MAGNETIC-FIELD-INDUCED LIQUID PHASE CATALYSIS OVER ELECTRICALLY CONDUCTING SURFACE CONTAINING TITANIUM DIOXIDE

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For the LORD almighty

Glory be Yours forever…

Rom 11: 36

My beloved DAD, MUM, Brothers - Augustine and Arnold,
Aunties, Uncles, cousins - Step and Phing,
My family in Christ (especially Jael), and
some of my ex-course mates……

For their love , support , encouragement …

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ABSTRACT

In general, heterogeneous catalytic reactions in liquid phase can be enhanced by manipulation of relevant local environment conditions. Since the magnetic field may affect the molecular processes of catalytic reaction on the catalyst's surface, it is of interest to explore the effect of magnetic field on the liquid phase reaction over a heterogeneous catalyst's surface. Therefore, the ultimate goal of this study is to design a new heterogeneous catalytic system based on the idea that the catalytic activity can be controlled by applying electricity to induce magnetic field. Polypyrrole and titanium dioxide have been used as electrically conducting materials and catalytic active site, respectively. The magnetic field effects over electrically conducting surface loaded with titanium dioxide to induce the adsorption of organic substrate has been confirmed by oxidation of benzhydrol to benzophenone by using hydrogen peroxide as an oxidant. The results suggest the occurrence of the synergistic effect with the generated magnetic field and titanium dioxide. The study was also extended to the removal of methylene blue enhanced by the magnetic field effect. One suggests that the magnetic field generated by electric current induced the removal of methylene blue over electrically conducting polypyrrole containing titanium dioxide. As a global guide for future actions, this work opens new perspectives for the use of electrically conducting surface containing titanium dioxide for liquid phase magnetic-field-induced oxidation catalysis.

ABSTRAK

Pada amnya, tindak balas pemangkinan heterogen dalam fasa cecair boleh dipertingkatkan dengan memanipulasikan keadaan persekitaran tempatan yang relevan. Disebabkan medan magnet boleh mempengaruhi proses pemangkinan di peringkat molekul pada permukaan mangkin, adalah menarik untuk menyelidiki kesan medan magnet terhadap sesuatu tindak balas fasa cecair yang berlaku pada permukaan mangkin heterogen. Oleh itu, matlamat utama kajian ini adalah merekabentuk satu sistem pemangkinan heterogen yang baru berdasarkan idea bahawa aktiviti pemangkinan boleh dikawal dengan menggunakan elektrik untuk menghasilkan kesan kemagnetan. Polipirol dan titanium dioksida masing-masing telah digunakan sebagai bahan mengkonduksi elektrik dan tapak aktif pemangkinan. Kesan kemagnetan ke atas permukaan mengkonduksi elektrik yang mengandungi titanium dioksida dalam mengaruhkan penjerapan substrat organik telah dibuktikan oleh tindak balas pengoksidaan benzhidrol membentuk benzofenon dengan menggunakan hidrogen peroksida sebagai pengoksida. Keputusan menunjukkan bahawa terdapat kesan sinergi secara bersama medan magnet yang terjana dan titanium dioksida. Kajian tersebut juga telah dilanjutkan dalam meningkatkan penyingkiran metilena biru di bawah pengaruh medan magnet. Adalah dicadangkan, medan magnet yang dihasilkan oleh arus elektrik tersebut akan mengaruhkan penyingkiran metilena biru pada polipirol yang mengandungi titanium dioksida. Sebagai satu panduan global untuk tindakan masa depan, kajian ini membuka perspektif baru tentang penggunaan permukaan mengkonduksi elektrik yang mengandungi titanium dioksida bagi pemangkinan pengoksidaan medan magnet teraruh dalam fasa cecair.

CONTENTS

1 INTRODUCTION

2 LITERATURE REVIEW

3 METHODOLOGY

LIST OF ABBREVIATIONS

PPy	-	Polypyrrole
Ti	-	Titanium
TiO_2	-	Titanium dioxide
OTS	-	Octadecyltrichlorosilane
$Ti(SO_4)_2$	-	Titanium (IV) sulfate
DC	-	Direct current
XRD	-	X-ray diffractometry
FTIR	-	Fourier transform infrared spectroscopy
IR	-	Infrared
FESEM	-	Field emission scanning electron microscope
UV-Vis	-	Ultraviolet-visible spectroscopy
UV/Vis/Nir	-	Ultra violet– visible-near infrared
GC	-	Gas chromatography
FID	-	Flame ionization detector
EDX	-	Energy dispersive X-ray spectroscopy
t_r	-	Retention time
PDMS	-	Polydimethylsiloxane
CB	-	Conduction band
VB	-	Valence band
e^-	-	Negatively charged electron

h^+ - Positively charged hole

e^-_{cb} - Negatively charged electrons (e^-) in the conduction band

h^+_{vb} - Positively charged hole (h^+) in the valence band

H_2O - Water

H^+ - Proton

$\cdot OH$ - Hydroxyl radical

$(C_6H_5)_2C{=}O$ - Benzophenone

$(C_6H_5)_2CHOH$ - Benzhydrol

TON - Turnover number

$SrTiO_3$ - Strontium titanate

Fe_2O_3 - Iron (III) oxide

CdS - Cadmium sulfide

WO_3 - Tungsten (VI) oxide

ZnS - Zinc sulfide

$FeTiO_3$ - Iron titanium oxide

ZrO_2 - Zirconium oxide

V_2O_5 - Vanadium oxide

Nb_2O_5 - Niobium oxide

SnO_2 - Stannic oxide

E_g - Energy gap

[O] - Oxidizing agent

RCH_2OH - Primary alcohol

$RCH{=}O$ - Aldehydes

RCOOH - Carboxylic acids

R_2CHOH - Secondary alcohol

$R_2C=O$ - Ketones

PCC - Pyridinium chlorochromate

DDQ - Dichlorodicynoquinone

$-N=N-$ - Azo

$-C=O$ - Carbonyl

$-C=C-$ - Carbon-carbon double bonds

$-NO_2$ - Nitro functional groups

$–CH=N-$ - Carbon-nitrogen functional groups

$C=S$ - Carbon-sulfur functional groups

$-NO$ - Nitroso functional groups

RNA - Ribonucleic acid

DNA - Deoxyribonucleic acid

E_0 - Ground state energy

E_1 - First excited state energy

KBr - Potassium bromide

ε - Molar absoptivities

T - Transmittance

A - Absorbance

He - Helium

I_0 - Intensity of reference beam

I - Intensity of sample beam

Aq - Aqueous

B_W - Magnetic field generated by wire

B_E - Earth magnetic field

B_T - Total magnetic field

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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 particularly chemical and petroleum industries since the vast majority of industrial processes and the synthesis of new materials are based on catalytic reactions [1]. 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.

Basically, catalysts are classified into three subdisciplines according to their structure, composition, area of application, or state of aggregation. The three subdisciplines of catalysts classes are 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 [2-9].

Until 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]. In recent years, magnetic field effect has been applied on chemical reactions like photocatalytic reaction [18, 19]. However, there is no report on the effect of magnetic field generated by external electric field in heterogeneous catalytic system.

Indeed, it has been a challenge to prepare catalysts with high activity and design catalytic systems with high efficiency 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 in these experiments to control catalytic chemistry had resulted in deeper insights into catalysis and allowed 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 had further provided new fundamental knowledge for the catalysis research community.

As this study intends to design a new heterogeneous catalytic system to enhance the heterogeneous catalytic system by applying electric field to generate magnetic field on the catalyst system, 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 Catalyst System

Great efforts have been undertaken internationally to understand the fundamental processes of the chemisorption at heterogeneous surfaces. These efforts also aimed to obtain a basic understanding of the bonding and reaction concepts with the aid of surface science techniques and the fast-growing insight into research in catalysis.

Therefore, the ultimate goal of this study is to design a new heterogeneous catalytic system to improve the efficiency of adsorption and desorption in catalytic cycle processes. This can be done by applying electric field to generate magnetic field on the surface of catalyst. Figure 1.1 shows the proposed design of the desired heterogeneous catalytic system.

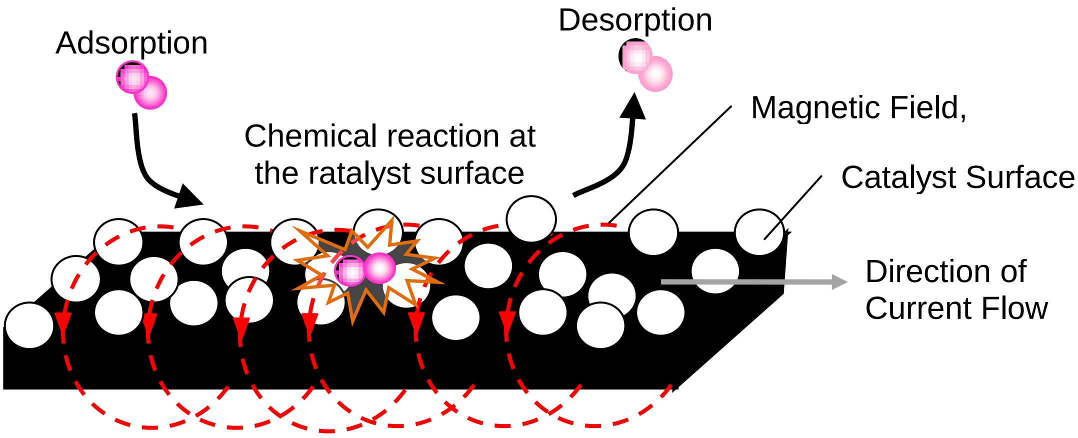

Figure 1.1 : The conceptual model for the desired heterogeneous catalytic system

One suggests that external electric field does bring forth changes in the chemisorption and catalytic properties of semiconductors [13-17]. Hence, this new catalytic system design is basically based on the idea that the surface properties of the catalyst can be controlled by the presence of magnetic field. Moreover, magnetic field will be generated on a conductor when an electric field is switched on. As a result, the different physicochemical processes occur and this can stimulate adsorption and catalytic reactions on the surface of the catalyst [13-17]. In other words, when there is an application of an electric field which bring forth the magnetic field effects, the efficiency of adsorption and desorption (interaction between the catalyst and reactant) in catalytic cycle processes can be controlled.

Figure 1.2 shows the model of a new integrated catalytic system using polypyrrole and titanium dioxide as conducting and catalytic active site, respectively. Polypyrrole is a conducting polymer and act as “solid” solvent to control the amount of titanium dioxide in catalytic system. Polypyrrole is one of the conducting polymers with "back bone" of alternating double and single bonds, along which electrons can flow [20]. 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 aqueous solution [17, 21]. It is also efficient electron donor and good hole transporter upon visible light excitation [22].

On the other hand, titanium dioxide was used to provide active sites for reaction to occur because it is resistant to photo-corrosion and has high oxidative power [23]. Due to its electrical conductive properties, it would be of great interest to study the adsorption and desorption behaviour of polypyrrole- titanium dioxide mixture under magnetic field.

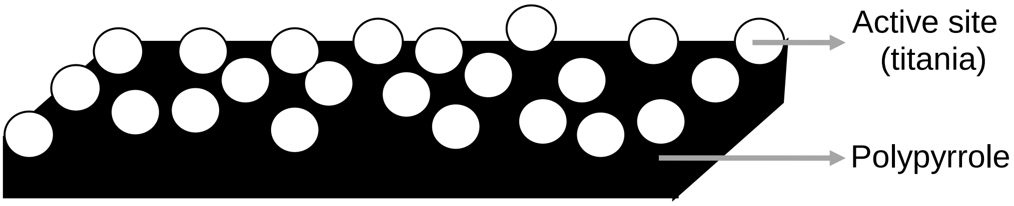

Figure 1.2 : The model of the polypyrrole and titanium dioxide

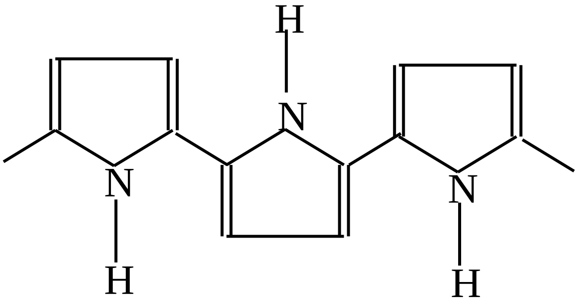

Figure 1.3 : The chemical structure of polypyrrole polymer chain

By applying these concepts into the new integrated catalytic system, this model will be introduced with the expectation of combining the effects of adsorption ability of polypyrrole and the reactivity of titanium dioxide to enhance the overall catalytic activity.

The effect of magnetic field on catalytic activity was investigated through several chemical reactions and adsorption experiments. In this study, epoxidation of alkane, oxidation of alcohol and also adsorption of dye were used to demonstrate the effect of magnetic field on the catalytic activity. The research questions and statement of the problem are shown in Figure 1.4.

Development of a new integrated catalytic system based on electrically conducting surface (polypyrrrole) containing titanium dioxide under magnetic field

Research Question

- What is the applicable design to demonstrate the effect of magnetic field induced by electric current in heterogeneous catalytic system?
- How the effects of magnetic field generated by electric fields influence the catalytic activity in liquid phase oxidation reaction?
- What chemical reaction is applicable to the magnetic-field-induced catalytic system?

Statement of the Problem

Can magnetic field effects generated by electric field increase catalytic activity in liquid phase reaction over solid catalyst?

Figure 1.4 : Schematic representation of the research question and statement of the problem

1.3 Objective of Study

Main objectives of this study are:

(a) To develop a new magnetic-field-induced catalytic system based on electrically conducting surface containing titanium dioxide.

(b) To study the influence of magnetic field effects generated by external electric field on the catalytic activity in liquid phase catalysis over electrically conducting surface containing titanium dioxide.

1.4 Scope of Study

This study investigated the magnetic field effect generated by external electric field in heterogeneous catalysis by using several integrated chemical system containing polypyrrole and titanium dioxide as model of new catalytic system. The models are tested for several chemical reactions like epoxidation of 1-octene, photodegradation of methylene blue reaction and the oxidation of benzhydrol by using aqueous hydrogen peroxide to clarify the effect of generated magnetic field on catalytic activity. The new catalytic system was introduced as a new approach to improve the activities of the heterogeneous catalysts by applying the magnetic field. Another experiment on dye adsorption was done to prove the effect of generated magnetic field on adsorption activity of the catalytic system.

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