming happened when the abundant of CO_2 in atmosphere absorbs heat from UV light and emits the heat to the earth. Due to this problem, some technologies like adsorption by using activated carbon and air stripping were used to capture CO_2 and hence reduced its concentration in atmosphere. However, this method is difficult to be applied in industry because of high cost consumption. Therefore, in this study we proposed an alternative method that offers lower cost and profitable yields which is advanced oxidation process (AOP). The AOP process used in this study is photocatalytic reduction of CO_2 by using heterogeneous catalyst (ZnS-Kaolin) assisted by UV light irradiation. Hence, this study focuses on performances of catalysts in photoreduction process that prepared from hydrothermal and impregnation method. The effect of parameters such as effect of irradiation time and dosage of ZnS-K catalyst used were studied in order to find the optimum condition for this process.

1.3 Objectives of Study

Based on research background and problem statement described previously, the objectives of this research are as follows:

- To prepare ZnS-Kaolin (ZnS-K) as a catalyst to be used in photoreduction process of CO_2.
- To characterize the developed ZnS-Kaolin catalyst.
- To study the performance of both catalysts prepared from hydrothermal and impregnation method in photoreduction process.

1.4 Scope of Research

In order to accomplish the objectives of this research, the following scopes were drawn:

- Synthesizing the new photocatalyst by doping ZnS semiconductor on surface of the kaolin by using hydrothermal and impregnation method.
- Characterizing the developed ZnS-Kaolin catalyst by using Scanning Electron Microscope (SEM) and Thermal Gravimetric analyser (TGA).
- The performances of both catalysts that prepared from hydrothermal and impregnation method were studied in photoreduction process using two different parameters that affect the reaction process; effect of catalyst dosage (0, 0.50 and 0.70 g) and irradiation time (1-5 hours).
- Analyzing the main product (methanol) by using High Performance Liquid Chromatography (HPLC) analyzer.

1.5 Rationale and Significance

Reduction of CO_2 by force (conventional method) is highly cost since the process requires high pressure, high temperature and high cost of materials. The application of photocatalytic reduction process by semiconductor catalyst assisted by UV light is purposely to provide an alternative treatment with low cost because the process could be performed at room temperature under atmospheric pressure and also to form useful products. With using different preparation methods, catalyst with best properties will produced highest concentration of methanol.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The reduction of anthropogenic CO_2 emissions to address of the consequences of climate change is a matter of all developed countries (Pevida et. al., 2008). The conventional method used is to capture the CO_2 by using solid sorbents such as molecular sieves, zeolites and activated carbon. The method involved adsorption-desorption on the solid sorbents. This method is applied at large stationary source of CO_2 such as power station, cement plants and refineries. The adsorption properties of solid sorbent are determined by its porous structure and surface chemistry. Activated carbon is widely used in industrial process due to its well developed microporosities and mesoporosities, high surface area and high surface reactivity. The capacity of CO_2 adsorbed by the activated carbon was determined by the mass uptake recorded from the expose towards pure CO_2. The adsorbed amount was calculated using ideal gas law at low pressure prevailing, by measuring the pressure drop caused by CO_2 adsorption (Somy et. al., 2009).

Instead of using conventional method, CO_2 concentration can also be reduced by using Advanced Oxidation Processes (AOPs). AOPs are technologies based on the intermediary of hydroxyl or other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to inert end-products. AOP includes heterogeneous and homogeneous photocatalysis based on near ultraviolet (UV) or solar visible irradiation, electrolysis, ozonation, the Fenton's reagent, ultra-sound and wet air oxidation (Klavarioti et. al, 2008). In reduction process of CO_2, the AOP used is heterogeneous photocatalysis or photocatalytic reduction process under UV light irradiation. Heterogeneous photocatalysis involves light absorption of sufficient energy by a photocatalytic semiconductor such as TiO_2, ZnS, ZrO_2, V_2O_5, ZnO, CeO_2 and NbO_5 that causing excitation of its valence band electrons into conduction band (Li et. al., 2004). The reaction for photocatalysis is shown in Figure 2.1.

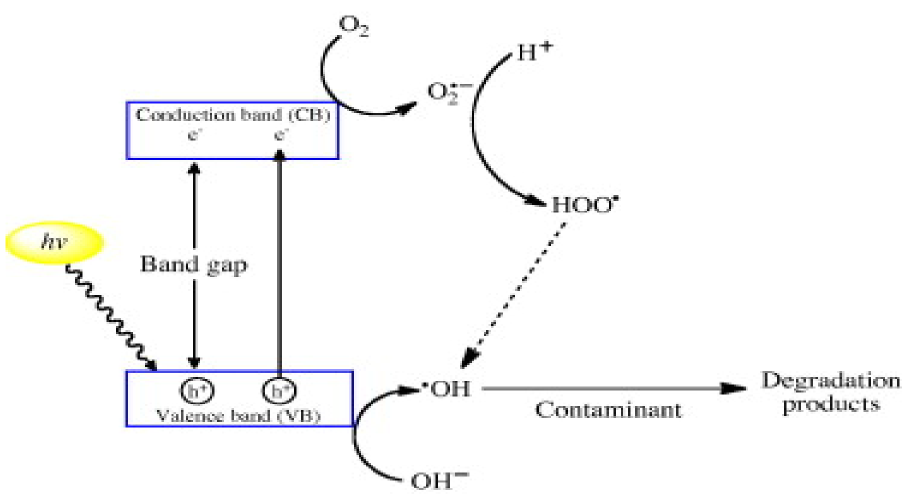


Figure 2.1: Schematic diagram of reaction occurring via photocatalysis

2.2 Photocatalyst Semiconductor

A semiconductor (SC) such as ZnS can be prepared from chemical solution. The methods of preparation include slow addition of Na_2S and bubbling H_2S through an aqueous precursor solutions, coprecipitation, microwave irradiation method and hydrothermal method (Wu et. al., 2008). A semiconductor is characterized by an electronic band structure in which the highest occupied energy band, called valence band (vb) and the lowest empty band called conduction band (cb), are separated by a band gap (Marta, 1999). Photocatalytic activity of the semiconductors is mainly determined by crystal structure, surface area, size of particles, bang-gap energy and morphology (Taghvae et. al., 2009). The process is considered as the direct absorption of a photon by band gap of the materials and generation of electron–hole pairs in the semiconductor particles. The excitation of an electron from the valence band to the conduction band is initiated by light absorption with energy equal to or greater than the band gap of the semiconductor (Pan et. al., 2007).

Energy will be absorbed by the semiconductor when the photon energy is higher or equal to the band gap energy. An electron from the valence band will be promoted to the conduction band and generates a hole (h^+) in the valence band. Subsequent anodic and cathodic redox reaction in Figure 2.2 will be initiated when the electron (ec^{b-}) and hole (hv^{b+}) react with donor (D) and acceptor (A).

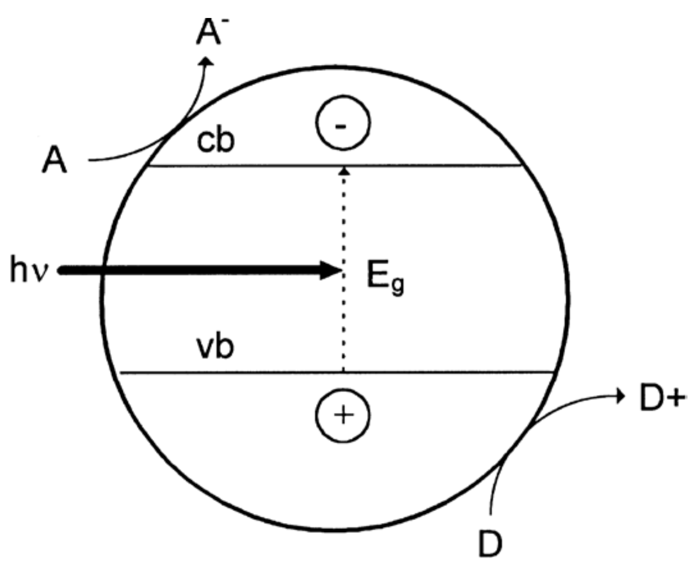


Figure 2.2: Simplified diagram of the heterogeneous photocatalytic process occurring on an illuminated semiconductor particle.

TiO_2 semiconductor has been widely used as catalyst for UV irradiation and was considered the best choice among several other oxides because it has low band-gap values of approximately 3.0 and 3.2 eV for rutile and anatase, respectively. Besides fulfilling the thermodynamic requirements needed for the occurrence of most of the photocatalytic reactions usually investigated, TiO_2 is reasonably cheap, photo-stable and non-toxic that making it a perfect candidate for photocatalytic process (Tan et. al., 2006).

Meanwhile, ZnS semiconductor behaves as an effective catalyst with wide band gap (E_g~3.6 eV) together with its distinguished energy band properties. It becomes good host material and possesses photoluminescence and electroluminescence characteristics (Taghvae et. al., 2009). However, Kočí et. al., (2010) has proved that the performance of heterogeneous semiconductor catalyst is better than raw semiconductor catalyst.

2.3 ZnS-Kaolin as photocatalyst

Photocatalysts are important materials that provide a relatively simple means for the conversion of solar energy for use in oxidation and reduction process (Casbeer et. al., 2011). These photocatalysts use their interlayer space as reactions sites, where the electron–hole recombination process could be retarded by physical separation of the electron–hole pairs generated by photo-absorption. One characteristic of these layered materials is that the interlayer guests are ion-exchangeable with various foreign species. The pillaring of layered compounds by inorganic compound is a promising method for fabricating function materials. Cationic species such as Pt, Fe_2O_3, TiO_2, CdS and SiO_2 have been introduced into interlayer galleries as precursors of photocatalytically active sites (Huang et. al., 2009).

Incorporation of a semiconductor catalyst in the interlayer region of a lamelar compound via chemical reactions is a promising method for fabricating a nanocomposite consisting of host layers with ultrafine particles in the interlayer and enhancing photocatalytic activity of the semiconductor. Another interesting feature is that the catalytic activity can be highly improved by partial substitution on A-and /or B-site, with only small changes in the average structure. It is well-known that the photocatalytic activity of a semiconductor is largely determined by the energetic of position of the band gap. Initially, a variety of transition metals (such as Cr, Fe and others) was employed to dope photocatalyst in order to reduce the band gap and allow it to absorb visible light (Huang et. al., 2009).

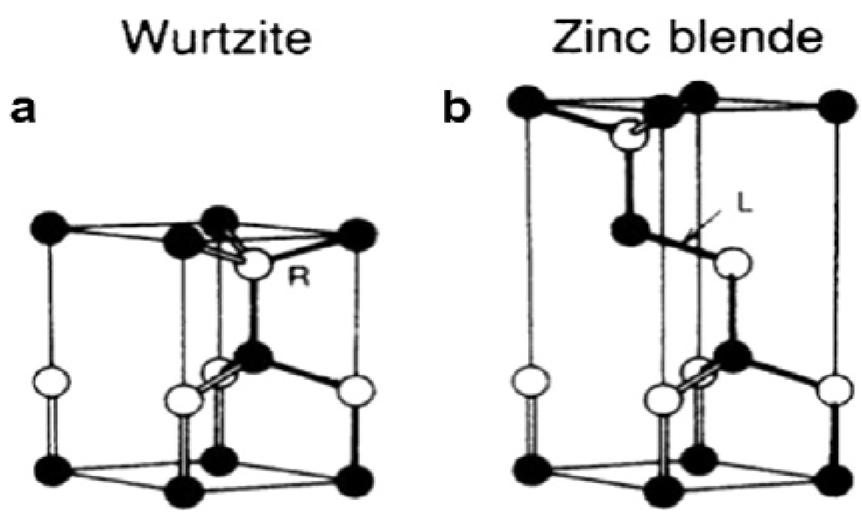
ZnS-Kaolin photocatayst is a kind of heterogeneous photocatalyst formed from the combination of semiconductor, ZnS and inert supporter of kaolin. It can be prepared through some methods such as sol-gel method, ion-exchange method, impregnation method and hydrothermal method. The semiconductor, ZnS has wide direct band gap energy which is 3.7 eV which performed rapid generation of electron-hole pairs by photoexcitation with lower wavelength of UV light. It also has highly negative reduction potentials of excited electrons (Miao et. al., 2006).

Meanwhile, Kaolin or China clay contains as the mineral kaolinite, which is a hydrated aluminiumsilicate (Al_2O_3•$2SiO_2$•$2H_2O$) (Chandrasekhar et. al., 2001). It has fine particle size, brightness and whiteness, chemical inertness and platy structure. Kaolin acts as supporter for ZnS nanoparticles. It also can act as an immobilizer that will prevent the semiconductor to aggregate in the NaOH solution. These properties will increase the effective surface area and photocatalytic efficiency. Kaolin also can changes the asidobasic properties of the catalyst surface and prevents the crystallite growing. Kočí et. al., (2010) has proved that heterogeneous semiconductor catalyst will performed better in photocatalytic reduction process. It provides effective surface area due to lower agglomeration in suspension, lower recombination rate of electron–hole pairs, changes of the acidobasic properties of the catalyst surface and lower crystallite size where the yields of the CO_2 photocatalytic reduction products increase with the decrease of crystallite size (Kočí et. al., 2010).

2.4 Zinc Sulphide (ZnS)

ZnS is one of the first nanostructured materials discovered and has shown remarkable fundamental properties versatility and a promise for novel diverse applications, including light-emitting diodes (LEDs), electroluminescence, flat panel displays, infrared windows, sensors, lasers and biodevices. Its atomic structure and chemical properties are comparable to more popular and widely known ZnO. However, certain properties pertaining to ZnS are unique and advantageous compared to ZnO. ZnS has a larger bandgap of 3.72 eV and 3.77 eV (for cubic zinc blende (ZB) and hexagonal wurtzite (WZ) ZnS, respectively) than ZnO which is 3.4 eV (Fang et. al., 2010).

ZnS has two commonly available allotropes, one with a ZB structure and another one with a WZ structure. The cubic form, ZB is the stable low-temperature phase, while the latter, WZ is the high-temperature polymorph which forms at around 1296 K. Figure 2.3 shows three different views of these structures. Alternatively, ZB consists of tetrahedrally coordinated zinc and sulphur atoms stacked in the ABCABC pattern, while in WZ, the same building blocks are stacked in the ABABAB pattern. The WZ phase has a higher band gap of 3.77 eV while the ZB structure of 3.72 eV that describes ranges of energy that an electron is forbidden or allowed to have (Fang et. al., 2010).



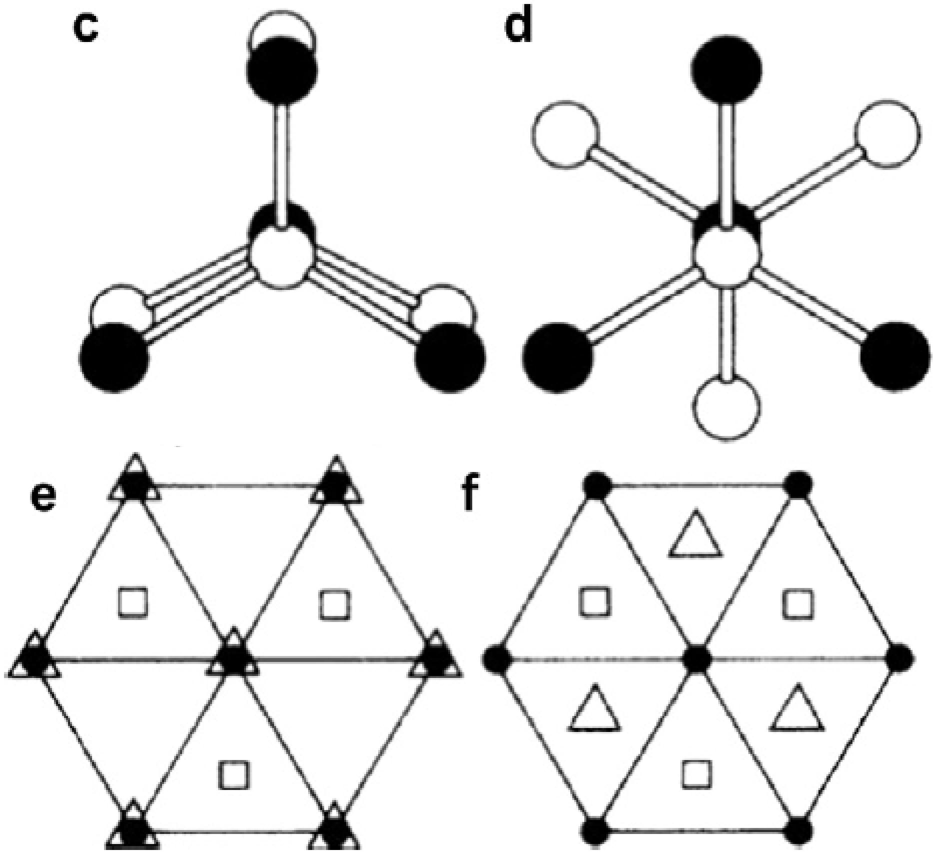


Figure 2.3: Model of wurtzite, WZ and zinc blende, ZB crystal structures where a and b show handedness of the fourth interatomic bond along the right (R) for wurtzite and along the left (L) for zinc blende, c and d show the respective eclipsed and staggered dihedral conformations, meanwhile e and f show atomic arrangement along the close packing axis.

2.5 Kaolin

Clays are nanoparticles with layered structures that possess net negative charge that is neutralized by cations such as Na^{+}, K^{+} and Ca^{2+} which occupy the interlamellar space. The amazing amenability of clays formodification is the fact that these interlamellar cations can be very easily replaced by other cations or other molecules. Molecules can be covalently anchored to layer atoms. This provides tremendous scope for altering the properties of clays like acidity, pore size, surface area, polarity and other characteristics that govern their performance as catalysts (Nagendrappa, 2010).

Clays are widespread, easily available and low-cost chemical substances. Clays are versatile materials that catalyze a variety of chemical reactions, both in their native state and in numerous modified forms. (Nagendrappa, 2010). It is estimated that millions of tons of kaolin, a kind of clay are used each year in the world for different applications like paper coating and filling, ceramics, paint, cracking catalyst, cements, waste water treatment and pharmaceutical industries (Lu et. al., 2009).

Kaolin is a commercial available and low cost clay material (Lu et. al., 2009). Kaolin belongs to the kandites mineral group and is a clay mineral with the chemical composition of $Al_2Si_2O_5(OH)_4$ as shown in Figure 2.4.

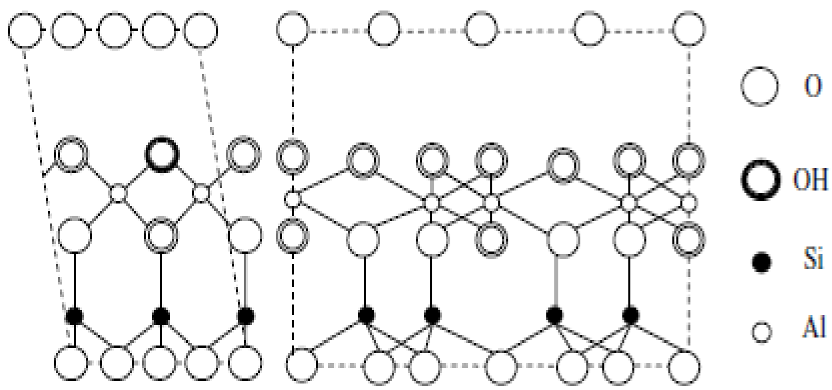


Figure 2.4: The Crystal Structure of Kaolinite

It is a layered silicate mineral with one layer of octahedral, which reacts with one sheet $(Si_2)_3(OH)_2)n$, resulting in a two-layer sheet structure. The siliceous side of Kaolin presents a surface of oxygen, while the aluminous side provides a surface of hydroxyl groups. These double layers are then stacked upon one another with the –OH groups of one such sheet against the oxygen of the next sheets. The interaction between the stacked layered in Kaolin are bonded covalently to each other, rather than Van der Waals or electrostatic forces. This interaction force makes Kaolin suitable as a structurally rigid substrate for supporting and immobilizing the TiO_2. The strong interaction forces make the immobilized particles chemically stable from swelling and can endure high