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MECHANOCATALYSIS WITH ELECTRICALLY INDUCED CONTRACTIVE ELECTRO-ACTIVE POLYMER

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ABSTRACT

One of the largest challenges in heterogeneous catalysis is how to control the adsorption and desorption catalytic cycle on the surface of catalyst. Therefore, the ultimate goal of this study is to design a new heterogeneous catalytic system based on an idea that the surface charge of the solid catalyst can be controlled by applying electric field in order to improve the efficiency of adsorption and desorption in catalytic cycle processes. Electric-field-induced oxidation of benzhydrol to benzophenone over electrically conducting surface containing titanium dioxide has been carried out by using hydrogen peroxide as oxidant. Polypyrrole and titanium dioxide have been used as electrically conducting materials and catalytic active site, respectively. The results suggest the occurrence of the synergistic effect of the electric field and titanium dioxide. The electric field on the generation of surface charge to induce the adsorption of organic substrate has been confirmed by methylene blue adsorption experiments. The study is also extended to photocatalysis in which the removal of methylene blue under the irradiation of UV light and electric field is chosen as a model catalytic system. One expects that the electric field will induce the degradation of metylene blue over polypyrrole containing titanium dioxide. There is no significant effect of the irradiation of UV light was observed in this process although the removal of methylene blue increased under electric field. As a global guide for future actions, this work opens new perspectives for the use of electrically conducting surface containing titanium dioxide in electric-field-induced liquid phase oxidation catalysis.

ABSTRAK

Salah satu cabaran terbesar dalam pemangkinan heterogen adalah bagaimana untuk mengawal penjerapan dan penyahjerapan pada permukaan mangkin dalam kitaran pemangkinan. Oleh itu, matlamat utama kajian ini adalah merekabentuk satu system pemangkinan heterogen yang baru berdasarkan idea di mana cas-cas pada permukaan pepejal mangkin boleh dikawal dengan mengaplikasikan keupayaan elektrik untuk memperbaiki kecekapan penjerapan dan penyahjerapan kitaran pemangkinan. Aruhan medan elektrik dalam pengoksidaan benzidrol ke benzofenon di atas permukaan mengkonduksi elektrik yang mengandungi titanium dioksida telah dijalankan dengan menggunakan hidrogen peroksida sebagai pengoksida. Polipirol dan titanium dioksida masing-masing telah digunakan sebagai bahan mengkonduksi elektrik dan tapak aktif pemangkinan. Keputusan menunjukkan terdapat kesan sinergi dalam medan elektrik dan titanium dioksida. Medan elektrik yang terjana oleh cas-cas permukaan untuk mengaruhkan penjerapan substrat organik telah dibuktikan oleh eksperimen penjerapan metilena biru. Kajian tersebut juga telah dilanjutkan untuk fotokatalisis di mana penyingkiran metilena biru di bawah sinaran cahaya UV dan medan elektrik telah dipilih sebagai satu model sistem pemangkinan. Jangkaan adalah bahawa medan elektrik tersebut akan mengaruhkan degradasi metilene biru atas polipirol yang mengandungi titanium dioksida. Tidak terdapat sebarang kesan yang ketara bagi sinaran cahaya UV yang diperhatikan dalam proses tersebut walaupun penyingkiran metilena biru miningkat di bawah pengaruh medan elektrik. Sebagai satu panduan global untuk tindakan masa depan, kerja ini membuka perspektif baru tentang penggunaan permukaan mengkonduksi elektrik yang mengandungi titanium dioksida dalam pemangkinan untuk pengoksidaan dalam fasa cecair atas aruhan medan elektrik.

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CHAPTER III METHODOLOGY

LIST OF ABBREVIATIONS/SYMBOLS/TERMS

$EDTA^{4-}$ - Ethylenediaminetetraacetate
Fe - Iron
Fe^{2+} - Ferrous, iron(II) ion
Fe^{3+} - Ferric, iron(III) ion
MnO_4^- - Manganate ion
Mn^{2+} - Manganese ion
H^+ - Proton
e^- - Electron
OH^- - Hydroxide ion
X^- - Halide
F^- - Fluoride
Cl^- - Chloride
Br^- - Bromide
I^- - Iodide
CN^- - Cyanide
NO_2^- - Nitrite
NCS^- - Thiocyanate
R- - Alkyl groups
RO- - Alkoxy group
RCO_2- - Acyl group
H_2O - Water
NH_3 - Ammonia
CO - Carbonyl group
bipy - 2,2-bipyridyl
en - Ethylenediamine
phen - 1,10- phenanthroline
$FeCl_2$ - Iron chloride
FAS - Ferrous ammonium sulfate hexahydrate, $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$
$KMnO_4$ - Potassium permanganate
MeOH - Methanol

H_2SO_4	-	Sulfuric acid
NaOH	-	Sodium hydroxide
KBr	-	Potassium bromide
MO	-	Molecular orbital
M	-	Metal
L	-	Ligand
[reactant]	-	Concentration of reactant
[A]	-	Concentration of A
[B]	-	Concentration of B
A	-	Absorbance
c	-	Speed of light, 3 x 10^8 m s^{-1}
h	-	Planck’s constant, 6.62 x 10^{-34} J s
k	-	Rate constant
t	-	Time
V	-	Rate of the reaction
?	-	Wavelength in cm^{-1}
$?_{max}$	-	Wavelength of maximum absorbance
e	-	Molar absorptivity
$?_o$	-	Energy separation between t_{2g} and e_g
N_A	-	Avogadro number, 6.02 x 10^{23}
M_1	-	Initial concentration of stock solution
V_1	-	Volume of stock solution needed
M_2	-	Desired concentration of standard solutions
V_2	-	Desired volume of standard solutions
E_1	-	Energy at first excited state
E_0	-	Energy at ground state
S_N^1	-	Unimolecular nucleophilic Substitution
CF	-	Crystal Field
CHN	-	Carbon, Hydrogen and Nitrogen
ESR	-	Electron spin resonance
FTIR	-	Fourier transform infrared
IR	-	Infrared
MS	-	Mass spectroscopy
UV-Vis	-	Ultraviolet-visible

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CHAPTER I

INTRODUCTION

1.1 Research Background and Problem Statement

In the 21st century, industrial catalyst technologies affect nearly all areas of the chemical and petroleum industries since the vast majority of industrial processes are based on catalytic reactions [1]. Much of the synthesis of new materials is certainly going to happen through catalysis. Moreover, catalysts are utilized as a critical component of emerging technologies for improving the quality of life and also for environmental protection and alternative energy sources.

Catalysts can be classified according to their structure, composition, area of application, or state of aggregation. However, it is customary to distinguish the catalysis into three subdisciplines, which is homogeneous catalysis, biocatalysis and heterogeneous catalysis. At present, heterogeneous catalytic reaction system is of fundamental importance in the chemical industry and in other technologically relevant applications since most of the catalytic chemical reactions are heterogeneous and adsorption is a necessary [2-9].

Recently, several attempts have been made to assist the heterogeneous catalysis in order to improve and to increase the efficiency of the heterogeneous catalytic reaction. For instance, the chemical effects of ultrasound, "sonochemistry", have been applied to heterogeneous catalysis during the past decade [10-12]. Another method is the application of an external electric field to enhance the heterogeneous catalytic reactions [13-17]. The development of new electrocatalysis holds a place on most “top ten” lists for catalysis where electrocatalysis at nanoparticle surface is a modern, authoritative treatise that provides comprehensive coverage at recent advances in nanoscale catalytic and electrocatalytic reactivity [7].

Indeed, the preparation of catalysts with high activity and the design catalytic systems with high efficiency have been a challenge in organic chemistry, organometallic chemistry, inorganic chemistry, and catalytic chemistry. However, many fundamental atomic-scale and nanoscale understanding of catalysis has been developed. The success of both scientists and engineers that involve experiment and theory on how to design catalysts to control catalytic chemistry, result in deeper insights into catalysis and allow the design of new catalysts and catalytic processes that approach the ultimate goal in the studies of catalysts. Moreover, the breakthrough in computational chemistry, measurement techniques and imaging, has further provided new fundamental knowledge for the catalysis research community until so many interesting developments could not be mentioned.

As this study is intended for designing a new heterogeneous catalytic system to improve the efficiency of adsorption and desorption in catalytic cycle processes by controlling the surface charge of catalyst by applying modulating electric field on the surface of catalyst, more emphasis will be given to the set-up of the new heterogeneous catalytic system and the relevant heterogeneous catalytic reactions.

1.2 Development of New Heterogeneous Catalysts System

With the advent of surface science techniques in decades past and the fast-growing insight into research in catalysis, there is great effort undertaken internationally to understand the fundamental processes of the initial stages of chemisorption at heterogeneous surfaces to obtain a basic understanding of the bonding and reaction concepts, and on the other hand, to highlight new properties that may appear by controlled modification at the atomic level of the surfaces.

Therefore, the ultimate goal of this study is to design a new heterogeneous catalytic system to achieve a coherent picture of catalytic processes at the fundamental level that able to improve the efficiency of adsorption and desorption in catalytic cycle processes. This can be done by controlling the surface charge of catalyst by applying modulating electric field on the surface of catalyst. Figure 1.1 is the proposed design of the desired heterogeneous catalytic system.

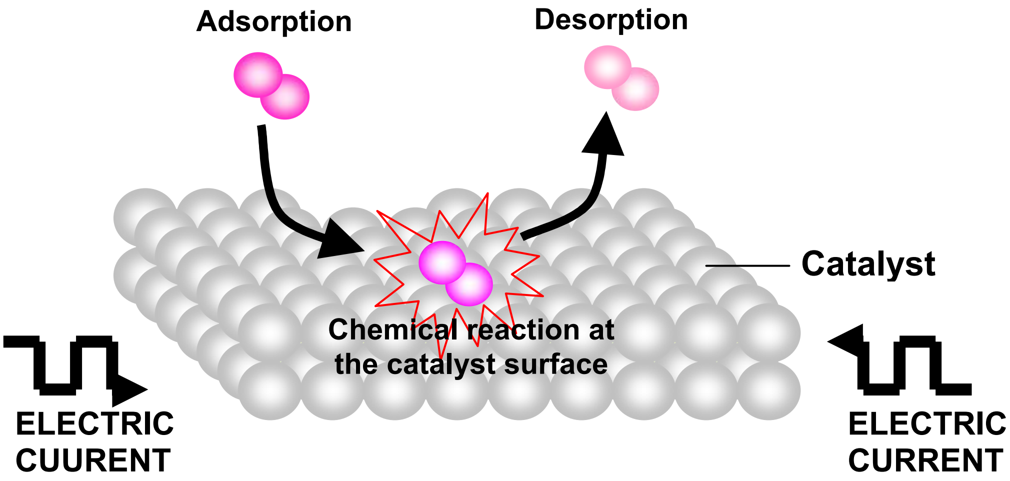


Figure 1.1 : The conceptual model for the desired heterogeneous catalytic system.

An external electric field does bring forth changes in the chemisorption and catalytic properties of semiconductors in heterogeneous catalytic reactions [13]. Hence, this new catalytic system design is basically based on an idea that the surface charge of the catalyst can be enhanced by the presence of electric potential. When an electric field is switched on, an additional surface charge is induced by the electric field. As a result, the different physicochemical processes occur and this can stimulate adsorption and catalytic reactions on the semiconductor surface [13-17]. In other words, when there is an application of an electric field, the efficiency of adsorption and desorption (interaction between the catalyst and reactant) in catalytic cycle processes can be control.

In this study, polypyrrole and titanium dioxide is used. Figure 1.2 shows the model of the polypyrrole and titanium dioxide as a new integrated catalytic system. Polypyrrole is chosen to be used in this research because it is one of the conducting polymers which are molecules with a "back bone" of alternating double and single bonds, along which electrons can flow as shown in Figure 1.3 [19]. Polypyrrole with extending π-conjugated electron systems have been extensively studied due to its good electrical conductivity and thermal stability, redox properties, environmental stability and easy preparation by both electrochemical and chemical approaches in various organic solvents and in aqueous solution [17, 18]. It is also efficient electron donor and good hole transporter upon visible light excitation [21]. Due to its electrical conductive properties, it would be of great interest to study the adsorption and desorption behaviour of polypyrrole under applied electrical potential.

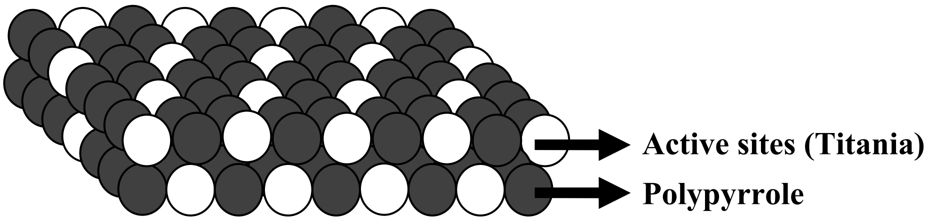


Figure 1.2 : The model of the polypyrrole and titanium dioxide.

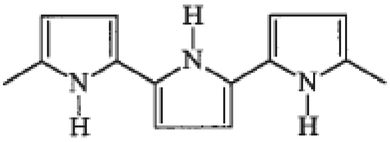


Figure 1.3 : The structure of polypyrrole polymer chain.

On the other hand, titanium dioxide was used to provide an active site for reaction to occur because it is resistant to photo-corrosion and has high oxidative power [20].

A lot of researches have been done on conjugated polymer/TiO_2 system where conjugated polymers act as stable photosensitizers combined with wide band gap inorganic semiconductors like titanium dioxide for optical, electronic and photoelectric conversion applications. In this conjugated polymer/TiO_2 system, polymer that bound to titanium dioxide is able to harvest the visible light matching the semiconductor energy levels, and then inject electrons into the conduction band of titanium dioxide. The electron-transfer paths in Fig. 1.4 are possible since the lowest unoccupied molecular orbital (LUMO) levels of polymer are energetically higher than the conduction band edge of titanium dioxide. The injected electron delocalizes from bulk to surface, simultaneously relaxing to the bottom of the conduction band owing to coupling to vibrations. Electron which remains trapped at the surface will react with the electron acceptor such as oxygen or hydrogen peroxide residing on the electrolyte mediator. As a conclusion, this conjugated polymer/TiO_2 system is very important in providing a vital prerequisite for the interfacial charge transfer between photosensitizer and semiconductor takes place [21]. Therefore, the study of this conjugated polymer/TiO_2 system is a very important for surface catalytic reactions.

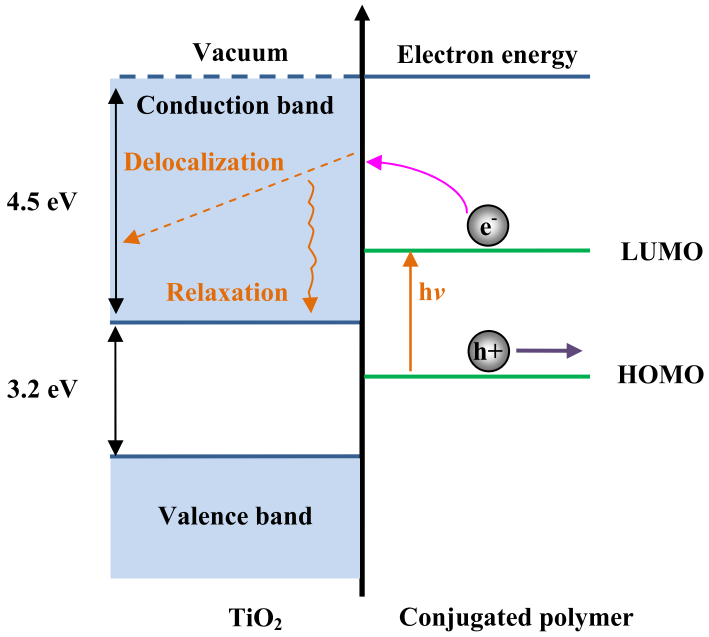


Figure 1.4 : Schematic diagram of conducting polymer/TiO_2 junction and free charge carrier photogeneration mechanism.

By applying this concept into the new integrated catalytic system under electric field, this model will be introduced as a new way to enhance the overall catalytic activity with the expectation of combining the effects of adsorption capacity of Polypyrrole and the reactivity of titanium dioxide.

The effect of an electric field on the adsorption of reactant on the surface of the catalytic system was investigated through the oxidation of benzhydrol by using aqueous hydrogen peroxide. Besides, the experiments employing methylene blue dye are performed so as to evaluate and to provide a better understanding of the effect of the electric field in the catalytic system.

1.3 Objective of Study

Main objectives of this study are:

(a) To develop a new integrated catalytic system based on electrically conducting surface (polypyrrrole) containing titanium dioxide under applied electric field.

(b) To study the influence of electric fields on the adsorption and catalytic properties of semiconductor catalysts in the new design catalytic system.

(c) To examine the usage of the polypyrrole and titanium dioxide as new catalytic system in the oxidation of benzhydrol and dye adsorption reactions.

1.4 Scope of Study

This study would cover the study of the effect of applied electric field in heterogeneous catalysis by using polypyrrole and titanium dioxide as a model of new catalytic system. The new catalytic system is introduced as a new way to improve the activities of the heterogeneous catalysts by controlling the surface charge of catalyst. The main chemical reaction that used to investigate the effectiveness of the electric field on regulating the adsorption capacity and the reactivity of catalyst in the new designed catalytic system was oxidation of benzhydrol by using aqueous hydrogen peroxide. Another experiment on dye adsorption was done as a further study to prove the impact of electric field on adsorption activity of the catalytic system. The supplied electric current was fixed at 5.0 A and 2.0 V for every experiments. The instruments that involved in characterization purpose are gas chromatograph (GC) equipped with a flame ionization detector (FID), Ultraviolet and Visible (UV/Vis) spectroscopy, Fourier

Transform Infrared Spectroscopy (FTIR), field-emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD).

CHAPTER II

LITERATURE REVIEW

2.1 Introduction to Catalysis

"Catalyst" is a word taken from a combination of two Greek words, κατα (kata, which mean down) and λύειν (lysein, meaning to annul or to untie). In another word, a catalyst is a substance that accelerates a chemical reaction by transforming reactants into products without itself being consumed in the process [36]. On the other hand, catalysis is an action where catalyst takes part in a chemical reaction process to alter the rate of reactions and yet itself will return to its original form without being consumed or destroyed at the end of the reactions. In autocatalysis, a reaction produces catalysts.

Actually, the development of catalysis as a concept is accorded to Jöns Jakob Berzelius who in 1835 realised that a number of isolated observations made by various investigators in the early part of the nineteenth century could be rationalised in terms of what he described as “catalytic power”. He defined the “catalytic power” as the ability of substances “to awaken affinities, which are asleep at a particular temperature, by their mere presence and not by their own affinity” [36]. The catalytic concept was then used to explain the contributions from Berzelius, Faraday, Davy, Döbereiner, Dulong, Thénard, Phillips, Ostwald, Henry, Wilhelmy and Kuhlmann in the early days of the phenomenon of catalysis.

Indeed, many types of materials can serve as catalysts. These include metals, metal compounds (e.g., metal oxides, sulfides, nitrides), organometallic complexes, and enzymes. However, a good catalyst of any type must exhibit a number of properties, like being high activity, selectivity, durability and regenerability.

As a conclusion, catalysis and catalyst help in new technology development. Therefore, a lot of fundamental atomic-scale and nanoscale research on bioscience, molecular science, surface science, computational science, and nanoscience has been invested to design new catalysts and new catalytic technology.

2.1.1 Catalysts and Reaction Energetics

A catalyst provides an alternative route (shown in red) to products where the catalytic route being subject to lower activation energy than in the uncatalyzed reaction as shown in Figure 2.1.

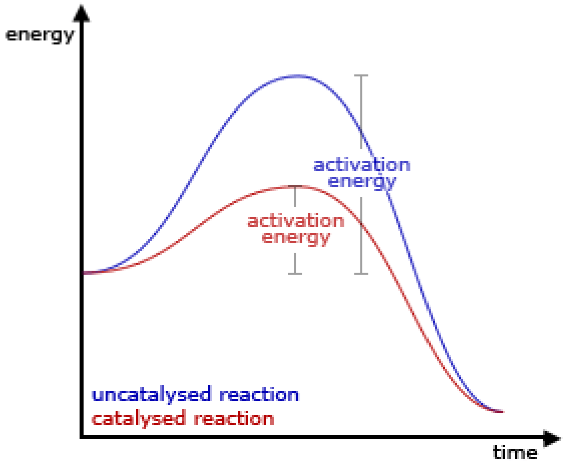


Figure 2.1: Potential energy diagram of the effect of a catalyst in a hypothetical exothermic chemical reaction.

The uncatalyzed reaction has to overcome a substantial energy barrier, whereas the barriers in the catalytic route are much lower. This means that catalysts reduce the amount of energy needed to start a chemical reaction. The effect of this is that more molecular collisions have the energy needed to reach the transition state. Lowered activation energy increases the reaction rate. However, catalysts cannot make energetically unfavorable reactions possible. They have no effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are equally affected. The net free energy change of a reaction is the same whether a catalyst is used or not because the catalyst just makes it easier to activate [37].

2.1.2 Importance of Catalysis

Catalysis plays a fundamental role in many areas particularly industrial chemicals and petroleum processing where it is useful in the production of chemicals. They are used heavily in polymerization processes, epoxidation, hydrocarbon cracking and so on. Since the catalysts are able to regenerate and can be reused multiple times, they help to save costs and energy and to reduce environmental impact from recycling or disposal of spent catalysts. Nearly 90% of all U.S. chemical manufacturing processes involve catalysis [36].

On the other hand, biocatalysis offers exciting opportunities for producing a broad range of pharmaceuticals, specialty chemicals and for bioremediation of the environment. A large fraction of chemical, refinery, and pollution and global warming-control processes involve catalysis, from the catalytic converter in automobiles to the alleged causes of the ozone hole. Catalytic, rather than stoichiometric reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated.

Catalysis also helps in encouraging application and advancement of new technologies and materials. For instance, many of the modern, cost-and energy-efficient environmental technologies are catalytic. In Nanotechnology, methods of Catalyst preparation are most suited for the preparation of nanomaterials like carbon nanotubes. Catalysis is of paramount importance in the academic field where research into catalysis is a major field in applied science, and involves many fields of chemistry, notably in organometallic chemistry, and physics.

2.1.3 Type of Catalysts

Catalysts can be either heterogeneous or homogeneous based on the ways it works.

2.1.3.1 Homogeneous Catalysts

Homogeneous catalysis is a chemistry term which describes catalysis where the catalyst is in the same phase as the reactants where the catalyst is a molecule which facilitates the reaction, typically a solution in common applications. The reactant(s) coordinate to the catalyst (or vice versa), are transformed to product(s), which are then released from the catalyst. Therefore, an understanding of the effects of solvents and solutes on the reaction chemistry is required.

If both the catalyst and reactants are in liquid phase, the two liquids can be different phases. For example, the petrochemical alkylation process features heterogeneous catalysis, although both the catalyst (acid) and reactants (hydrocarbons) are liquids.

In fact, homogeneous catalysis is of considerable commercial importance in the production of chemicals, and particularly in polymerization processes like carbonylation and hydroformylation. However, the drawback of homogeneous catalysis is the problem of separating the single-site-catalysts from the reaction media which is the major problem in industry of large scale applications. Only a few processes are applied nowadays in industry, such as the production of adiponitrile by Dupont, acetic acid by Monsanto and butanal by Celanese (former Ruhr Chemie) [36]. In each case an individual solution was developed to solve the problem of catalyst separation and recovery.

Therefore, substitution of these homogeneous catalytic systems with heterogeneous systems is desirable because of the simplicity of catalyst and product isolation from the reaction mixture and because of the possibility of operating the reaction continuously in heterogeneous systems [2].

2.1.3.2 Heterogeneous Catalysis

Heterogeneous catalysis is a catalysis process where the catalyst is present in a different phase to the reactants. Commonly, heterogeneous catalysts take the form of a solid catalyst which provides surface liquid or gaseous reactants for the chemical reaction to take place on.

At present, heterogeneous catalytic reaction system is of fundamental importance in the chemical industry and in other technologically relevant applications. For example, the oxidation of carbon monoxide to form carbon dioxide is the key reaction in car exhaust catalytic converters.

Other surface catalysts, such as metals and metal oxides, rely on catalytic action at sites on their surfaces. These catalysts are valuable in areas such as partial oxidation of hydrocarbons, or in the selective reduction of exhaust gasses.

Another broad class of these catalysts such as zeolites play a key role in the production of chemicals and fuels worth billions of dollars every year. Their complex pore structure and the character of the acidic sites within the framework offer an invaluable combination of shape-selectivity towards guest molecules and catalytic potential. They play key roles in refining, alkylation, hydrocracking and so on. But the usage of such catalysts produces a problem which is the difficulty of effective interaction between water-immiscible substrate(s) and catalyst particles owing to their hydrophilicity that hinders the contact with hydrophobic compounds in the organic phase [3].

In short, a simple model for heterogeneous catalysis involves the catalyst providing a surface on which the reactants or substrates temporarily become adsorbed. Bonds in the substrate become weakened sufficiently for new bonds in the product to be created. Then, the bonds between the products and the catalyst are weaker to release the products from the solid surface (desorption). Frequently, this transport of reactants and products from one phase to another plays a dominant role in limiting the reaction rate. Different possible mechanisms for reactions on surfaces are known, depending on how the adsorption takes place.

2.2 Electric field-induced chemistry

Electrical energy serves a useful purpose in our life. The flow of electrons or negative charges through a circuit called electric current. As current flows through any two points in a circuit, part of the electrical energy is converted into other forms of energy to produce light, heat, chemical reactions and mechanical power. The amount of electrical energy needed for the electrical charges to flow between the two points is the voltage (potential difference) between the two points. The region of space characterized by the existence of a force generated by electric charge is termed the electric field of the charge [45, 46].

The SI unit of voltage and electric current is volts (V) and amperes (A) respectively. The voltage voltage is measured using voltmeter whereas the quantity of electric current is measured using an ammeter.

Resistance is the property of an electrical conductor that opposes the flow of electrons through it ohms (Ω). Hence, resistance determines the amount of electric current that flows in a circuit and it is measured it . Ohm's law states that the current (*I*) that flows through a metal conductor is directly proportional to the potential difference or voltage (V) across it, if the resistance (R) remains constant. Therefore, Ohm's law is expressed as follows:

$$R = \frac{\mathrm{V}}{\mathrm{I}} \tag{2.1}$$

Electric field-induced chemistry is a phenomenon where the external electric fields caused a redistribution of the valence electrons in molecules and especially in molecules adsorbed on surfaces which then affect both internal bonds and the surface bond. Indeed, a number of different systems have been used in chemical reaction to reveal electric field-induced chemistry. For instance, Block and coworkers have developed a field pulse technique in the field ion microscope that allows the investigation of the field effect following earlier work by Inghram and Gomer [44]. It has been found that under the influenced of electric potential, the adsorption property of polypyrrole is improved toward the adsorption of dyes on the polypyrrole surface by enhancing surface charge [34, 47].

In conclusion, electricfield-induced chemistry opens up new reaction pathways in chemical reactions particularly in heterogeneous catalysis.

2.3 Adsorption and Desorption in Catalytic Cycles

Heterogeneous catalysis cycle involves the adsorption of reactant on the surface of solid catalyst, followed by the surface reaction and product desorption. According to Langmuir-Hinshelwood mechanism for catalyzed process, the rate of heterogeneous reaction is controlled by the reaction of the adsorbed molecules and that all adsorption and desorption process are equilibrium [49].

Adsorption is a process in which molecules from gas, vapour, or liquid phase land on, interact with and attach to a solid surface due to the unbalanced or residual forces or valencies which act along the surface of the molecule and the solid surface. The term 'adsorption' was first of all used by Kayser at the suggestion of du-Bois Reymond in the year of 1881 [48].

The material on the surface of which adsorption takes place is called the adsorbent and the substance adsorbed is called the adsorbate. Adsorption is an interface phenomenon whereas absorption is a bulk phenomenon. When the amount of adsorbate taken up by a solid at a fixed pressure and temperature is proportional to its surface area and not its volume, then it is an adsorption process and not absorption predominates. In certain reaction, the initial rapid adsorption is followed by a slow process of absorption of the substance into the interior of the solid until the effects of adsorption cannot be distinguished from the effect of adsorption. Hence, sorption is a term suggested by Mcbain to describe a process in which both adsorption and absorption take place simultaneously [49].

The reverse process of adsorption is a process which adsorbed molecules escape from solid surfaces and it is called desorption. In conclusion, adsorption and desorption is an important surface reaction in catalytic cycles.

2.3.1 Physisorption and Chemisorption

Indeed, adsorption is a fundamental physic-chemical property of solids and liquids. Therefore, adsorption can be divided into two types because of the different forces involved. Physisorption is a physical adsorption whereas chemisorption is a chemical adsorption.

Physisorption is a type of adsorption in which the adsorbate adheres to the surface only through weak interparticle bonds like Van der Waals , Hydrogen and dipole-dipole interactions which involves low activation energy [38]. It takes place in multilayers and is reversible in the majority of cases. Solid heterogeneous catalysis proceeds via physisorption where reacting molecule adsorb onto the surface of the catalyst without changing their internal bonding. Therefore, physical adsorption constitutes a very important means of investigating the properties of heterogeneous catalyst.

In chemisorption, molecule adheres to a surface through the formation of a covalent and ionic bond between adsorbate and surface. These strong interparticle bonds present due to an exchange of electrions which involves high activation energy [38]. This kind of absorption takes place only in a monolayer and reversible only at high temperature. Chemisorption process is pivotal to the role of heterogeneous catalysis where the catalyst is in a solid phase where chemical reagents bind to the catalytic surface. Then, chemical bonds are formed and draw electrons away from the chemisorption bonds. This caused the increase in electron density in the adsorbent-adsorbate interface. The molecule then desorbs and is free to leave the surface. The heat of chemisorption is in the same order of magnitude of reaction heat whereas the heat of physisorption is in the same order of magnitude of condensation heat [49].

2.3.2 Application of Adsorption in Industries

The phenomenon of adsorption has found in many applications in the industries as described below:

(a) The dehydration and purification of CO_2, O_2, N_2, He and Cl_2 by using silica gel and alumina due to their strong adsorptive force.

(b) Decolourisation of coloured solutions by passing the solution over animal charcoal.

(c) Catalysed reactions.

(d) Chromatographic analysis.

(e) Dyeing process where dyes are absorbed on the surface of cloth.

(f) Human body used the principle of purification by adsorption for certain removal functions.

2.3.3 Adsorption in Electrochemistry

For adsorption in electrochemistry, the potential difference at the interface can be controlled and varied independently. In this way, an additional degree of freedom exists and the equilibrium constant for adsorption can be change at constant temperature and bulk concentration. Additionally, higher reproducible surfaces can be produced in rigorously purified solutions by keeping the electrode at a fixed potential or taking it through a programmed cycle of potential variation [50].

The tendency of molecules to adsorb on electrode surfaces is offset by a stronger energy of bonding to the surface in one of the possible configurations. The extent of adsorption also depends strongly on the solubility of the adsorbate where the lower the solubility, the higher the adsorbability. Besides, the size of the molecule and the dipole moment also play an important role in this area.

Accordingly, the two prerequisites for adsorption in electrochemistry are the identity of species in the bulk of the solution and the occupancy of the surface of the electrocatalyst [50].

2.4 Carbon Conductive Grease

Carbon conductive grease helps in improving electrical conductivity to an otherwise nonconductive surface. It is uses for lubricating switches and improving electrical connecting between sliding surfaces as well. Besides, carbon conductive grease is lubricates and also provides protection for moisture and corrosion on the surface.

According to material safety data sheet (MSDS) provided by MG Chemical, carbon conductive grease consists of 20-22% carbon black and 78-86% polydimethylsiloxane.

2.4.1 Carbon Black

Carbon black is a material produced through the incomplete combustion of heavy petroleum products such as coal tar, ethylene cracking tar and vegetable oil. It is a form of amorphous carbon, an allotrope of carbon that does not have any crystalline structure but it has a high surface area to volume ratio. Amorphous carbon also has localized π electrons where its bonds form with lengths and distances that are inconsistent with any other allotrope of carbon. It contains a high concentration of dangling bonds, which cause deviations in interatomic spacing of more than 5%, and noticeable variation in bond angle.

As a matter of fact, carbon black is neither graphite nor diamond. However, it is also not truly amorphous because it consists of the crystallites of graphite or diamond with varying amounts of amorphous carbon holding them together to make polycrystalline or nanocrystalline materials within an amorphous carbon matrix. Therefore, the ratio of sp^2 to sp^3 hybridized bonds present in a material determined the allotropes of carbon. Graphite and diamond consist purely of sp^2 hybridized bonds and purely of sp^3 hybridized bonds respectively. Material that consists of mixed sp^2 and sp^3 hybridized bonds are referred to as amorphous carbon.

2.4.2 Polydimethylsiloxane

Polydimethylsiloxane (PDMS) is a silicon-based organic polymer and its molecular formula is $(H_3C)_3[Si(CH_3)_2O]_nSi(CH_3)_3$, where n is the number of repeating monomer $[SiO(CH_3)_2]$ units. Figure 2.2 shows the structure of polydimethylsiloxane.

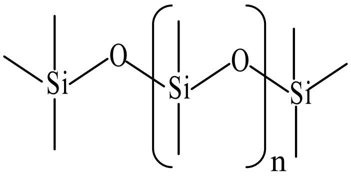


Figure 2.2: The structure of polydimethylsiloxane with $[SiO(CH_3)_2]$ as the repeating monomer units.

Polydimethylsiloxane is well known for its unusual rheological property which gives the carbon grease the lubricating ability. This is due to the molecules of polydimethylsiloxane have quite flexible polymer backbones due to their siloxane linkages.

Polydimethylsiloxane is optically clear, non-toxic, non-flammable and present an external hydrophobic surface. Thus, this surface chemistry leads to adsorption of hydrophobic contaminants. Organic solvents infiltrate into the material and cause it to swell. Therefore, the chemical reaction that used in this study must be water-based reaction in order to maintain the fuction of polydimethylsiloxane.

2.5 Polypyrrole

Polypyrrole is one of the conducting polymers which have been extensively studied due to its good electrical conductivity and thermal stability, redox properties, environmental stability and easy preparation by both electrochemical and chemical approaches in various organic solvents and in aqueous solution [17, 18]. Polypyrrole conducting polymers exhibit a wide range of surface conductivities (10^{-3} S $cm^{-1} < \sigma < 100$ S cm^{-1}) depending on the functionality and substitution pattern of the monomer and the nature of the counter ion or dopant.

The structure of polypyrrole is believed to be pyrrole unit coupled through their 2- and 5-positions shown by solid-state nuclear magnetic resonance (NMR), infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The mechanism of pyrrole polymerization can be deduced from several observations as shown in Figure 2.3 [18].

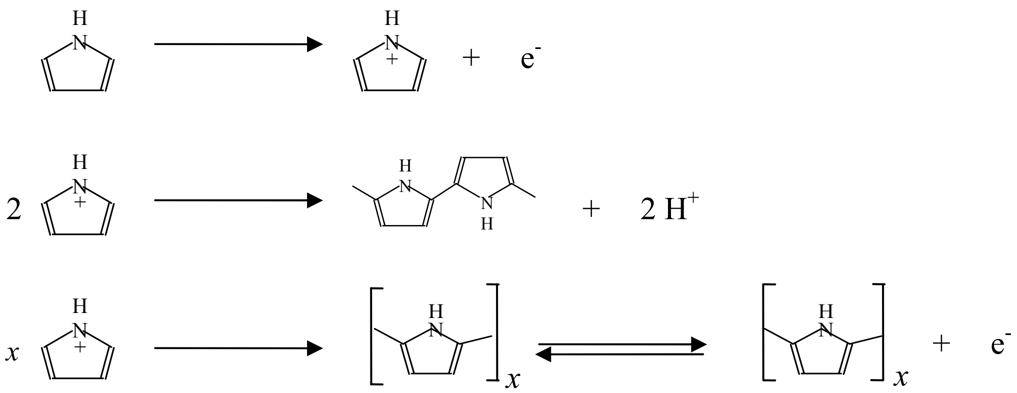


Figure 2.3: Mechanism of pyrrole polymerization.

Firstly, the initial oxidation step produces a radical cation which can either react with another radical cation to produce a dimmer or undertake electrophilic attack on a neutral monomer. Since the electrochemical polymerization reaction occurs only when the applied potential is sufficient to oxidize the monomer, the coupling of two radicals is the more likely reaction because, at the potential applied, the number of neutral species at the electrode surface will be essentially zero. Secondly, the charge consumed during polmer formation has a linear time dependence (at least initially) and is independent of pyrrole concentration during a constant potential electrolysis. This indicates that the entire electrochemical reaction occurs at the electrode surface. Thirdly, the dimer, bipyrrole, the trimer, terpyrrole, and the polymer, polypyrrole, are all more readily oxidized than pyrrole monomer and will thus be in an oxidized state during polymerization. Therefore, coupling will occur between oligomer radical cations and pyrrole radical cations at the electrode surface. An outline of the polymerization scheme is given in Figure 1.3. The growth of polypyrrole chains is most likely terminated when the ends of the growing chains become blocked sterically [18].

Figure 2.4 and Figure 2.5 show the structure of the monomer and polypyrrole polymer chain, respectively.

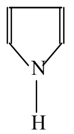


Figure 2.4: The structure of monomer of pyrrole.

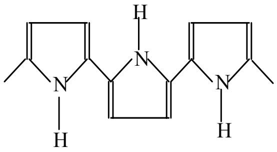


Figure 2.5: The structure of polypyrrole polymer chain.

The degree of polymerization, *x*, is not known precisely. Most conducting polymers will have a range of chain lengths which will include some relatively short oligomers. By comparing the radioactivity of the monomer to that of the polymer, an *x* value can be determined, which is equivalent to a relative molar mass of 100 000 [18].

Actually, polypyrrole is largely-produced and commercially available in various types of composite form, such as polypyrrole doped with carbon black. Due to its electrical conductive properties, it would be of great interest to study the adsorption and desorption behaviour of polypyrrole under applied electrical potential. The alternating single double bonds in polypyrrole chain make it easily lose or gain an electron, or simply displace an electron along the polymer backbone. The localization of the bonds on alternating sites creates an energy gap between the valence band and conduction band. In the presence of an applied electric field, the removal of an electron during oxidation of polypyrrole generates an unpaired electron and a hole or a positive charge. The formation of this localized radical which occurs in the backbone which is called a "polaron" is the charge-carrying entity of polypyrrole and it is correspond to a new energy state in the band gap. Such changes in the electronic structure are very important to the conduction mechanism. "Bipolaron", a doubly charged unit derived when a second electron is removed from the polaron at higher levels of oxidation. The holes alongside the polypyrrole chain allow electrons to pass along the polymeric chain thus increasing the negative polarity of polypyrrole. Figure 2.6 shows the chemical structures of polarons (radical-ions) and bipolarons (diions) in polypyrrole.

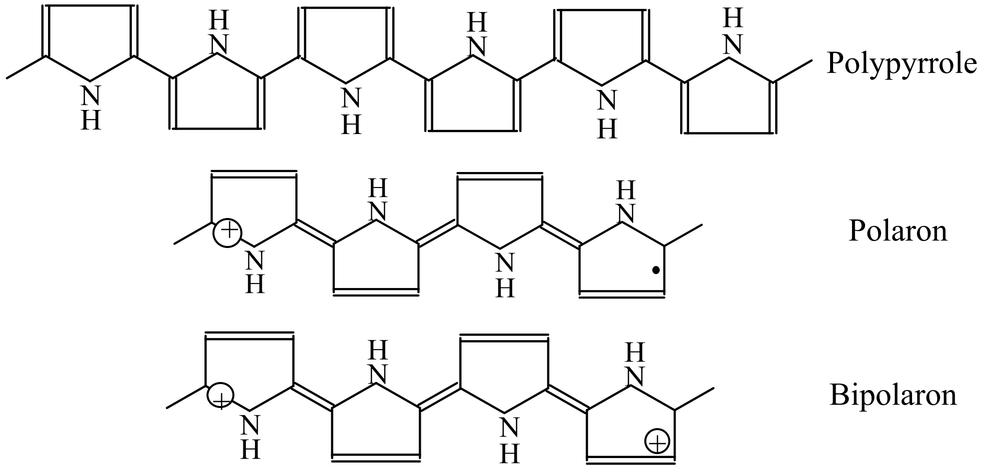


Figure 2.6: Structures of polarons and bipolarons in polypyrrole.

The electrochemistry of polypyrrole has been discussed in numerous review papers from various points of view because of its promising properties like its high electrical conductivity, air stability, and good mechanical properties. Many studies have been devoted to the relationship between the preparation conditions and the electrical properties of PPy films [51, 52]. It was found that the high conductivity of polypyrrole was obtained by the use of doping techniques. Indeed, the detailed reasons of electrical conductivity of conjugated polymers are still not quite clear up to now [52]. However, the charge transport in polypyrrole is described by three fundamental processes:

(i) Transport along the conjugated parts of the polypyrrole chains

(ii) Transport by hopping between the polypyrrole chains

(iii) Tunneling processes in high doping regions

2.6 Titanium dioxide

Titanium dioxide is the naturally occurring oxide of titanium, chemical formula TiO_2. It occurs in four forms, which is titania, rutile, anatase and brookite. Titanium dioxide occurrences in nature are never pure because it is found with contaminant metals such as iron. The oxides can be mined and serve as a source for commercial titanium. The metal can also be mined from other minerals such as ilmenite or leucoxene ores, or one of the purest forms, rutile beach sand.

Titanium dioxide is the most widely used as pigment in cosmetic and paint products. It is also used as catalyst due to its characteristic of high crystallinity and high surface area that provides active sites for adsorption and for catalysis to occur to a larger extent. For example, it is well known that titanium dioxide is the dominant semiconductor found in practical applications of UV activated photocatalysis. This is attributed to its crystallinity, surface area, moderate purity, stability in aqueous solutions, safety for living organisms, and low price. Many laboratories are doing research on modifying titanium dioxide in attempts to solve environmental problem through photocatalysis.

2.6.1 Titanium dioxide as Photocatalyst

Photocatalysis is basically a reaction which uses light to activate a catalyst (photocatalyst) to alter the speed of a chemical reaction by either direct irradiation or by the irradiation of a catalyst that in turn lowers the activation energy for the primary reaction to occur. The catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction [25].

By exploiting the energy of light, photocatalysts induce the formation of strongly oxidizing reagents which can decompose some organic and inorganic substances present in the atmosphere. For instance, chlorophyll (a type of photocatalyst in nature) captures sunlight to turn water and carbon dioxide into oxygen and glucose. Specially designed machines or equipment are needed in this field because inconveniences and detrimental factors in direct solar photolysis are the lack of sunlight adsorption by the substrates, attenuation of the sunlight, and the relatively shallow penetration depth of sunlight in natural aquatic bodies.

Today, many semiconductors are selected as photocatalysts including TiO_2, $SrTiO_3$, Fe_2O_3, CdS, WO_3, ZnS, $FeTiO_3$, ZrO_2, V_2O_5, Nb_2O_5, SnO_2 and so on. This is because of semiconductors have a narrow gap between the valence and conduction bands. In order for photocatalysis to proceed, the semiconductors need to absorb energy equal to or more than its energy gap. This movement of electrons forms negatively charged electron (e^-) or positively charged hole pairs (h^+) where the hole can oxidize donor molecules.

Among the possible semiconductors, titanium dioxide is most extensively used in the field of photocatalysis in terms of research, characterization, and applications because it has many advantages. It is nontoxicity, recyclability, and it requires little post-processing which make it inexpensive. Besides, it has moderate band gap and can react under mild-operating conditions. The characteristic inert and resistant to corrosion of TiO_2 make the TiO_2 has chemical and photochemical stability. However, ultraviolet light is required for photocatalysis to occur [25]. Titanium dioxide in anatase form that used in this study possess a large band gap where its E_g is 3.2 eV. Figure 2.7 presents the band edge positions of several semiconductors [32].

The photochemical activity of titanium dioxide is modified by promoting or suppressing the recombination of electron and hole pairs which are formed by UV light excitation. In other words, electron-hole pair was created once excitation occurs across the band gap for a sufficient lifetime. Then, the charge transfer to adsorbed species on the surface of titanium dioxide from solution phase contact to allow chemical reaction happen. The ability of titanium dioxide to undergo electron transfer to adsorbed species on its surface is governed by its band energy positions and the redox potentials of the adsorbate. Thermodynamically, the relevant potential level of the acceptor species must be more positive than the conduction band (CB) potential of the semiconductor whereas the potential level of the donor must be more negative than the valence band (VB) position of the semiconductor in order to donate an electron to the vacant hole.

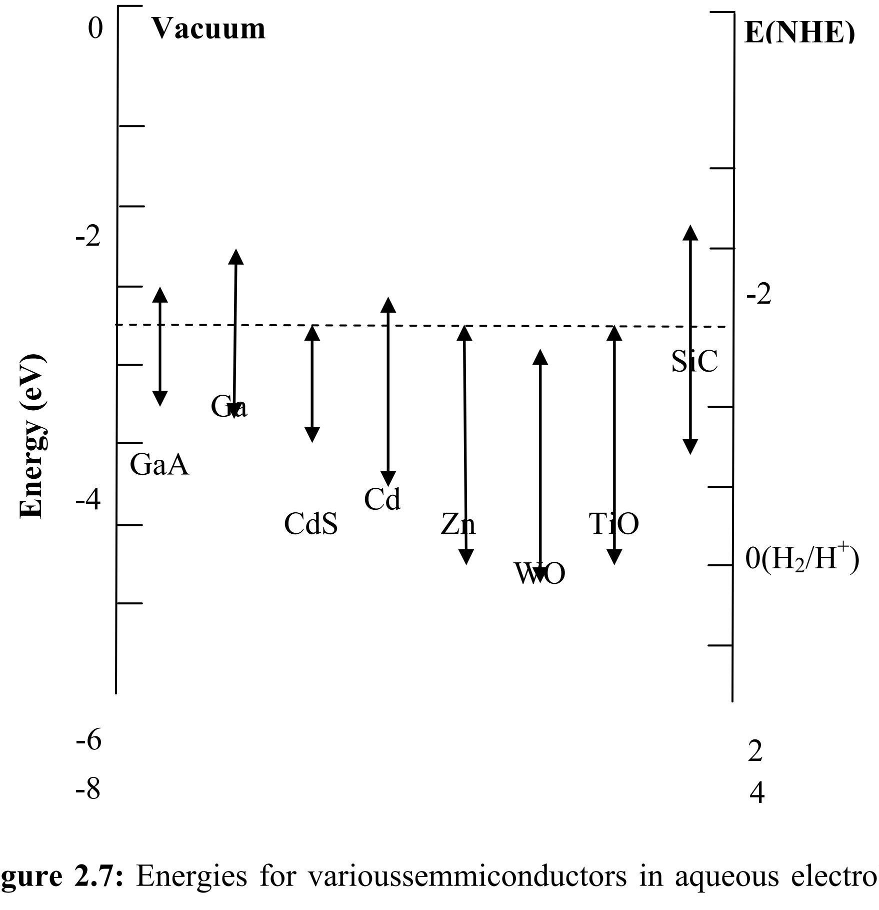


Figure 2.7: Energies for varioussemmiconductors in aqueous electrolytes at pH = 1

Therefore, the generation of electron-hole pairs in the titanium dioxide particles is the initial process for heterogeneous catalysis of organic compounds to occur (pathway 1). The enlarged section of Figure 2.8 shows the excitation of an electron from the valence band to the conduction band with energy equal to or greater than the band gap of titanium dioxide.

However, several of the possible reaction pathways can be taken by the separated electron and hole once they are generated and it is depend on the bulk and surface properties of titanium dioxide. Pathway 2 and pathway 3 can be respectively described as volume and surface recombination and are the dominant fate of electron-hole pairs which lead to low catalytic efficiencies. Hence, the recombination of electron-hole pairs is necessary in order to improve the efficiencies of a catalytic system. Indeed, recombination processes can be decreased by reducing the particle size although the recombination processes will increase again near quantum sizes. Apart from that, an increasing of crystallinity of the lattice by reducing the surface and bulk defects and impurities and increasing the charge transfer rate by preadsorbing reactant species on the surface can decrease the frequency of recombination processes as well.

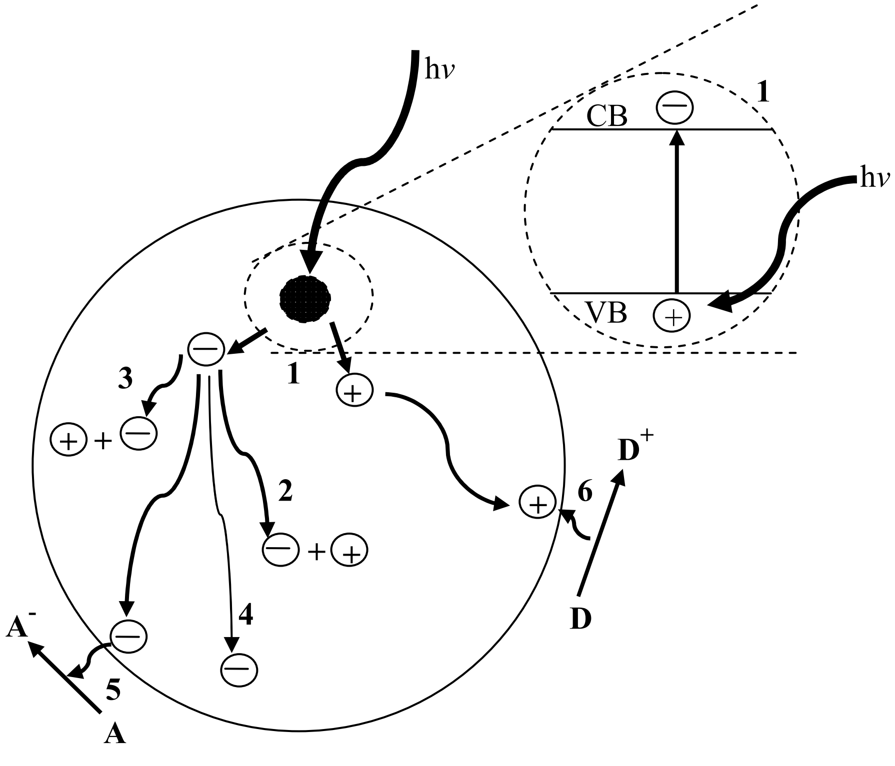


Figure 2.8: Possible reaction pathway for generated electron-hole pairs in titanium dioxide

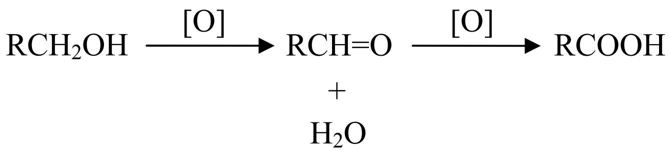
On the other hand, charge trapping (pathway 4) can occur in localized energy levels in the band gap region. Eventually, the charge carriers that trapped in these energy levels decay slowly by bimolecular and geminate recombination on the order of micro or nanoseconds. Pathway 5 occurs when an electron acceptor is reduced by removing a migrating electron from the surface of the particle. An oxidation reaction occurs (pathway 6) when an electron from a donor species combines with a hole that has migrate to the surface where the surface hole oxidizing the donor species [25, 32]. As a conclusion, the probability and rate of the charge transfer processes for electrons and holes depends upon the respective positions of the band edges for the conduction and valence bands and the redox potential levels of the adsorbate species.

In this study, titanium dioxide was intergrated with polypyrrole to be introduced as a new integrated catalytic system under electric field.

2.7 Oxidation of Alcohols

One of the most important reaction that alcohols are known to undergo is oxidation. The development of new oxidation processes continues to attract attention in spite of the availability of numerous oxidizing agents. The demand for eco-friendly chemical processes has encouraged the development of clean reactions and awaits further development of high yielding and economical methods for the oxidation of alcohols [30].

Primary alcohols (RCH_2OH) are converted to aldehydes ($RCH=O$) by oxidation easily but the aldehydes are easily oxidized further to carboxylic acids ($RCOOH$) as shown in Figure 2.9 [54]. Hence, the oxidation of primary alcohol is not an ideal and practical method to synthesis aldehydes.



$$RCH_2OH \xrightarrow{[O]} \underset{\displaystyle H_2O}{\underset{+}{RCH{=}O}} \xrightarrow{[O]} RCOOH$$

Figure 2.9: Generalized oxidation of primary alcohol in which the oxidizing agent is represented by [O].

Oxidation of secondary alcohol yield ketones which will not undergo further oxidation except by very drastic procedures that break carbon-carbon bonds or by combustion. Therefore, almost any desired ketone can be made from the corresponding secondary alcohol by the action of an appropriate oxidizing agent as shown in Figure 2.10. The oxidation of primary alcohol and secondary alcohol involve the removal of two hydrogen atoms from the alcohol molecule. One of these hydrogens is from the —OH group and the other is from the carbon atom to which the —OH group is attached.

$$R_2CHOH \xrightarrow{[O]} R_2C{=}O + H_2O$$

Figure 2.10: Oxidation of secondary alcohol

Actually, the oxidation of secondary alcohols to carbonyl compounds is an important synthetic transformation and various transition metal based catalysts, such as methyltrioxorhenium dinuclear iron complexes, vanadium phosphorus oxide, cobalt(II) complexes and sodium tungstate using hydrogen peroxide as oxidant have been reported. However, most of these methods are associated with the limitations such as use of toxic, expensive metals, lower yields of the products and oxidation of only activated such as benzylic and allylic alcohols. Hence, the development of transition metal free ecofriendly synthetic methodologies is emphasized to avoid the use of toxic and expensive metals and their complexes [29].

Since there is no hydrogen atom is directly bonded to the carbon atom that is attached to the —OH group in a tertiary alcohol, the tertiary alcohol cannot be oxidized except by such drastic procedures as combustion [53, 54].

In this study, oxidation of benzhydrol by using aqueous hydrogen peroxide was done in order to investigate the effect of an electric field on the adsorption of reactant on the surface of the catalytic system to yield benzophenone.

Benzhydrol is used in many organic syntheses and it is also used as an intermediate in pharmaceuticals, agrochemicals and other organic compounds. In polymerisations and perfumery, benzhydrol is used as a terminating group and fixative, respectively [56]. Hydrogen peroxide was used as an oxidant because water is the only by-product, which is easy to deal with after reactions. Hydrogen peroxide is also known as an attractive, atom-economic, and environmentally benign oxidant as it is cheap, easily available, and produces only water as by-product. In the recent years, it has been extensively used in developing a variety of synthetically important oxidation methodologies like epoxidation, oxidation of alcohols, aldehydes, and sulfides using transition metal based catalysts both in homogeneous and heterogeneous phases [29, 30].

In summary, a variety of different catalytic systems for the oxidation of alcohols have been developed and there is ongoing interest in the search for new efficient metal catalysts for this system [30]. For instance, most benzophenones are conveniently obtainable by oxidation of the corresponding benzhydrols by pyridinium chlorochromate (PCC) and other oxidants. Besides, a convenient and mild protocol for oxidation of electron rich benzhydrols using catalytic amount of dichlorodicynoquinone (DDQ) has been developed [55]. In the presence of a phase-transfer catalyst, benzhydrol is oxidized to benzophenone by sodium hypochlorite (commonly known as bleach). Moreover, benzophenone was observed to be the sole product in the TiO2 photocatalyzed oxidation of benzhydrol in oxygen purged acetonitrile [56].

2.8 Dye absorption

2.8.1 Dyes

Dyes are chemicals which on binding with a material will give color to the material. It is used in many industries such as food, paper, carpet, rubber, plastics, cosmetics and textiles. Dyes are ionic, aromatic organic compounds with structures including aryl rings which have delocalised electron systems. Such complex aromatic molecular structures make dyes more stable and more difficult to biodegrade [41].

Basically, all aromatic compounds absorb electromagnetic energy. However, only those that absorb light with wavelengths in the visible range (~350-700 nm) are coloured. Dyes contain chromophore group which is a delocalised electron systems with conjugated double bonds, and *auxochromes*, electron-withdrawing or electron donating substituents that cause or intensify the colour of the chromophore by altering the overall energy of the electron system. The example of chromophores are azo (-N=N-), carbonyl (-C=O), carbon (-C=C-), carbon-nitrogen (>C=NH or –CH=N-), sulphur (C=S), nitroso (-NO or N-OH) and nitro (-NO_2 or =NO-OH). The chromogen which is the aromatic structure normally containing benzene, naphthalene or anthracene rings is part of a chromogen-chromophore structure along with an auxochrome. The presence of ionishing groups, the auxochromes (-NH_3, -COOH, -HSO_3, -OH) results in a much stronger alteration of the maximum absorption of the compound and providesa bonding affinity [38].

2.8.2 Dye Classification

Normally, dyes are classified according to their chemical structure or chromophore, colour index and other dye classes (Food dyes and Natural dyes). Around thirty different groups of dyes can be discerned based on chemical structure. Azo (monoazo, disazo, triazo, polyazo), anthraquinone, phthalocyanine and triarylmethane dyes are quantitatively the most important groups. Other groups are diarylmethane, indigoid, azine, oxazine, thiazine, xanthene, nitro, nitroso, methine, thiazole, indamine, indophenol, lactone, aminoketone and hydroxyketone dyes and dyes of undetermined structure (stilbene and sulphur dyes). Dyes can be classified as acid, direct reactive dyes (anionic), basic dyes (cationic) and disperse dyes (nonionic) according to their dissociation in an aqueous solution. Commercial dyes are usually a mixture of large complex and have often unreported structure and vary widely in chemical composition [12, 34, 47].

2.8.3 Dye Removal Techniques

Most dyes are chemically and photolytically stable and resistant to environmental conditions like light, effects of pH and microbial attack. As a consequence, these colored compounds inhibit sunlight from penetrating into the stream and reduce the photosynthetic reaction. Some dyes are even toxic or carcinogenic. The release of dyes introduces the potential danger of bioaccumulation that eventually affects man by transport through the food chain [12, 39, 41].

Therefore, various physical, chemical and biological pre treatment, main treatment and post treatment techniques have been conducted to remove colour from dye containing wastewaters. These include membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic mineralisation, electrolysis, advanced oxidation (chlorination, bleaching, ozonation, Fenton oxidation and photocatalytic oxidation) and chemical reduction. Biological techniques include bacterial and fungal biosorption and biodegradation in aerobic, anaerobic, anoxic or combined anaerobic/aerobic treatment processes [40, 41, 61]. However, the use of one individual process may often not be sufficient to achieve complete decolourisation because each technique has its limitations. Hence, most of the dye removal strategies consist of a combination of different techniques.

Since this study is concerning the effect of electric field in improving the efficiency of adsorption and desorption in catalytic cycle processes, only the electrolysis and adsorption methods of removing dye are referred here.

Basically, electrolysis is a chemical change especially decomposition which is produced in an electrolyte by an electric current. Organic compounds like dyes react through a combination of electrochemical oxidation, electrochemical reduction, electrocoagulation and electroflotation reactions. In several studies, electrochemical methods have been successfully applied to achieve decolourisation of dye solutions and dye containing wastewaters. However, the process is expensive due to large energy requirements and the limited lifetime of the electrodes. Furthermore, foaming or uncontrolled formation of unwanted breakdown products may occur as radical reactions are involved [61].

On the other hand, adsorption techniques have been found to be useful means for removing organic compounds from water due to their high efficiency and ability to separate a wide range of chemical compounds like dyes [34, 39, 47, 61]. It offers the most economical and effective treatment method in terms of simplicity of design, ease of operation and insensitivity to toxic substances [58, 59]. Adsorption technique is influenced by many factors including dye and sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time [38]. Among all the adsorbent, activated carbon is most commonly used adsorbent for color removal since it is efficient in adsorbing a broad range of different types of adsorbates but its use is limited due to its high cost [40, 39]. Therefore, several studies have been done on the use of alternative materials which involve lower costs although it is less efficient. Those alternative materials are agricultural, forest, animal and several low-cost industrial by-products such as fly ash [40, 41, 59], Kapok hull activated carbon [42], bentonite [40], clay-wood sawdust mixture [43], peat, wood, tree barks, chitin, silica gel, bauxite and certain synthetic polymeric adsorbents [40]. Clay has been accepted as one of the most appropriate low cost sorbents. In addition, mixed sorption systems, such as the sorption of lead (II) on china clay and wollastonite, heterogeneous micture of alumina and clay to remove the color of dye and mixture of activated clay and activated carbon have also been investigated [58].

In this study, the effect of applied electric potential on the adsorption of methylene blue over electrically conducting surface containing titanium dioxide has been carried out.

2.8.4 Methylene Blue

Among the dyes, methylene blue is a thiazine (cationic) dye, which is most commonly used for coloring among all other dyes of its category [60]. Methylene blue is a heterocyclic aromatic chemical compoundas shown in Figure 2.11. There are three nitrogen atoms that could interact with water through H-bonds. However, the methyl groups linked to the two non-aromatic nitrogen atoms decrease the capability of such interactions due to the stabilization provided by its electron donating character and by stereo hindrance [62]. It appears as a solid, odorless, dark green powder at room temperature. Methylene blue appears as a blue solution when its dye powder is dissolved in water.

Methylene blue is an important basic dye widely used for printing calico, dyeing, printing cotton and tannin. In purified zinc-free form, it is used as an antiseptic and for other medicinal purposes like examine RNA or DNA under the microscope or in a gel. Methylene blue is also widely used as a redox indicator in analytical chemistry. Solutions of this substance are blue when in an oxidizing environment, but will turn colorless if exposed to a reducing agent [60].

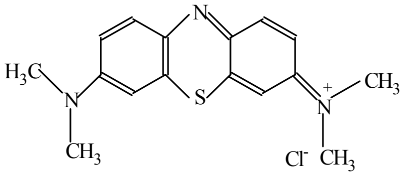


Figure 2.11: Structure of methylene blue

According to the MSDS of methylene blue, the dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. Methylene blue causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting,and diarrhea if it is swallowed. Finally, the dye also causes methemoglobinemia, cyanosis, convulsions, tachycardia and dyspnea when it is being inhaled.

A lot of research has been done on the removal of methylene blue from waters. Among these methods, adsorption is the most widely used method because of its initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances. A number of agricultural waste and by-products of cellulosic origin have been used as the absorbent to adsorb methylene blue. For instances, barley husks, sugarcane bagasse, wheat straw, wheat bran, corncobs, barley husks, tree ferns, wood chips, corn-cob shreds, fly ash and baggase [41, 59, 60].

In order to confirm the effect of the electric field to generate surface charge to induce the adsorption of organic substrate in the new designed catalytic system, the experiment on methylene blue adsorption was chosen.

2.9 Instrumental Analysis

X-ray diffractometer (XRD), Fourier Transform Infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscope (FESEM), Ultraviolet-Visible (UV-Vis) spectroscopy and Gas chromatograph (GC) are the methods which used for characterizing PPy/TiO_2 composite and the reaction samples. All these characterization methods help to identify the presence of functional groups, the actual structural formula and the percentage of the certain element or yield.

2.9.1 X-ray diffractometer (XRD)

The X-ray diffraction (XRD) measurements in this study were carried out by using a Bruker AXS D8 Automatic Powder Diffractometer. It is used to investigate the microstructure of crystalline materials of the titanium dioxide powders.

Figure 2.12 shows the principle of XRD. Firstly, an incident x-ray beam is sent to the surface of a crystal. However, the beam can penetrate only first few micrometers of a crystal; thus part of the beam will reflect on each one of the crystal lattice plane and this results in a large number of reflected beams will interfere. The large number of coherent interfering beams causes the destruction of interference in all the cases except when all the reflecting beams are in phase. The intensity of the reflected beam is measured for a continuous range of angles when the experiment is in the process. Different peaks of intensity corresponding to the different inter-planar distances present in the crystalline sample are observed.

The experiments are completely remote-controlled via a computer where the x-ray specimen chamber is separated from the outside by a shield. The XRD instrument automatically scans a given range of angles between the x-ray source, the sample and the detector. The resulting data is analyzed using the software provided.

The sample preparation involved is simple and the analysis is done with computer-controlled and automated. Moreover, the sample preparation and analysis involves a non-destructive technique whereby samples can be reanalyzed at a later date. However, XRD method is not an elemental analysis. The used of XRD is highly specific; the location of diffraction peaks requires both elemental and structural parameters to be "just right". This is true for both analytes and interferences. Substitution of one element for another in a given structure results in a different diffraction line pattern. Substitution of one structure for another likewise results in a different pattern.

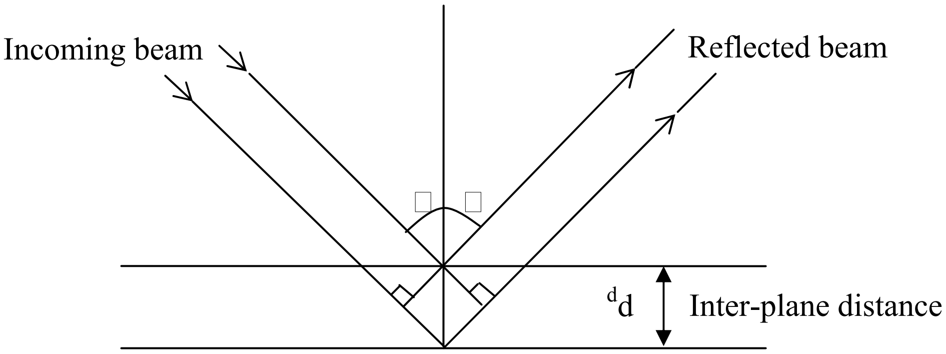


Figure 2.12: The principle of XRD

The X-ray technique is based on the Bragg equation:

$$n\lambda = 2d \sin \square \qquad (2.2)$$

Where:

n = order of diffracted beam

λ = wavelength of X-ray beam (in angstroms)

d = distance between diffracting planes (in angstroms)

θ = angle between incident X-ray and the diffracting planes (in degrees)

A disadvantage of using XRD is the high cost of instrumentation and maintenance. On the other hand, it is the requirement of a known particle size distribution and a sample weight compatible with a thin-layer deposition for sample analysis.

2.9.2 Fourier Transform Infrared (FTIR) Spectroscopy

Characterization of sample with FTIR spectroscopy is essential to reveals information on molecular vibrations that cause a change in the dipole moment of molecules based on the presence of functional groups in the molecule. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. Generally, inorganic compounds usually have much simpler spectra.

Infrared radiation is that part of the electromagnetic spectrum between the visible and microwave regions. When a compound absorbs infrared (IR) radiation, molecular bonds are promoted to higher-energy vibrational modes that consist of bond stretching or bending. Different types of bonds absorb infrared radiation of different wavelengths. The characteristic regions for common infrared stretching and bending vibrations are given in Figure 2.13.

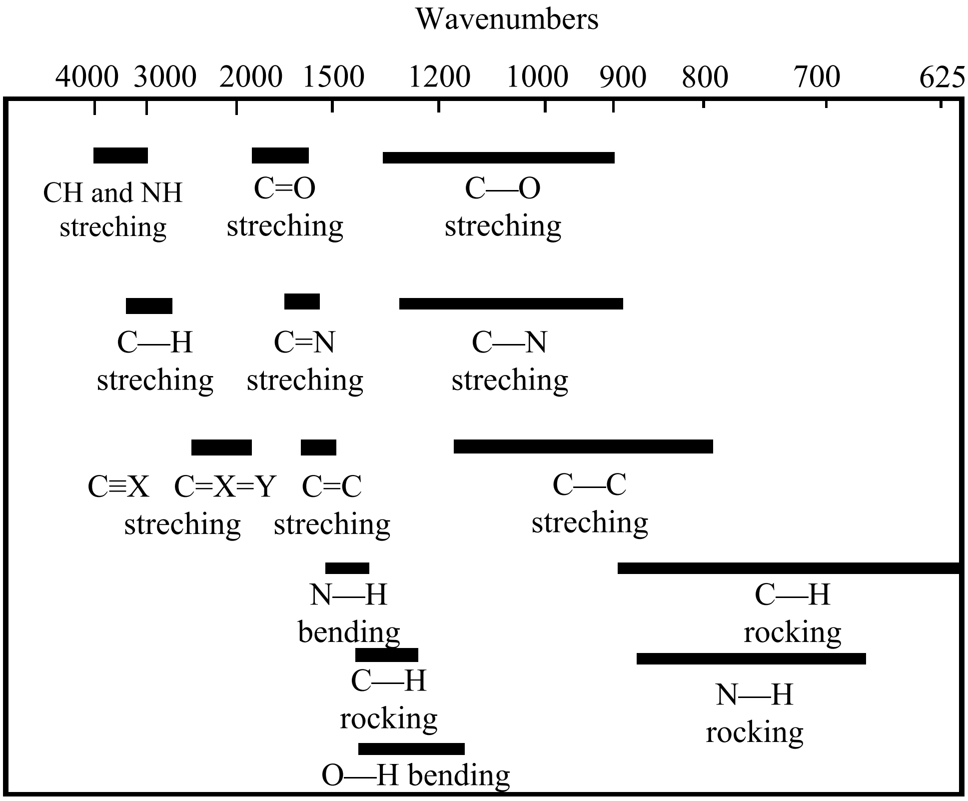


Figure 2.13: The characteristic regions for common infrared stretching and bending vibrations.

According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E_0) and the first excited state (E_1)]. The magnitude of the enthalpy is given by Equation 2.3.

$$\Delta E = E_1 - E_0 = h\,c\,/\,\lambda \tag{2.3}$$

IR absorption energies are very sensitive to molecule structural changes that include ligand coordination to a metal center. Between 4000 and 400 cm^{-1}, molecular vibrations can be observed due to organic ligands. However, metal-ligand bonds can only be observed between 400 and 50 cm^{-1} using Far-IR spectroscopy. Therefore, the absorptions for metal-ligand bonds are not included in this study.

Perkin Elmer Spectrum One FTIR spectrometerwas used to record infrared spectrums of samples. Samples were prepared using potassium bromide (KBr) pellet technique with the ratio of potassium bromide towards samples was 100:1. In general, an infrared spectrometer consists of a glowing filament that generates infrared radiation (heat), which is passed through the sample to be studied. Then, a detector measures the amount of radiation at various wavelengths that is transmitted by the sample. Lastly, this information is recorded on a chart where the percent of the incident light that is transmitted through the sample (% transmission) is plotted against wavelength in microns (um) or the frequency (cm^{-1}).

2.9.3 Field Emission Scanning Electron Microscope (FESEM)

Field Emission Scanning Electron Microscope (FESEM) is used to visualize very small topographic details on the surface or entire or fractioned objects that may be as small as 1 nanometer. The FESEM has been employed to study cell organelles and DNA material, synthetical polymeres, and coatings on microchips.

As shown in Figure 2.14, electrons are liberated from a field emission source and accelerated in a high electrical field gradient under vacuum. These electrons are called primary electrons. Within the high vacuum column, the primary electrons are focussed and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result, the secondary electrons are dislocated from each spot on the object. Then, a detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor. Actually, the composition of the sample has an effect on the number of deflected electrons and the position of each point in the sample relative to the detector is of great influence on the strength of the signal. The smaller the angle of incidence of the electron beam is with respect to the sample surface. On the other hand, the higher a certain point is in the sample, the more secondary electrons are able to reach the detector and the lighter this dot will appear in the final image following electronic signal amplification and digitalization.

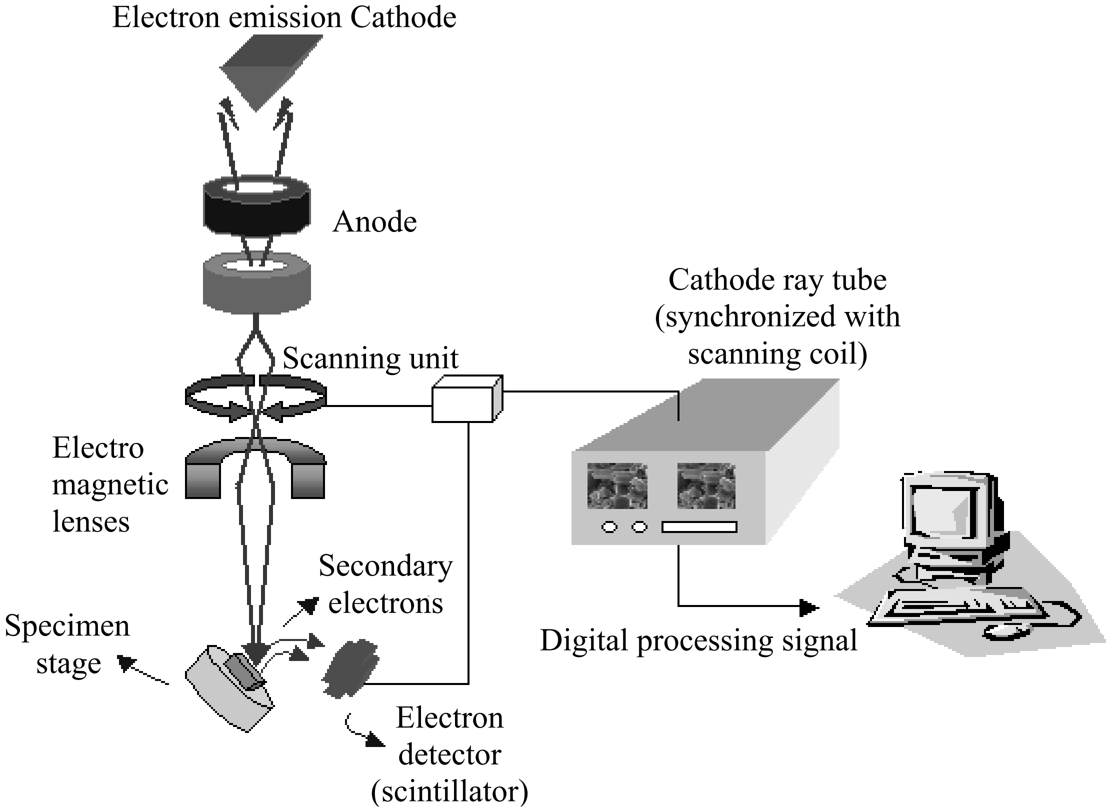


Figure 2.14: Field emission scanning electron microscope (FESEM) principle

FESEM produces clearer, less electrostatically distorted images with spatial resolution down to 1 1/2 nm which is three to six times better than conventional SEM. Each of the signals detected gets specific information about topography, crystallography, surface characteristics, specimen composition and other properties. In FESEM, smaller area contamination spots can be examined at electron accelerating voltages compatible with Energy Dispersive X-ray Spectroscopy.

2.9.4 Ultraviolet-Visible (UV-Vis) spectroscopy

The ultraviolet (UV) region scanned is normally ranged from 200 to 400 nm, and the visible portion is from 400 to 800 nm. Molecular moieties that favored to absorb light in the 200 to 800 nm region are π-electron functions and hetero atoms having non-bonding valence-shell electron pairs. In terms of the colour of the light absorbed, greater energy corresponds to shorter wavelengths [64].

The wavelength of maximum absorbance is a characteristic value, designated as λ_{max}. The absorbance of a sample at particular λ is gives by Beer's Law as shown in Equation 2.4 where ε is a constant of proportionality, called absorbtivity. Absorbance, A, is directly proportional to the length of light path through the cuvette in cm, b, and the sample concentration in moles/liter, c, of the absorbing species. For strongly absorbing compounds, molar absoptivities may be very large ($\varepsilon > 10{,}000$) and very small ($\varepsilon = 10$ to 100) if absorption is weak. The magnitude of ε reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore. Chromophores refer to light absorbing groups [65].

$$A = \varepsilon bc \tag{2.4}$$

As shown in Figure 2.15, a beam of light from a visible and/or UV light source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic beam with single wavelength in turn is split into two equal intensity beams by a half-mirrored device. The sample beam passes through a small transparent container which is a sample cuvette that contains a solution of the compound being studied in a transparent solvent. The other reference beam passes through an identical reference cuvette which only contains the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described.

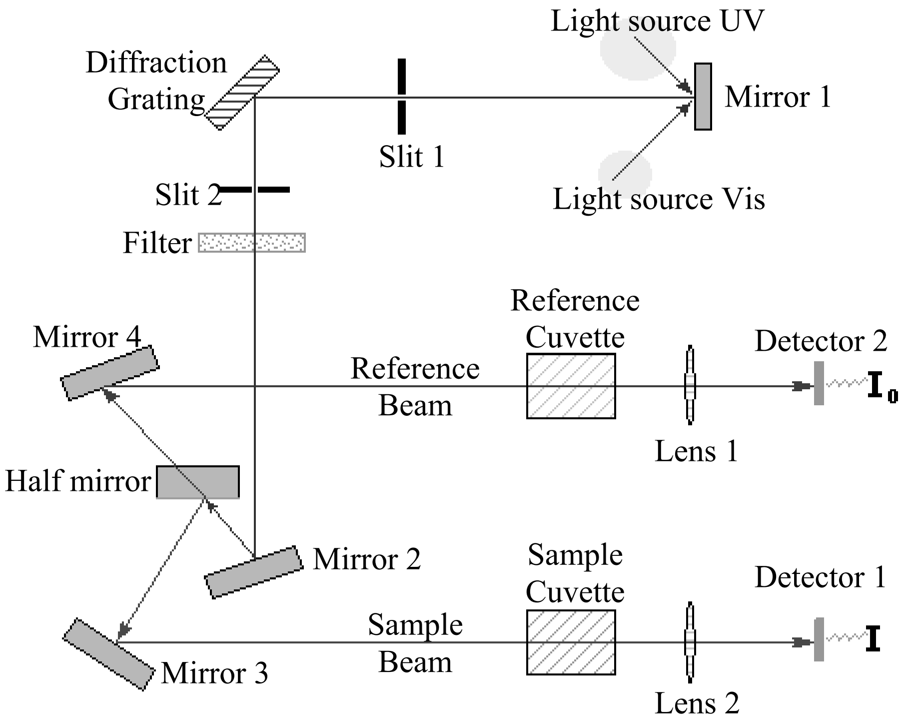


Figure 2.15: The principle of Ultraviolet-Visible (UV-Vis) spectroscopy.

If the sample compound does not absorb light of of a given wavelength, $I = I_0$. On the other hand, I is less than I_0 when the sample compound absorbs light and this difference may be plotted on a graph versus wavelength. Absorption may be presented as transmittance, T, or absorbance, A, where $T = I/I_0$ and $A = \log I_0/I$, respectively. $T = 1.0$ and $A = 0$ when no absorption has occurred. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λ_{max}. Dilute solution is used to examine absorbing compounds so that significant light energy is received by the detector. Therefore, the completely transparent (non-absorbing) solvents are used like water, ethanol, hexane and cyclohexane instead of using solvents having double or triple bonds, or heavy atoms.

The UV spectrophotometer used in this experiment is UV-160PC by SHIMADZU Company and the concentration of methylene blue over time was measured at maximum wavelength 664.20 nm in this study.

2.9.5 Gas Chromatograph (GC)

In this study, An Agilent Technologies gas chromatograph was used to identify the reaction product from the oxidation of benzhydrol. It was equipped with a flame ionization detector (FID) and a high resolution Gas chromatograph column (Agilent 19091N-133:260$_o$C, 30m x 250μm x 0.25 μm) and with helium (He) as the carrier gas.

Gas chromatography (GC) is a technique used to analyze, identify and quantitate individual components in a mixture. This instrument allows mixtures to be separated and the amount of each component present to be determined even to a few microliters samples can be analyzed.

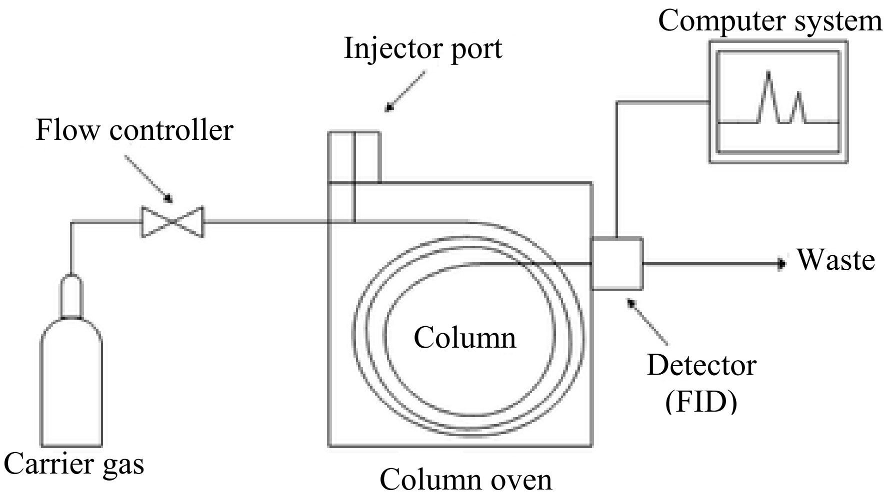


Figure 2.16: The basic components of a gas chromatograph

Figure 2.16 shows the basic components of a gas chromatograph. The injection port introduced the sample via a syringe whereby the samples that need to be analyzed in a gas chromatograph must be vaporized easily. Once the sample is vaporized, it is carried by a carrier gas which is a nonreactive gas such as helium through a long tube called a column containing a porous material whereby the oven regulates the temperature of the column. The porous material plays a role as a stationary phase where analytes are sorbed onto the thin layer of stationary phase. On the other hand, the gas cylinder supply high purity carrier gas which is used as the mobile phase which carries the sample through the chromatographic system and the flow control valve controls the carrier gas flow [68, 69].

The sample is separated to its own smaller components in GC because not all the components of the sample travel through the column at the same rate. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. The sample components are selectively retained by the stationary phase depending on their affinity for the stationary phase. This affinity is measured by a distribution coefficient, K, which relates the ratio of solute in the stationary and mobile phase as shown in Equation 2.5 [68]. As a result, analyte separated into discrete bands within the column.

$$K= [A]_S/[A]_M \tag{2.5}$$

K = distribution coefficient
A = concentration of solute
S = stationary phase
M = mobile phase

Then, the carrier gas continues to move analytes along the column until they reach the detector. As each of the components pass over the detector, the detector sends a signal by generating a voltage to a data system like computer systems which collects the signal and generates a chromatogram. A chromatogram is a plot of time versus the output signal generated from the detector as individual sample components elute from the column.

In GC, the time that a substance takes to pass through the instrument from injection port to detector is called retention time, t_r. The retention time, t_r, is measured from the injection point to the peak height as shown in Figure 2.17. The peak height is the highest point of the peak and is the only reproducible point on the peak. The correct peak for related component is identified by referring the t_r of the individual standards or by using reproducible conditions. These methods are practical unless there are two peaks with exactly the same retention time under the analysis conditions.

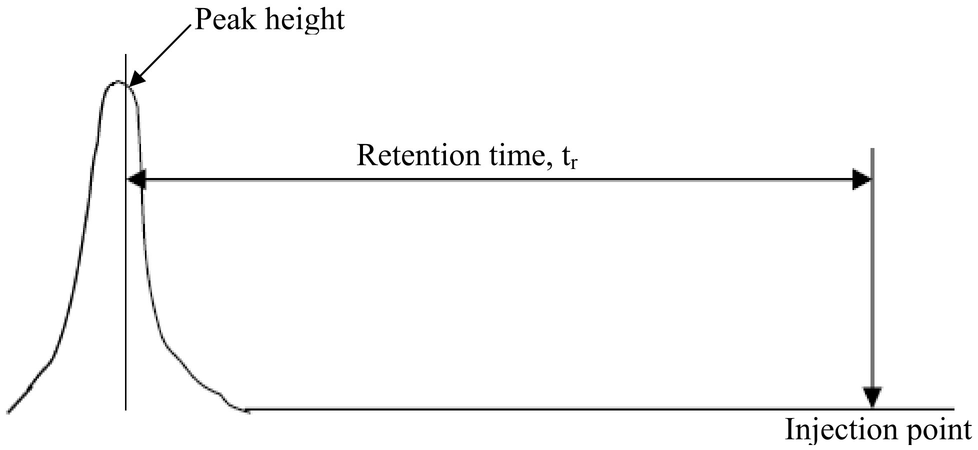


Figure 2.17: Figure used to define the retention time, t_r.

The amount composition of each component in the sample is determined by referring the chromatogram where the composition of each component is directly related to the area of each peak of that substance in the chromatogram. However, the proportionality constant is different for each substance and detector.

Flame ionization detector (FID) is the most widely used GC detector. Moreover, FID is an ionization detectors invented specially for GC. The column effluent is burned in a small oxy-hydrogen flame producing some ions in the process. Then, these ions are collected and form a small current that becomes the signal. The small current (10^{-14} A) arises from the impurities in the hydrogen and air supplies when there is no sample is being burned. Hence, FID is a specific property-type detector with characteristic high sensitivity. FID responds to all organic compounds that burn in the oxy-hydrogen flame where he signal is approximately proportional to the carbon content and giving rise to the so-called *equal per carbon* rule. However, this constant response factor decreases when hetero-atoms like oxygen or nitrogen are present. The advantages of using FID are good sensitivity, large linearity, simplicity, ruggedness and adaptability to all sizes of columns [69].

CHAPTER III

METHODOLOGY

The overall methodology of this study is showed in flowchart in Figure 3.1.

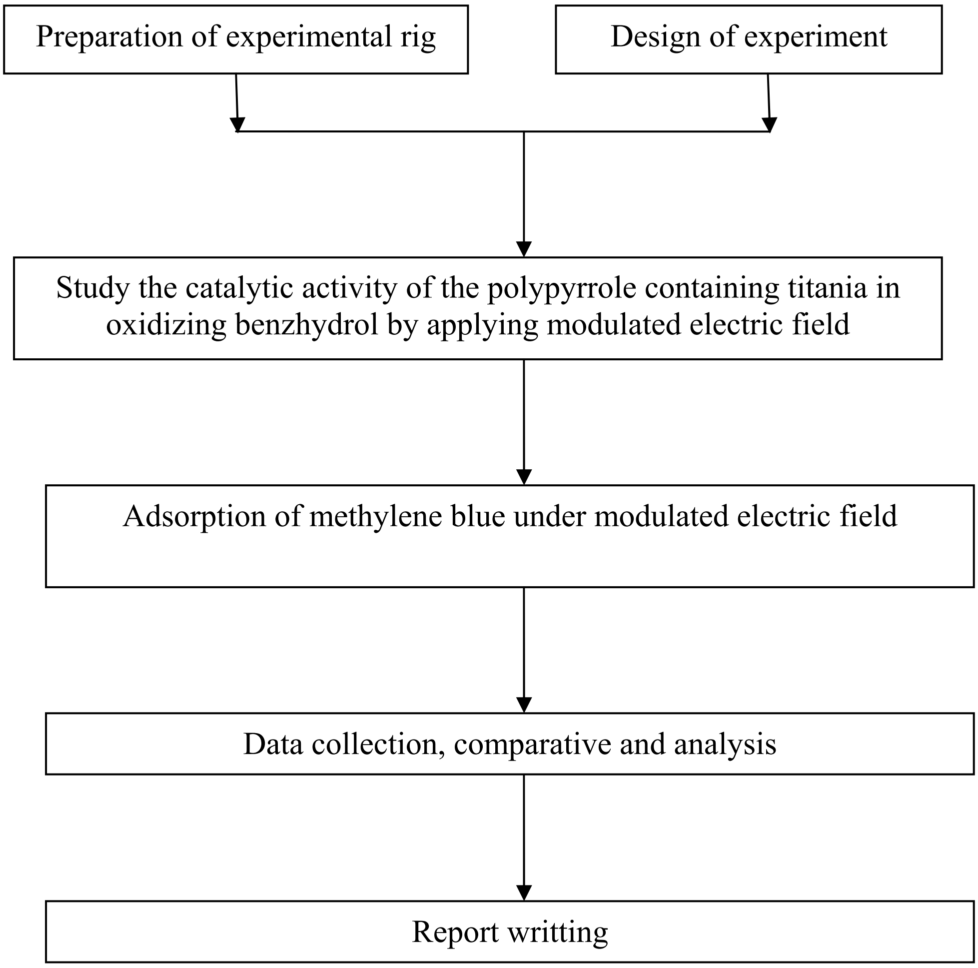


Figure 3.1: Methodology of this study in flow chart.

3.1 Chemicals and Apparatus

3.1.1 Chemicals

All reagents used were of analytical grade (Analar). Double distilled deionized water of nanopure type and bronze foil (10mm x 100mm x 0.1mm) was used in this study. Chemicals used for preparation of polypyrrole intergrated with titania in the new design catalytic system were polypyrrole doped (supplied by Aldrich) and titanium dioxide (supplied by Merck) powder which were used as obtained. In addition, carbon conductive grease supplied by MG Chemicals was used to stick polypyrrole doped and titanium dioxide powder on the bronze foil and at the same time to conduct electricity.

To examine the activity and effectiveness of the new design catalytic system, the oxidation of benzhydrol (99%, supplied by Aldrich) by using H_2O_2 (35%, supplied by Scharlau) was used as the probe reaction. Diethyl ether was supplied by Sigma-Aldrich and it was used to extract the product derived from the oxidation reaction. To assess the extent of the activity and effectiveness of the new design catalytic system, the process of adsorption of dye under the presence of electric field was conducted where methylene blue (supplied by Fischer Chemical) was used as absorbate.

3.1.2 Apparatus

The chemicals were weighed by using electronic analytical balance. Volumetric flasks (10mL and 100 mL) were used to prepare the desired solutions. Apparatus used to measure and fill the chemicals were beakers (25 mL, 50 mL and 100 mL), dropper, disposable transfer pipettes (3.5 mL), adjustable-volume pipettors (200 μL), Serological pipette (5mL) and pipette filler. Other apparatus was thermometer (100°C), retort stand, stirring rod, hot plate and magnetic stirrer. Separatory funnel (100mL) was used to separate the organic solvent from aqueous. Syringe (10 mL) was used to suck organic solvent into vials (12 x 32 mm) through syringe filter (PTFE 0.45μm). A low-volume syringe with needle (10μL) was used to suck and inject the organic solvent into the gas chromatography. All glasswares were washed and soaked with detergent for one day to get rid of all contaminates on apparatus. After that, the apparatus were rinsed with distilled water and dried in the drying oven. Apart from that, direct current voltage-stabilized power source (supplied by Dazheng direct current power supply) was used in supplying current in the new design catalytic system. A True-rms Multimeter (models 175, 177, 179 supplied by Fluke) was used to measure the current and voltage flow in the catalytic system.

3.2 Chemical preparation

3.2.1 Preparation of Polypyrrole Loaded with Titania in various Proportions

In this research, polypyrrole doped powder and titanium dioxide powder have been used as electrically conducting materials and catalytic active site, respectively. The titanium dioxide powder was incorporated onto polypyrrole doped powder and the composite is then denoted PPy/TiO_2. Eleven series of PPy/TiO_2 in various proportions as shown in Figure 3.2 were prepared to check the optimization of the new catalytic system based on the activity of the polypyrrole and the titanium dioxide under the present of the electric field.

Figure 3.2: Eleven series of the PPy/TiO_2 composite with the weight (g) ratio of

PPy/TiO_2 composite at: (i) 1.0:0; (ii) 0.9:0.1; (iii) 0.8:0.2; (iv) 0.7:0.3; (v) 0.6:0.4; (vi) 0.5:0.5; (vii) 0.4:0.6; (viii) 0.3:0.7; (ix) 0.2:0.8; (x) 0.1:0.9; and (xi) 0:1.0.

The PPy/TiO_2 composite is prepared by just mixing a specified amount of polypyrrole doped powder and a specified amount of titanium dioxide powder physically. This is an easy and direct method of preparing the PPy/TiO_2 composite. Table 3.1 show the composition of titanium dioxide in polypyrrole doped powder varied in the range of 0.0 to 1.0 g which keeps the weight (g) ratio of PPy/TiO_2 at 1:0 to 0:1.

Table 3.1: Polypyrrole loaded with titanium dioxide in various proportions.

Series	Weight (g)		Percentage(%)	
	Polypyrrole	**Titanium Dioxide**	**Polypyrrole**	**Titanium Dioxide**
1	0.00	1.00	0	100
2	0.10	0.90	10	90
3	0.20	0.80	20	80
4	0.30	0.70	30	70
5	0.40	0.60	40	60
6	0.50	0.50	50	50
7	0.60	0.40	60	40
8	0.70	0.30	70	30
9	0.80	0.20	80	20
10	0.90	0.10	90	10
11	1.00	0.00	100	0

3.2.2 The Preparation of Dye Solutions

For this study, methylene blue was used as model compound to test the performance of adsorption system under applied electric potential. In preparing the standard solutions used for calibration, 10 ppm stock solution of methylene blue was prepared by dissolving 1 mg methylene blue powder in 100 cm^3 double distilled water by using a 100 cm^3 volumetric flask. This stock solution was diluted to five standard solutions for calibration purpose. It is done by diluting the stock solution into 5 volumetric flask of 100 cm^3 to prepare five standard solutions of concentration 0.5 ppm, 1.0 ppm, 1.5 ppm, 2.0 ppm and 2.5 ppm. The concentration of these standard methylene blue solutions were measured using UV using Perkin Elmer UV/Vis/Nir spectrophotometer Lambda 900 and 10mm UV/Vis spectroscopy cells (LID, NIR-Quartz) at ambient condition in the range of 550 nm to 700 nm. The absorbance of standard solutions were then recorded and transformed into calibration graph. For experiment purpose, methylene blue in aqueous solutions with concentration 2.0 ppm was used as the initial concentration.

3.3 Experimental Setup for this New Design Catalytic System

The new designed heterogeneous catalytic system consists of 3 parts, which is the medium for catalytic processes to occur, catalyst and direct current supply. In other words, an open circuit system was implemented which incorporated a direct current generator and PPy/TiO_2 composite to study the effect of applied electrical potential towards adsorption capability of the catalytic system.

In order to establish the new design catalytic system, PPy/TiO_2 composite has been immobilized onto bronze foil as a layer of coating. Besides, the bronze foil also has been used to conduct electric to the PPy/TiO_2 composite while it is immersed in an aqueous solution in the catalytic system. The PPy/TiO_2 composite was connected to the DC power supply using wires that were attached to the bronze foil whereby the electrical wires were joined with the bronze foil using soldering method. This immobilization method of preparing the model catalyst coating was appeared as a convenient and suitable technique in term of practical application.

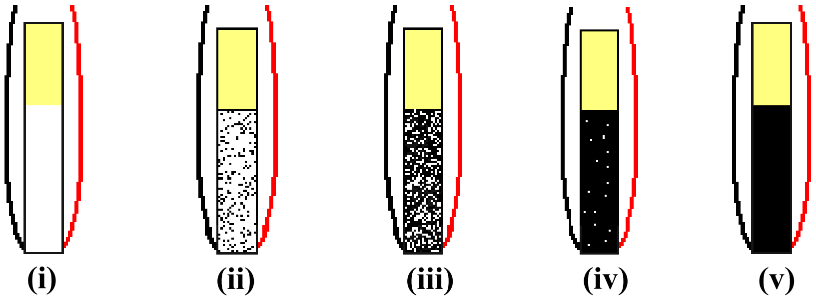


Figure 3.3: Five examples of bronze foils of attached PPy/TiO_2 composite with the weight (g) ratio at: (i) 0:1.0; (ii) 0.1:0.9; (iii) 0.5:0.5; (iv) 0.9:0.1; and (v) 1.0:0

Firstly, electrical wires were joined with the bronze foil using soldering method. Then, the moderate yellowish bronze foil with electrical wires joined at its end was weighed and followed by applying a thin layer of carbon grease on its surface for 1 cm x 5 cm area in order to hold the PPy/TiO_2 composite while still allowing electric to conduct through it. The bronze foil with a layer of carbon grease was then being weighed. Finally, it was dipped into a glass tube that filled with the specified PPy/TiO_2 composite in order to attach the PPy/TiO_2 composite on the surface of the bronze foil through the layer of carbon grease. Figure 3.3 shows five of the various proportions of PPy/TiO_2 composite which have been immobilized onto the bronze foil.

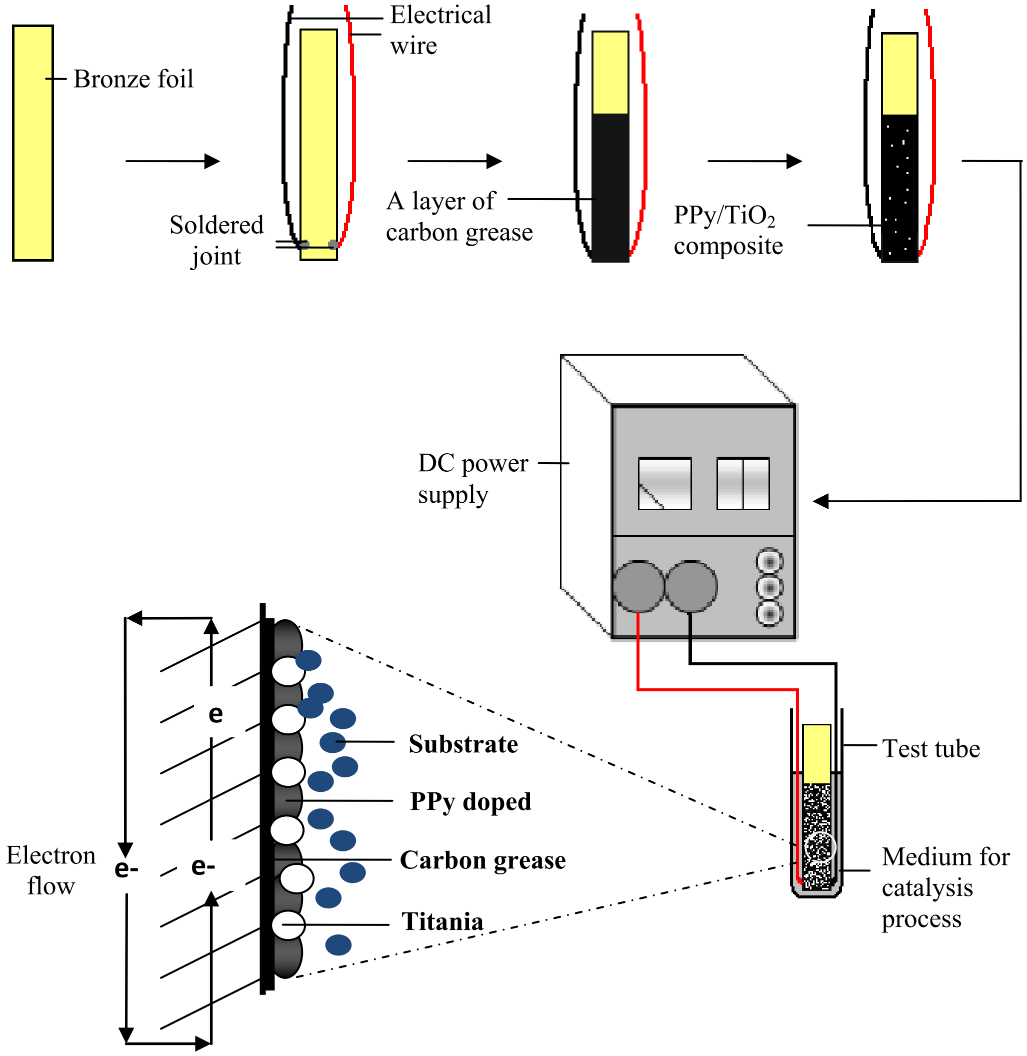


Figure 3.4: Diagram of experimental setup for this new design catalytic system

The resulting bronze foil of attached PPy/TiO_2 composite was again being weighed and ready to be used in the catalytic system. As shown in Figure 3.4, the bronze foil is submerged into a mediumin a test tube, which is apparently responsible for the adsorption and catalytic processes. A direct current electric field is discharge in proximity to the PPy/TiO_2 composite through the electrical wires which are joined at the end of the bronze foil through soldering paste. In all the experiments, 5.0 A and 2.0 V of electric current was supplied to the catalytic system by using a direct current voltage-stabilized power source while the current and voltage flow in the catalytic system were measured using a True-rms Multimeter. The purpose of the experimental setup for this new design catalytic system as shown in Figure 3.4 is to provide intimate contact of the reactant and substrate through the enhancemenet of electric field.

3.4 The Study of Catalytic Activity of the Polypyrrole containing Titania as Integrated Catalytic System by applying Modulated Electric Field

As mentioned in the previous section, the idea of this study is to improve the activities of the heterogeneous catalysts in the presence of external electric fields. Therefore, two types of chemical reactions were studied to check the effect of an electric field on regulating the adsorption capacity of polypyrrole and the reactivity of titanium dioxide in the new catalytic system; the first chosen chemical reaction was oxidation of benzhydrol by using aqueous hydrogen peroxide, while the second chosen chemical reaction was photocatalysis of methylene blue. Indeed, the dye adsorption experiments are done as a further study about the new catalytic system in order to confirm and reassure the effect of the electric field in the catalytic system. The chosen chemical reactions must be water-based reactions. In other words, the medium involved in the chemical reaction must be organic solvent-free because the use of organic solvents will dissolve the carbon grease layer that hold the PPy/TiO_2 composite and keep a good contact between PPy/TiO_2 composite and electric fields.

3.4.1 Oxidation of Benzhydrol

The oxidation of benzhydrol which synthesize benzophenone by reaction with aqueous hydrogen peroxide was chosen as a model reaction to examine the effectiveness and impact of the activity of the catalysts system. Figure 3.5 shows the conversion of benzhydrol to benzophenone by using hydrogen peroxide.

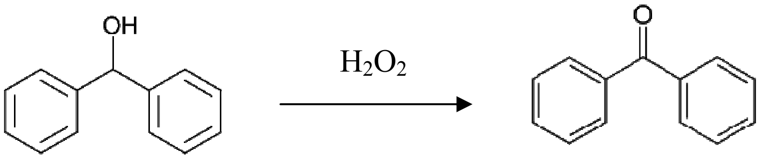


Figure 3.5: Oxidation of Benzhydrol to synthesis Benzophenone

The oxidation of benzhydrol was carried out firstly by dissolving 2 mmol of benzhydrol in 10 mL warm water of 70°C in a test tube. The temperature of the solution was maintained between 70-75°C by heating it on a hot plate and stirred it with magnetic stirrer. Then, 10 mmol of hydrogen peroxide was added. The resulting solution was used as reactant for the synthesis of the benzophenone.

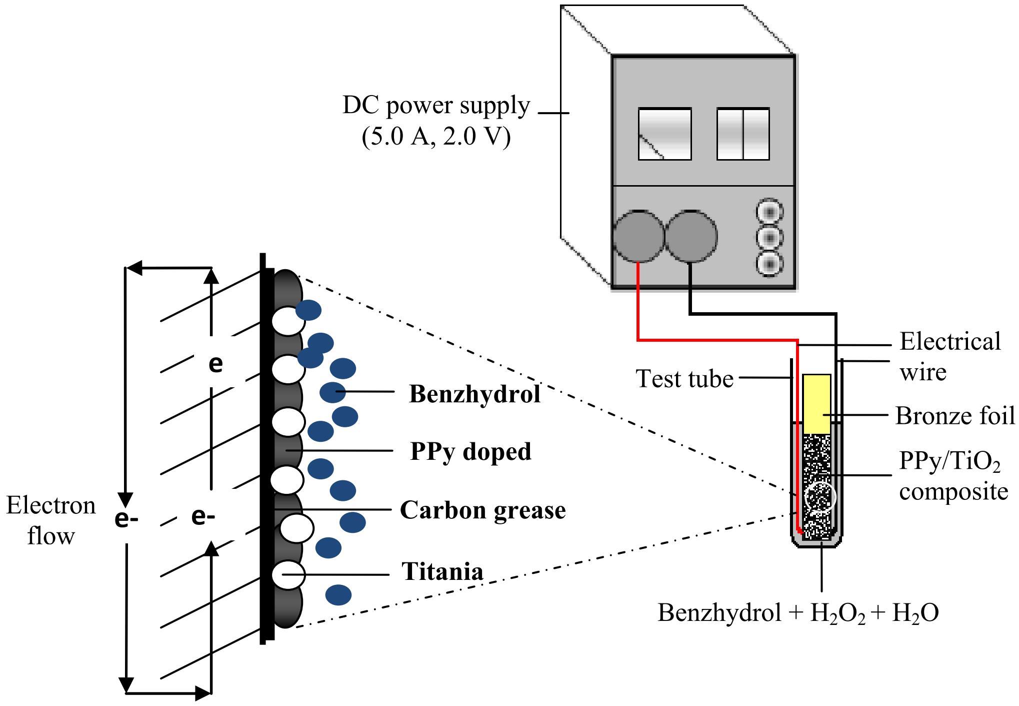


Figure 3.6: Schematic diagram of the basic experimental set-up used in oxidizing benzhydrol to benzophenone reaction.

Then, the bronze foil of attached PPy/TiO_2 composite submerged into the reacting mixture to start the oxidation process under the influence of external electric field. The temperature of this system was maintained between 70-85 °C and the reaction time was set for the period of 20 minutes at room temperature. For this experiment, the electric current was fixed at 5.0 A and 2.0 V and it was supplied to the catalytic system by using a direct current voltage-stabilized power source. The current and voltage flow in the catalytic system were measured using a True-rms Multimeter on and on to make sure the consistency of the current and voltage flow in the catalytic system. The basic experimental set-up used in this study is presented graphically in Figure 3.6.

After 20 minutes, the resulting solution was removed from the catalytic system and was cooled slightly for 5 minutes at room temperature. Then, the solution was transferred into a separatory funnel and extract with 3ml of diethyl ether. Finally, a portion of the diethyl ether solution was withdrawn and subjected to an Agilent technologies gas chromatograph equipped with a high resolution gas chromatograph column (Agilent 19091N-133:260$_o$C, 30m x 250μm x 0.25 μm) and a flame ionization detector, using He as the carrier gas. It was done so to verify the concentration of benzophenone which is the resulting product. This attempt was done for PPy/TiO_2 composite in various proportions which are listed in Table 3.2 with purpose of investigating the optimization of the new catalytic system based on the activity of the polypyrrole and the titanium dioxide under the present of the external electric field.

The oxidation of benzhydrol was also carried out by using hydrogen peroxide and PPy/TiO_2 composite in various proportions for 20 minutes, but with no external electric field in order to distinguish the electric field effect of this new designed catalytic system. Further, the oxidation of benzhydrol was carried out under the presence of the electric field by just applying carbon grease in the system without any PPy/TiO_2 composite to test the influence of PPy/TiO_2 composite. The oxidation reaction was also performed in the absence of catalyst system and only the reacting mixture was heated for 20 minutes. The resulting solution was used as reference to explain the effect of the catalytic system on converting the benzhydrol to benzophenone process. Eventually, the concentration of the resulting benzophenone in all the conditions was observed and compared to evaluate the effectiveness of the new catalytic system in oxidizing benzhydrol.

3.4.2 Adsorption of Dyes Process

The using of PPy/TiO_2 composite for dye adsorption under the influences of electric fields was conducted as an experiment to reaffirm the effectiveness of the new catalytic system toward oxidation of benzhydrol under the influences of electric field. Methylene blue was chose to be used as model compounds in checking the performance of photoreducing under applied electric potential.

In order to obtain more information about the work of the external electric fields on the chemisorption and catalytic properties of PPy/TiO_2 composite in methylene blue adsorption, three parameters that involved in this process were investigated: the temperature of the solution, the use of PPy/TiO_2 composite and the applied electric field.

For methylene blue adsorption, methylene blue in aqueous solutions with concentration 2.0 ppm was used as the initial concentration to start the experiment under modulated electric field. Experiments were done under two conditions with purpose of distinguishing between influences of the electric fields in methylene blue adsorption process. The two conditions are mentioned as below:

(i) under the influence of electric field
(ii) without the presence electrical field

For each experiment operation, 10 mL of methylene blue solution with the same initial concentration (2.0 ppm) was transferred into a test tube and it was stirred by a magnetic stirrer. Then, the bronze foil which attached with PPy/TiO_2 composite and connected to the direct current voltage-stabilized power source was immersed into the methylene blue solution to start the dye adsorption process under an applied electric potential of 5.0 A and 2.0 V at room temperature.

The activity of electric field toward the catalytic system is estimated by measuring the residual concentration of methylene blue in the solution. Therefore, the sampling interval for every experiment was 15 minutes for 75 minutes at room temperature (approximately 25 °C) where 3.0 ml of the mixture was withdrawn using a disposable transfer pipettes (3.5 mL) to measure the concentration of the methylene blue. The concentration of methylene blue over time was measured using Perkin Elmer UV/Vis/Nir spectrophotometer Lambda 900 and 10mm UV/Vis spectroscopy cells (LID, NIR-Quartz) at ambient condition in the range of 550–700 nm where its maximum wavelength is 665.02nm with double distilled water as blank.

The experimental set-up for methylene blue adsorption in this system are shown in Figure 3.7.

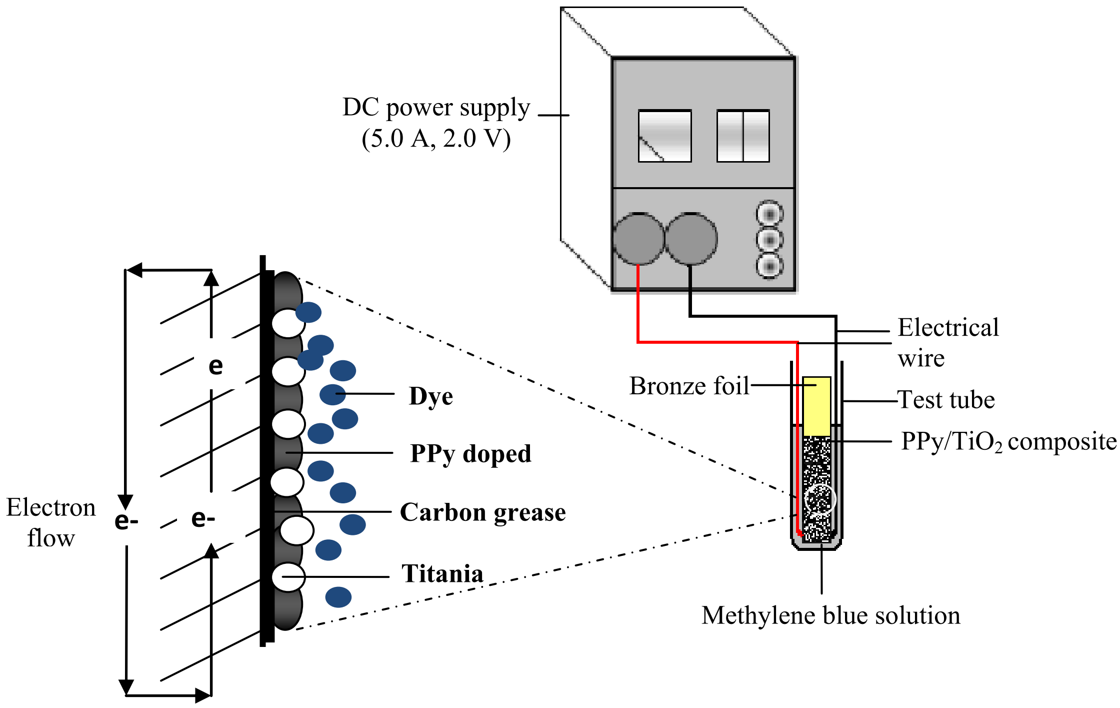


Figure 3.7: Experimental set-up used in the photocatalytic degradation of methylene blue under modulated electric field.

Since the catalytic system involved the application of current which caused the increasing of temperature of the dye solution throughout the whole process, the effect of increment of temperature toward the degradation of dye also studied. The test tube contained of 10 cm^3 of dye was placed in a beaker which filled with boiling water to increase the temperature of the dye solution. The catalytic system was not involved in this attempt and the sampling was done few times for every different temperature.

Further points of comparison have been conducted by running the experiment without photocatalyst. It was done at constant room temperature in the absence of catalyst system and the resulting solution was used as reference to explain the impact of the photocatalytic on this reaction.

In this experiment, only four PPy/TiO_2 composite were chose to be used because higher content of titanium dioxide lead to turbidity in dye solution that caused difficulty in measuring the concentration of methylene blue solution using UV–Vis spectroscopy. Hence, the chosen four PPy/TiO_2 composite were the composite with the weight (g) ratio of PPy/TiO_2 at 1:0, 0.9:0.1, 0.5:0.5 and 0.1:0.9.

3.5 Characterization

The PPy/TiO_2 composite and the reaction samples were characterized with a variety of spectroscopic techniques including Fourier Transform Infrared (FTIR) Spectroscopy, UV/Vis spectroscopy, Field Emission Scanning Electron Microscope (FESEM), X-ray diffractometer and Gas chromatograph (GC).

3.5.1 Fourier Transform Infrared (FTIR) spectroscopy

FTIR is used to characterize the eleven series of PPy/TiO_2 in various proportions. Characterization of sample is essential to give the information regarding to the structure and the presence of functional groups in a molecule of interest. It reveals information on molecular vibrations that cause a change in the dipole moment of molecules.

For characterization of samples, infrared spectrums were recorded using Perkin Elmer Spectrum One FTIR spectrometer. Samples were prepared using potassium bromide (KBr) pellet technique with the ratio of potassium bromide towards samples was 100:1. First, the mixture of sample and potassium bromide powder salt was mixed and grinded to a very fine powder by using mortar and pestle. Then, some the mixture was transferred into the steel die and compressed under the 7 tonnes of pressure for 3 minutes by using a manual hydraulic press to form a thin pellet film. Finally, the pellet sample was put in a sample holder and infrared spectrum was recorded at the wavelength of 450-4000 cm^{-1}.

3.5.2 Ultraviolet-Visible (UV-Vis) spectroscopy

The photocatalytic activity on methylene blue dye samples was evaluated by using the UV-Vis spectrometric to obtain the optical adsorption spectra where the photocatalytic activity is estimated by measuring the residual concentration of methylene blue in the solution. The residual concentration of methylene blue over time in the dye adsorption reaction under electric field was measured using Perkin Elmer UV/Vis/Nir spectrophotometer Lambda 900 and 10mm UV/Vis spectroscopy cells (LID, NIR-Quartz) at ambient condition in the range of 550–700 nm with double distilled water as blank. The maximum absorbance, λmax was determined from the recorded spectra.

Absorbance of standard solutions were recorded before the reaction samples and transformed into calibration graph. The concentration of each reaction samples was determined using the calibration graph of respective standard solutions and the concentration of methylene blue per gram adsorbent remove in 15 minutes interval was calculated and drawn into graph.

3.5.3 Field Emission Scanning Electron Microscope (FESEM)

The surface morphology or structure of the eleven series of PPy/TiO_2 composite particle in various proportions was studied by field emission scanning electron microscope (FESEM) and elemental analysis was performed with energy dispersive X-ray (EDX) spectroscopy. However, only six chosen PPy/TiO_2 composite (PPy/TiO_2 composite with the weight (g) ratio of PPy/TiO_2 at (0:1.0, 0.4:0.6, 0.5:0.5, 0.7:0.3, 0.9:0.1 and 100:0.1) were sent for determining its surface morphology.

Firstly, the PPy/TiO_2 composite was deposit at the specimen surface and later it was coated with a very thin layer of platinum which is a conductive material to provide a path to release the absorbed electrons in the specimen. This is done to clear away superfluous electrons and prevent those electrons that are not captured by the detector from hanging like a cloud masking around the sample. Then, a JEOL JSM-

6701F field emission scanning electron microscope operated at 20 kV (FESEM) was used for recording the images of the PPy/TiO_2 composite which a thin layer of gold had been deposited. Energy dispersive X-ray (EDX) attached to the JEOL JSM-6701F FESEM machine was used to carry out the surface morphologies for quantitative analysis as well as the elemental mapping.

3.5.4 X-ray diffractometer (XRD)

The X-ray diffractogram of the titanium dioxide powder was collected at room temperature by using a Bruker AXS D8 Automatic Powder Diffractometer with a Cu $K\alpha$ (λ= 1.5418 Å at 40 kV and 40 mA) radiation sources. The resulting X-ray diffractogram was then compared with the XRD spectra in the database to find out the form of the titanium dioxide which was used in this study.

3.5.5 Gas chromatograph (GC)

An Agilent technologies Gas chromatograph was used to identify the reaction product from the oxidation of benzhydrol. It was equipped with a flame ionization detector (FID) and a high resolution Gas chromatograph column (Agilent 19091N-133:260$_o$C, 30m x 250µm x 0.25 µm) and with helium (He) as the carrier gas. The samples of 0.2µl were injected to gas chromatography with 5 minutes as the hold time, with rate 10 ◦C min−1 until 220 ◦C and hold 5 min.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Oxidation of Benzhydrol with Aqueous Hydrogen Peroxide under Electric Field

The results of oxidizing benzhydrol to benzophenone under and without electrical field are presented in Table 4.1 and Table 4.2, respectively.

Table 4.1 : Oxidation of benzhydrol to benzophenone under the influence of electric field

Percentage of (%)		$[(C_6H_5)_2C{=}O]$	Weight of PPy/TiO_2	Weight of TiO_2
PPy	TiO_2	(µmol)	(mg)	(mg)
0	100	9.8736	42.8	42.8
10	90	16.1460	53.9	48.5
20	80	12.4175	38.1	30.5
30	70	11.7338	34.6	24.2
40	60	27.4346	24.4	14.6
50	50	31.6480	27.4	13.7
60	40	14.9932	19.0	7.6
70	30	43.3659	23.7	7.1
80	20	28.7861	21.0	4.2
90	10	30.8530	14.4	1.4
100	0	25.0020	7.5	0

Table 4.2 : Oxidation of benzhydrol to benzophenone without the presence of external electric field in the catalytic system

Percentage of (%)		$[(C_6H_5)_2C{=}O]$ (μmol)	Weight of PPy/TiO_2 (mg)	Weight of TiO_2 (mg)
PPy	TiO_2			
0	100	3.8958	29.2	29.2
10	90	3.7053	31.8	28.6
20	80	2.1240	28.1	22.5
30	70	4.3163	17.0	11.9
40	60	3.9030	18.7	11.2
50	50	5.2183	17.6	8.8
60	40	5.7358	13.0	5.2
70	30	5.5562	11.7	3.5
80	20	4.0611	9.6	1.9
90	10	6.2174	10.2	1.0
100	0	7.9605	9.7	0

Figure 4.1 shows the comparison of the effect of electric field toward the performance of this catalytic system in oxidizing benzhydrol to benzophenone. The catalyst system without electric field showed a low performance for benzophenone production, whereas it exhibits reasonably good performance for this reaction under electric field. The external electric field caused the yield of benzophenone to increase significantly in the ranges of 9–43 μmol which is higher than the yield of benzophenone under the condition that without the influence of electric field. The results of oxidizing benzhydrol without the presence of electric field show no significant effect by exhibiting the yield of benzophenone in the ranges of 2–8 μmol. The significant gap between the two curves presented in Figure 4.1 characterizes the effect of the electric field in the oxidation process. Hence, the presence of external electric field in the catalytic system plays significant roles in enhancement of the catalytic activity and adsorptive capacity in oxidizing benzhydrol.

According to the results obtained from the oxidation of benzhydrol in Figure 4.1, it was observed that the yield of benzophenone on the oxidation of benzhydrol using various composition of titanium dioxide under the influence of electric field gives a bell curve whereby the best performance appears to be the catalyst system containing 30% TiO_2. In other words, an increase in the amount of benzophenone was observed with an increasing amount of titanium dioxide until the amount of titanium dioxide reach 30% with the weight of 7.1 mg. Thus, the initial rates of reaction were found to be directly proportional to the mass of catalyst. This indicates a true heterogeneous catalytic regime. The increased yield of benzophenone at the beginning before it reach the maximum value can be attributed to the presence of more reactive sites on the PPy/TiO_2 composite which allow the oxidation of benzhydrol to occur to a larger extent. Titanium dioxide has both high crystallinity and high surface area that provides active sites for adsorption and for catalysis like oxidation to occur to a larger extent.

However, above a certain value of mass, the reaction rate levels off and becomes independent of mass. An optimum amount of TiO_2 was found equal to 30% TiO_2 on a fixed $5cm^2$ surface area in the catalytic system. These limits correspond to the maximum amount of TiO_2 in which all the particles are totally took part in the reaction by exposing all the surface of the catalyst. The yield of benzophenone decreased when the weight of titanium dioxide is more than 7.1 mg where the saturation of titanium dioxide is attained in the catalytic system. This is probably due to the increased of titanium dioxide particles on the catalytic system resulted a screening effect of excess particles occurs for higher quantities of titanium dioxide since the excess amount of titanium dioxide agglomerated and formed few layers which mask part of the surface. In addition, the increased of titanium dioxide particles on the catalytic system will reduce the electrical properties of the catalytic system since the electric field influences the adsorption and catalytic processes. Therefore, this optimum mass of catalyst has to be chosen in order to avoid excess of catalyst and to ensure a total adsorption of substrates.

Note that although the catalyst system containing 30% TiO_2 appears to be best when comparing different loadings, if we replot Figure 4.1 in terms of turnover number (TON) as shown in Figure 4.2, then 10% TiO_2 appears to be a better than the other TiO_2 loading, suggesting that amount of TiO_2 at 10% loading exhibited definite activity. This probably relates to the dispersibility of TiO_2 particles on the conducting surface of the catalyst system as shown in Figure. 4.3. EDX mapping of Ti (Figure 4.1b) shows that TiO_2 particles agglomerate into big particles when TiO_2 loading is 60%.

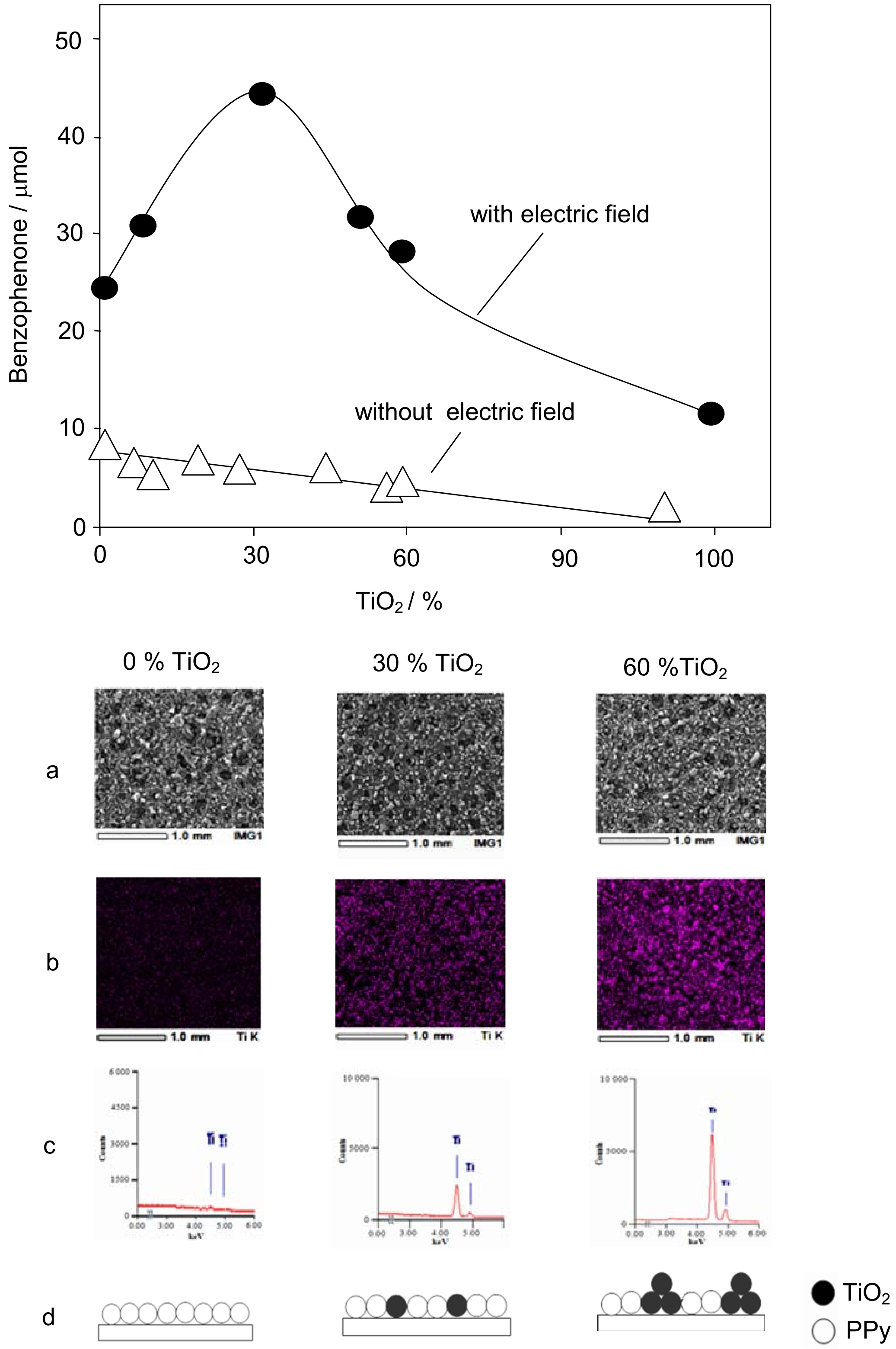


Fig. 4.1: The yield of benzophenone on the the oxidation of benzohydrol by aqueous hydrogen peroxide. All reactions were carried out at 70 °C for 20 min. The voltage and current of electric field measured during the reaction are 5 V and 2 A,

respectively. (a) The SEM photographs, (b) EDX mapping, (c) elemental Ti count image and (d) arrangement of TiO_2 on the surface of catalyst system. The violet points in the Fig. 2(b) denote Ti atoms.

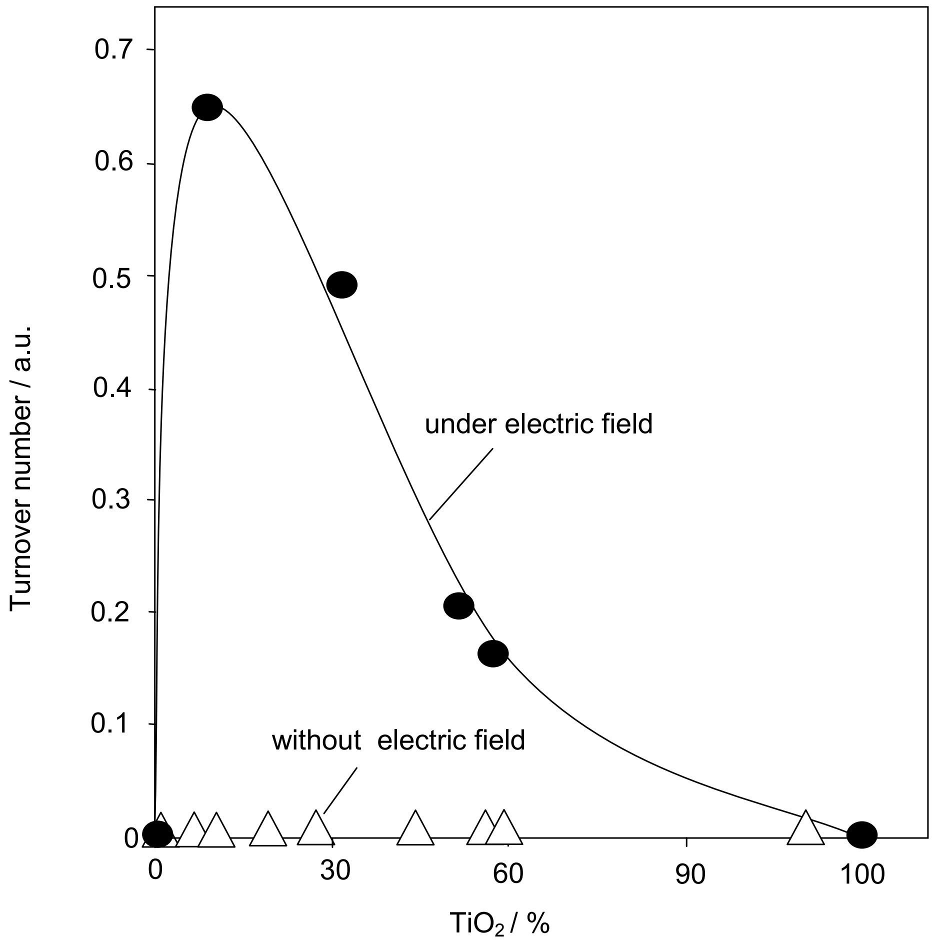


Fig. 4.2: The turnover number per Ti in the oxidation of benzohydrol by aqueous hydrogen peroxide. Reaction conditions are the same as given in Fig. 2.

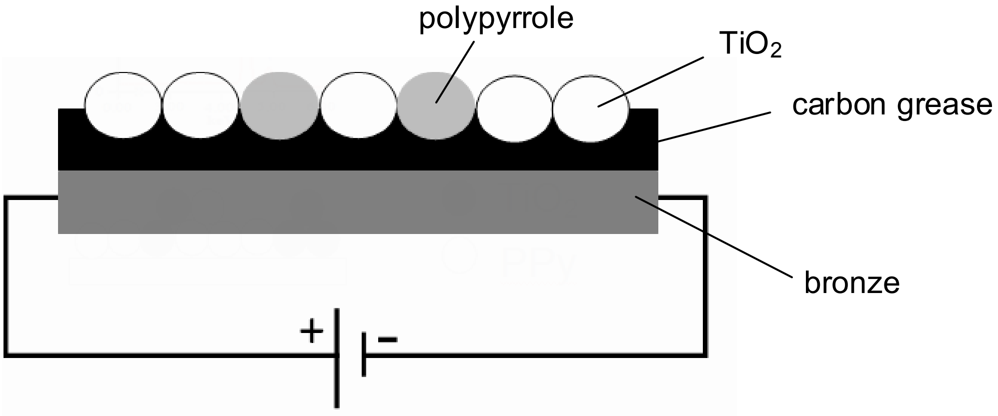
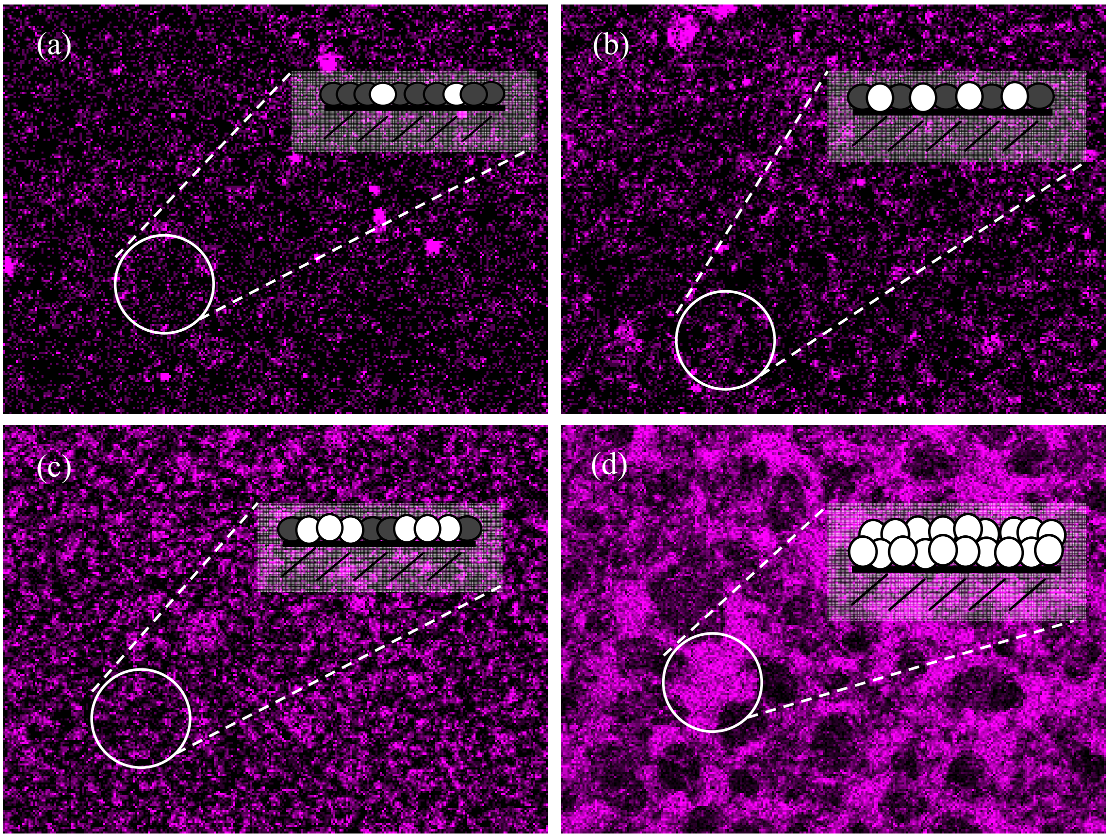


Fig. 4.3: The schematic representation of the catalyst system induced by electric field.

Figure 4.4 shows the surface morphology of 10%, 30% and 100% titanium dioxide when distributed on the polypyrrole doped powder. It is clear that titanium dioxide granules agglomerated into large particles and form more than one layer on the surface of polypyrole when the composition of titanium dioxide is higher and this condition deactivates the catalytic system.



● PPy ○ TiO_2

Figure 4.4 : The surface morphology of (a) 10%; (b) 30%; (c) 50% and (d) 100%
titanium dioxide when distributed on the polypyrrole doped powder.

The process of oxidizing benzhydrol to benzophenone by using hydrogen peroxide as oxidant but without attaching PPy/TiO_2 composite on the carbon grease layer was carried out for 20 minutes as well. In this attempt, 27.2µmol benzophenone was detected by GC. This amount of benzophenone is almost the same with the amount of benzophenone (25.0 µmol) derived from the same oxidation process by applying 100% polypyrrole particles on the surface of the carbon layer on the bronze foil under the presence of the electric field. In other words, polypyrrole functions like carbon grease in passing the electric charges. With or without the use of polypyrrole does not make a big difference because carbon grease which held the titanium dioxide can still conduct electric. However, polypyrrole was chosen to be used in this new designed catalytic system as a media to distribute the titanium dioxide particles as mentioned earlier.

Eventually, the oxidation reaction was performed in the absence of catalyst system and only the reacting mixture was heated. After 20 minutes, only 1.4µmol benzophenone was obtained. It is noted that the apparent rate of the oxidation of benzhydrol in the absence of catalyst system was much smaller than the oxidation of benzhydrol in the catalytic system.

As a conclusion, the catalytic system plays an importance role in providing an environment to improve the rate of the oxidation process and to increase the amount of benzophenone as well. Therefore, the ideal composition of titanium dioxide and polypyrrole at the surface is very important in pursuing high adsorption and catalytic activity for target reactions. However, the experimental procedures to demonstrate it seem difficult although the adsorption study of benzohydrol on the catalyst system is important to clarify the effect of electric field on catalytic activity. The only credible, tough complex, in the present study, we employed the feasible process of adsorption of methylene blue on the catalyst system as a model compound to evaluate the effect of electric field on the adsorption of organic substrates.

4.2 Adsorption of Dyes Process

The effect of the adsorption of the methylene blue on the surface of catalyst system under and without electric field is shown in Figure 4.5. Apparently, the electric field induced the adsorption of methylene blue on the catalyst system. Electric field gave a greater effect in absorbing the methylene blue solution where about 0.25 ppm more of methylene blue was absorbed in the catalytic system with the application of external electric field.

The amount of TiO_2 led to a considerable decrease of the adsorption of dye because the conducting surface was covered by non-conducting TiO_2 particles. Due to this reason, titanium dioxide did not play a role as a photocatalyst in degrading the color of methylene blue in this experiment. Since the electric current flow only in conducting region, a suggestion that can be made is that the dye molecules preferentially adsorb on PPy and carbon grease surfaces. Therefore, the degradation of methylene blue in this study is mainly an electric-field-induced adsorption process where the dye particles are absorbed on the surface of polypyrrole instead of titanium dioxide.

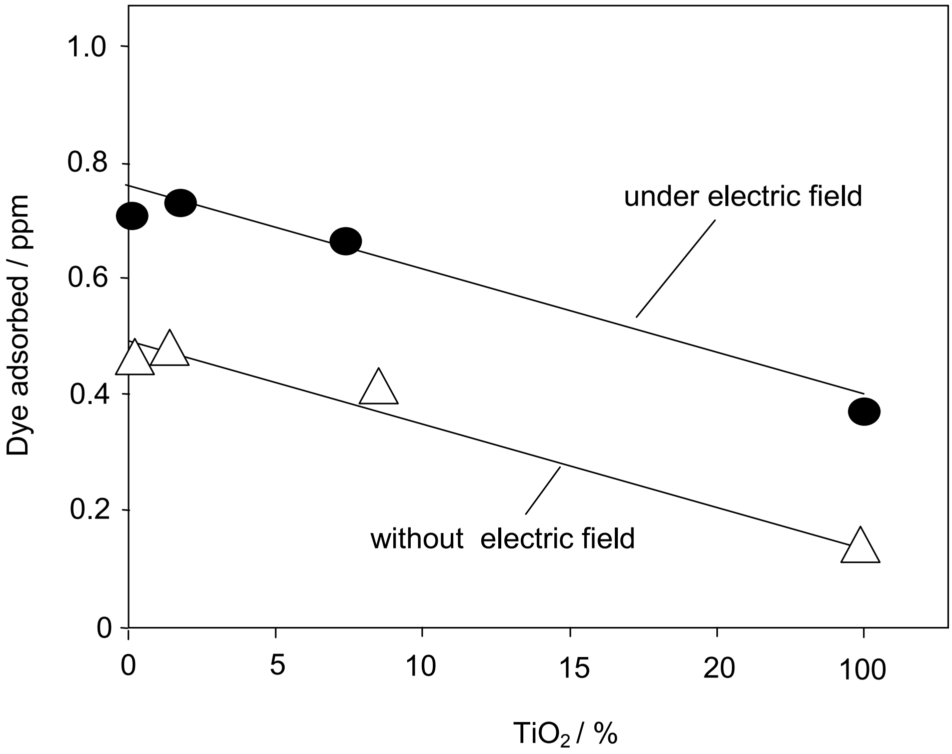


Fig. 4.5: Concentration of adsorbed methylene blue on the surface of catalyst system containing TiO_2.

Actually, the increasing amount of polypyrrole allows more charge carriers in response to enhance the adsorption of dye molecule. On the other hand, the high titanium dioxide concentrations impede the overall reaction since it is a insulator. Methylene blue appeared as cationic dye particles and it experienced attraction towards polypyrrole when an electric field is applied in the catalytic system. As shown in Figure 4.6, the cationic dyes started to move and consequently adsorbed to the surface of polypyrrole. As a consequence, the concentration of methylene blue in its aqueous solution decreased which caused by the simultaneous adsorption of methylene blue particles on the surface of polypyrrole.

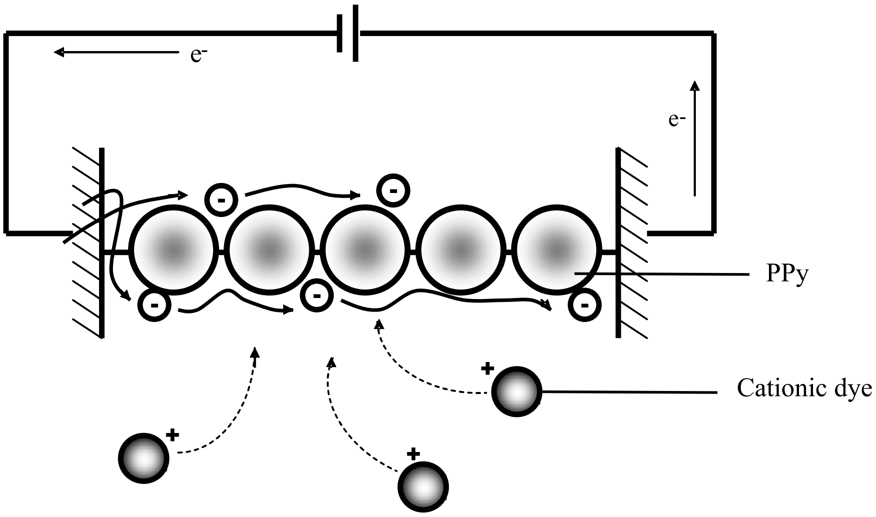


Figure 4.6: Model mechanism for the adsorption of cationic dye particles towards polypyrrole in an electric field induced system.

Table 4.3 : Adsorption of methylene Blue at different temperature

Temperature (^{o}C)	**Absorbance (A)**
23.5	0.28506
28.0	0.26372
39.0	0.27321
68.5	0.28534

The effect of the reaction temperature toward the adsorption of dye was also evaluated since the temperature of the dye solution increased during the adsorption process under the application of electric current in the catalytic system. Table 4.3 shows the absorbances of methylene blue solution at different temperature which was recorded at 665.02nm as well. As shown, there are no clear significant changes in the reading of the absorbance of methylene blue solution at different temperature. Hence, further increase in temperature give no significant effect on the degradation of methylene blue solution. These results also proved that the blue color of methylene blue that had faded was attributed to the adsorption of dye on the surface of the PPy/TiO_2 composite.

Further points of comparison have been conducted by running the experiment at constant room temperature in the absence of catalyst system. The sampling interval was 15 minutes for 75 minutes and the methylene blue solution exhibited absorbances of 0.2834 A, 0.2783 A, 0.2748 A, 0.2765 A, 0.2674 A and 0.2686 A at 665.02 nm over time. It can be observed a slower degradation of methylene blue when the catalytic system was not applied where degradation rate becomes quite limited, only 0.05 ppm dye disappeared after 75 minutes at room temperature. The little degradation of methylene blue still exists without the catalytic system, which is probably due to homogeneous decomposition of methylene blue by UV irradiation.

These results of the degradation test of methylene blue provide that the evidence of the adsorption activity depends on the specific surface area of polypyrrole which determine the amount of electric current on the generation of surface charge to induce the adsorption of dye molecules. As a conclusion, the electric field on the generation of surface charge to induce the adsorption of organic substrate has been confirmed by methylene blue adsorption experiments.

4.3 The Location of the most active Oxidation Site

The results of oxidation of benzhydrol and methylene blue suggested the occurrence of the synergistic effect of the electric field and titanium dioxide. The presence of polypyrrole was found to be essential in this catalytic system. The absence of polypyrrole in the oxidation of benzhydrol was found to give poor yield of the benzophenone. This is probably due to the electrically conducting properties of polypyrrole. Polypyrrole with alternating single double bond structures make it easily lose or gain an electron, or simply displace an electron along the polymer backbone. Therefore, the arrangement of both electronic and physical structure of polypyrrole is very important in controlling the conductivity of the catalytic system.

As described above, the catalyst system containing *ca.* 10-30% TiO_2, effectively catalyzed benzohydrol oxidation by using H_2O_2. The simple explanation for the decrease of the catalytic activity of the catalyst systems containing TiO_2 above 30% is that, as the TiO_2 loading increases, so does the effective interphase area between the TiO_2 particles. This is due to above a certain loading, the TiO_2 particles begin to agglomerate and overlap. One suggests that the catalyst system must satisfy the following requirements in order to achieve high catalytic activity: (i) existence of Ti active sites, and (ii) the presence electric field. Therefore, if the catalyst particles exist in the agglomerate form, the number of Ti active sites which are in contact with conducting surface are limited and efficient oxidation reaction cannot be expected. The use of a certain amount of TiO_2 is necessary in order to increase the effective interphase area between the TiO_2 particles and conducting surface. On the basis of these results, a model of the catalyst system induced by electric field is proposed as shown in Figure 4.7.

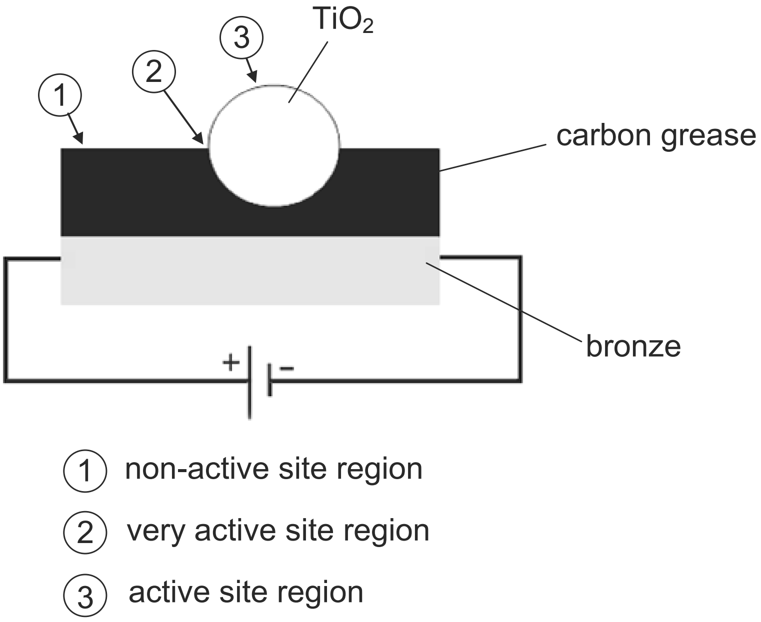


Fig. 4.7: Proposed model of an effective region for catalytic oxidation reaction induced by electric field.

Based on the results obtained from the oxidation of benzhydrol, it is suggested that the most effective active site for this catalytic system is on the surface area of the interface between the polypyrrole and titanium dioxide particles where both electric field and catalytic active site are found. In the process of oxidizing benzhydrol, the intensity of the electric current flowing through the catalytic system was 2.0 V with 5.0 A. The presences of the electric field enhance the effect of interfacial adsorption of the substrate. The process of adsorption is actually pivotal to the role of heterogeneous catalysis where the catalyst is in a solid phase. When the substrate is binded to the interface between the polypyrrole and titanium dioxide particles by the additional electric force, oxidation of the substrate (benzhydrol) took place on the active site on titanium dioxide to give benzophenone.

Indeed, oxidation of benzhydrol was also occurred on the active site of titanium dioxide. At this area, no electric field is found because titanium dioxide alone is an insulator. Therefore, the resulting benzophenone amount was lesser when compare with the oxidation process that take place on the surface where electric field is presence. This is proved by the curve presented in Figure 4.1 where benzophenone was derived with no electric potential applied to the catalytic system. At the same time, oxidation of benzhydrol was occurred on the surface area of polypyrrole as well. However, the amount of the resulting benzophenone was lesser without the presence of active site of titanium dioxide and the results was also presented in Figure 4.1. Therefore, it is proposed that the interface between titanium dioxide and polypyrrole is the most effective active site for the reaction of oxidizing benzhydrol to occur where it is based on the double aptitude of PPy/TiO_2 composite to adsorb reactant electrically and followed by the oxidation process at the active site. Due to the importance of electric field and titanium dioxide active sites, the optimum capacity of titanium dioxide in this catalytic system has to be known in order to make the system as effective as possible which enables maximum quantity of substrates to bind at the interface between polypyrrole and titanium dioxide particles.

All the results mentioned above seem consistent with the proposal that claimed the reaction takes place at the effective interphase area between the TiO_2 particles and conducting surface. However, the apparent rate of oxidation of benzohydrol was much lower than previously reported [9]. One of the reasons for the low activity in our catalyst is the presence of few four-coordinate Ti species which are considered to be the most active species in the oxidation reaction with H_2O_2 [10, 11]. It should be noted that we used the TiO_2 as an easily available material and the catalyst and the reaction conditions have not been optimized. Thus, we have shown that the oxidation reaction could be enhanced by electric field.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, a new heterogeneous catalytic system which is able to improve the efficiency of adsorption and desorption in catalytic cycle processes was designed to achieve a coherent picture of catalytic processes at the fundamental level. It is based on an idea that the surface charge of the solid catalyst can be controlled by applying electric field in order to improve the efficiency of adsorption and desorption in catalytic cycle processes.

The new designed catalytic system consists of 3 parts, which is the solid catalyst, medium for catalytic processes to occur and direct current supply. The solid catalyst consists of doped polypyrrole and titanium dioxide in anatase phases. Polypyrrole is used as a media to distribute the titanium dioxide particles because it is an electrically conducting material whereas titanium dioxide provides catalytic active site in the new catalytic system.

Eleven series of PPy/TiO_2 in various proportions which keeps the weight (g) ratio of PPy/TiO_2 at 1:0 to 0:1 was used to check the optimization of the activity of the polypyrrole and titanium dioxide under the present of the electric field. Furthermore, the incorporation of titanium dioxide in polypyrrole was confirmed by FESEM with EDX and FTIR spectroscopy.

The main chemical reaction that used to investigate the effectiveness of the electric field on regulating the adsorption capacity and the reactivity of catalyst in the new designed catalytic system was oxidation of benzhydrol by using aqueous hydrogen peroxide. Another experiment on dye adsorption was done as a further study to prove the impact of electric field on adsorption activity of the catalytic system. Indeed, the chemical reactions used in this new designed catalytic system was water-based reactions while the supplied electric current was fixed at 5.0 A and 2.0 V.

As a result, external electric field has significant effects on the oxidation of benzhydrol reaction. The external electric field caused the yield of benzophenone to increase significantly when compare to the yield of benzophenone under the condition that without the influence of electric field. The external electric field caused the yield of benzophenone to increase significantly in the ranges of 9–43 μmol whereas the results of oxidizing benzhydrol without the presence of electric field show no significant effect by exhibiting the yield of benzophenone in the ranges of 2–8 μmol.

Moreover, the results also suggested the occurrence of the synergistic effect of the electric field and titanium dioxide where the initial rates of oxidation of benzhydrol were found to be directly proportional to the mass of catalyst. This can be attributed to the presence of more reactive sites on the PPy/TiO_2 composite which allow the oxidation of benzhydrol to occur to a larger extent. However, the reaction rate levels off and becomes independent of mass when the amount of TiO_2 was found equal to 30% TiO_2 on a fixed $5cm^2$ surface area in the catalytic system in which all the particles are totally took part in the reaction by exposing all the surface of the catalyst. After the saturation of titanium dioxide is attained in the catalytic system, the yield of benzophenone decreased. This is probably due to the increased of titanium dioxide particles on the catalytic system resulted an excess amount of titanium dioxide agglomerated and formed few layers which mask part of the surface, thus reducing the electrical properties of the catalytic system since the electric field influences the adsorption and catalytic processes.

From the synergistic effect of the electric field and titanium dioxide, it is proposed that the interface between titanium dioxide and polypyrrole is the most effective active site for the reaction of oxidizing benzhydrol to occur where both electric field and catalytic active site are found. Hence, the proposed mechanism regarding this study is based on the double aptitude of PPy/TiO_2 composite to adsorb reactant electrically and followed by the oxidation process at the active site. The surface charge of polypyrrole is enhanced by the presence of electric potential thus increasing short-range attractive interactions between polypyrrole and particles of organic substrate. In other words, oxidation of benzhydrol either on the surface of titanium dioxide or polypyrrole alone are less effective.

On the other hand, the results of the degradation test of methylene blue revealed that the evidence of the adsorption activity depends on the specific surface area of polypyrrole which determine the amount of electric current on the generation of surface charge to induce the adsorption of dye molecules. The increasing amount of polypyrrole allows more charge carriers in response to enhance the adsorption of dye molecule but the high titanium dioxide concentrations impede the overall reaction since it is an insulator. As a consequence, electric field gave a greater effect in absorbing the methylene blue solution where about 0.25 ppm more of methylene blue was absorbed in the catalytic system with the application of external electric field. It is found that the further increases in temperature give no significant effect on the degradation of methylene blue solution. Therefore, the degradation of methylene blue is mainly an electric-field-induced adsorption process where the dye particles are absorbed on the surface of polypyrrole instead of titanium dioxide because titanium dioxide in low concentration did not play a role as a photocatalyst in degrading the dye.

In conclusion, the catalytic system has been successfully designed and it plays an importance role in providing an environment to improve the rate of the oxidation process and to increase the amount of benzophenone as well. Therefore, the ideal composition of titanium dioxide and polypyrrole at the surface is very important in pursuing high adsorption and catalytic activity for target reactions.

5.2 Recommendations

As a global guide for future actions, this study opens new perspectives for the use of electrically conducting surface containing titanium dioxide in electric-field-induced liquid phase oxidation catalysis.

In order to increase the reliability of the new designed catalytic system, the scope of study and application of titanium dioxide can be widen as well as improve the present study in different aspects. Below the ideas are some recommendations about the further works of this research:

a) To investigate the mechanism and kinetic of the chemical reaction under the application of electric field in this catalytic system.
b) To study the effect of electric field over the new catalytic system in other chemical reactions.
c) To apply this fundamental idea into larger scale like chemical process in industry field.

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