สมบัติการเร่งปฏิกิริยาและสมบัติทางเคมีไฟฟ้าของสารประกอบเชิงซ้อนเหล็ก

นางสาวธีราพร ทิมทอง

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2546

ISBN 974-17-4718-7

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

CATALYTIC AND ELECTROCHEMICAL PROPERTIES OF IRON COMPLEXES

Miss Teeraporn Timthong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2003

ISBN 974-17-4718-7

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Thesis title Catalytic and Electrochemical Properties of Iron Complexes
By Miss Teeraporn Timthong
Field of Study Petrochemistry and Polymer Science
Thesis Advisor Assistant Professor Orawon Chailaphakul, Ph. D.
Thesis Co-advisor Assistant Professor Warinthorn Chavasiri, Ph. D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

Thesis Committee

....Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

Orawon Chailaphakul
....Thesis Advisor
(Assistant Professor Orawon Chailaphakul, Ph.D.)

Warinthorn Chavasiri
....Thesis Co-advisor
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

W. Trakarnpruk
....Member
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

Nuanphun Chantarasiri
....Member
(Associate Professor Nuanphun Chantarasiri, Ph.D.)

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

ธีราพร ทิมทอง: สมบัติการเร่งปฏิกิริยาและสมบัติทางเคมีไฟฟ้าของสารประกอบเชิงซ้อนเหล็ก (CATALYTIC AND ELECTROCHEMICAL PROPERTIES OF IRON COMPLEXES) อ.ที่ปรึกษา : ผศ.ดร. อรวรรณ ชัยลภากุล อ.ที่ปรึกษาร่วม : ผศ.ดร. วรินทร ชวศิริ : 65 หน้า; ISBN 974-17-4718-7.

ในงานวิจัยนี้ได้สังเคราะห์สารประกอบเชิงซ้อนเหล็ก เพื่อใช้เป็นตัวเร่งปฏิกิริยาออกซิเดชันของไซโคลเฮกเซน โดยใช้ของผสมไพริดีนและแอซิโทไนไทร์ลเป็นระบบตัวทำละลาย ใช้ไฮโดรเจนเปอร์ออกไซด์ และเทอร์เชียรีบิวทิลไฮโดรเปอร์ออกไซด์เป็นตัวออกซิแดนท์ที่อุณหภูมิห้องและ 70 องศาเซลเซียส พบว่าได้ไซโคลเฮกซาโนนเป็นผลิตภัณฑ์หลัก ไซโคลเฮกซานอลเป็นผลิตภัณฑ์รอง ศึกษาความสัมพันธ์ระหว่างสมบัติการเร่งปฏิกิริยา และสมบัติทางเคมีไฟฟ้าของสารประกอบเชิงซ้อนเหล็ก โดยใช้เทคนิคไซคลิกโวลแทมเมทรี ใช้กลาสซีคาร์บอนเป็นขั้วทำงาน ลวดเงินเป็นขั้วอ้างอิงและลวดแพลทินัมเป็นขั้วช่วย พบว่าสารประกอบเชิงซ้อนเหล็กส่วนใหญ่ที่เกิดปฏิกิริยารีดอกซ์แบบผันกลับได้ และกึ่งผันกลับได้ จะแสดงสมบัติเป็นตัวเร่งปฏิกิริยาที่ดีกว่าสารประกอบเชิงซ้อนเหล็กที่เกิดปฏิกิริยารีดอกซ์แบบผันกลับไม่ได้ เนื่องจากสารประกอบเชิงซ้อนเหล็กส่วนใหญ่ที่เกิดปฏิกิริยารีดอกซ์แบบผันกลับได้และกึ่งผันกลับได้ จะให้ปริมาณผลิตภัณฑ์ที่สูงกว่า นอกจากนี้ได้ศึกษาจลน์ศาสตร์ของปฏิกิริยาออกซิเดชันของไซโคลเฮกเซนเปรียบเทียบกับเทคนิคไซคลิกโวลแทมเมทรี พบว่าผลที่ได้สอดคล้องกัน

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

4472289423: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORD: OXIDATION/ IRON COMPLEX/ CYCLIC VOLTAMMETRY

TEERAPORN TIMTHONG: CATALYTIC AND ELECTROCHEMICAL PROPERTIES OF IRON COMPLEXES. THESIS ADVISOR: ASST. PROF. ORAWON CHAILAPHAKUL, Ph.D. THESIS CO-ADVISOR: ASST. PROF. WARINTHORN CHAVASIRI, Ph.D.; 65 pp. ISBN 974-17-4718-7.

In this research, iron complexes were synthesized and exploited as catalyst in the oxidation of cyclohexane using a mixture of pyridine-acetronitrile as a solvent system. Hydrogen peroxide and *tert*-butylhydroperoxide as an oxidant at room temperature and 70 °C. Cyclohexanone was selectively obtained as a major product and cyclohexanol as a minor product. The relationship between oxidation reaction utilizing catalytic and electrochemical properties of iron complexes using cyclic voltammetry was studied. Cyclic voltammetry was performed using glassy carbon as a working electrode, silver wire as a reference electrode and platinum wire as an auxillary electrode. It was found that iron complexes exhibiting reversible and quasi-reversible reactions gaving better catalytic activity and provided better yield than iron complexes displayed irreversible reactions. In addition, the results obtained from kinetic study of cyclohexane oxidation and those from cyclic voltammetry were in good agreement.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Field of study...Petrochemistry and Polymer Science... Student's signature...T. Timthong...

Academic year...2003... Advisor's signature...................

Co-advisor's signature...W. Chavasiri...

ACKNOWLEDGEMENTS

This research could not have been successfully completed without the assistance and contribution from several people as well as Chulalongkorn University.

First of all, the author would like to express my sincere appreciation to her advisor, Assistant Professor Dr. Orawan Chailapakul and Dr. Warinthorn Chavasiri for their invaluable guidance, support and encouragement throughout the course of this research. She is grateful to Professor Dr. Pattarapan Prasassarakich, Associate Professor Dr. Wimonrat Trakarnpruk and Associate Professor Dr. Nuanphun Chantarasiri, serving as the chairman and members of her thesis committee, respectively, for their valuable comments and suggestions.

The author would like to thank for permitting to use some equipments, especially, from Natural Products Research Laboratory.

Above of all, I deeply thank to her parents for their support, encouragement, kindness and special someone, her close friends for their supports.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS (cont.)

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

Figures **Page**

LIST OF FIGURES (cont.)

LIST OF FIGURES (cont.)

Figures **Page**

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF SCHEME

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF ABBREVIATIONS

Fig	figure
°C	degree celsius
atm	atmosphere
mmol	millimole
NMR	Nuclear Magnetic Resonance
IR	Infrared spectroscopy
g	gram (s)
mL	milliliter (s)
min	minute (s)
h	hour (s)
cm^{-1}	unit of wavenumber
ppm	part per million
J	coupling constant (Hz)
m	multiplet (NMR)
dd	double of doublet (NMR)
d	doublet (NMR)
s	singlet (NMR)
m.p	melting point
dec	decomposed
lit	literature
R_f	retardation factor
acac	Acetylacetonate
salen	Bis(salicylaldehyde)-*N*,*N*′-ethylenediimine
TBHP	*tert*-butylhydroperoxide
ssp	*N*-salicylidene-2-aminobenzenethiolate
salophen	Bis(salicylaldehyde)-*N*,*N*′-trimethylenediimine
sap	*N*-salicylaldehydene-2-aminophenol
tdppcyme	*cis*-*cis*-1,3,5-tris(di-phenylphosphine)-*cis*,*cis*-1,3,5-tris (methoxycarbonyl)cyclohexane

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER I

INTRODUCTION

The basic concept of a catalyst is that of a substance in small amount causes a large change. More precise definitions of catalysis and of what constitutes a catalyst have gradually evolved as understanding of the causes of catalytic phenomena has grown. Even today there is no universal agreement on definitions, the point of view varying somewhat depending upon the investigator; as between the fundamental investigator, the practitioner and among researchers concerned with heterogeneous catalysis, homogeneous catalysis, polymerization reactions, and enzymes. A catalyst is a substance that increases the rate of reaction without being appreciably consumed in the process.

This basic concept, stemming from the chemical approach to catalysis, is that a reaction involves a cyclic process in which a site on a catalyst forms a complex with reactants, from which products are then desorbed, thereby restoring the original site. This leads to the idea that a catalyst is unaltered by the reaction it catalyzes, but this is misleading. A catalyst may undergo major changes in its structure and composition as a part of the mechanism of its participation in the reaction. A pure metal catalyst will frequently change in surface roughness or crystal structure on use. The ratio of oxygen to metal in a metal oxide catalyst will frequently change temperature and composition of the contacting fluid. In both cases, however, there is no stoichiometric between such changes and the overall stoichiometry of the catalyzed reaction. Many so-called polymerization catalysts or initiators are not termed catalysts within the above definition. Thus, in the use of an organic peroxide to initiate a polymerization reaction, the ratio of peroxide consumed to quantity of monomer reacted is indeed nonstoichiometric, but the peroxide becomes completely consumed in the process; hence it cannot be regarded as a true catalyst.[1]

A catalyst is defined as a substance; a creleration of a rate by energy-tranfer process is not regarded as catalysis by this definition. Excluded cases include excitation by thermal energy (increased temperature), by bombardment of reactants by charged or high–energy particles, by electric discharge, or by photochemical irradiation.[2] Catalyst can generally be classifed into two groups: heterogeneous catalysts and homogeneous catalysts.

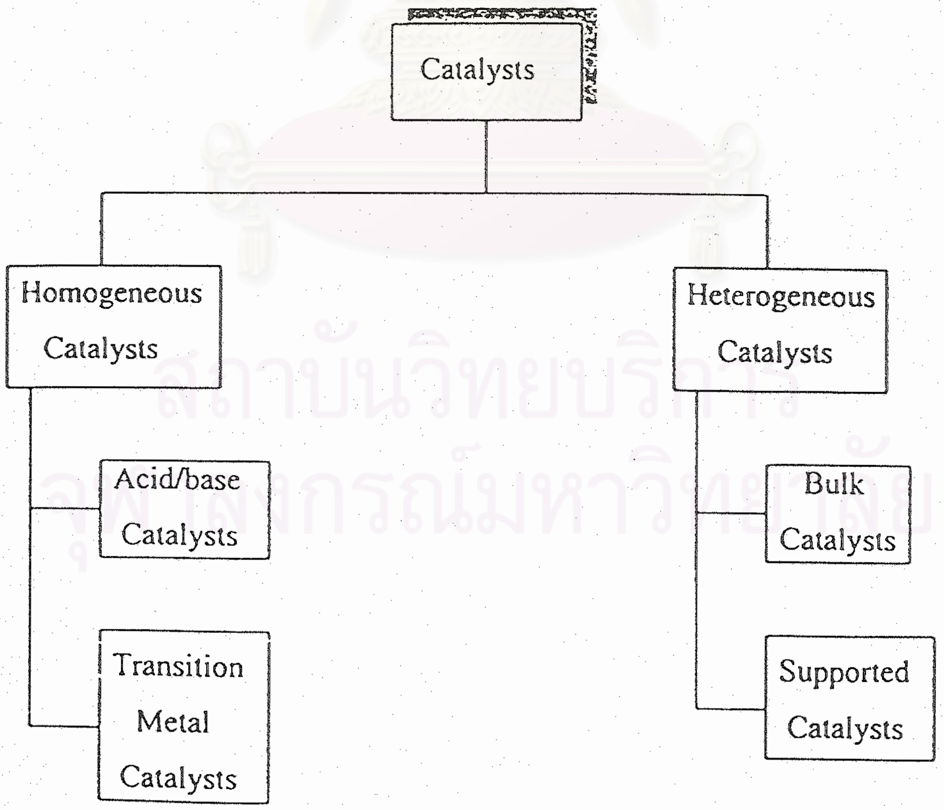
Heterogeneous catalyst[3]

A catalyst may sometimes act by generating free radicals, which then propagate a chain reaction in the bulk of the reacting fluid. Examples are well documented for various liquid-phase reactions in which free radicals have been trapped or otherwise identified. For gas- phase reaction the phenomenon is sometimes postulated to occur, especially for vapor-phase oxidation reactions at elevated temperatures. There is little solid experimental evidence to indicate the extent, if any, to which it is actually significant for conditions and systems of practical interest. Good evidence exists for heterogeneous catalysis in the reaction of hydrogen and oxygen gases at low pressures, where the mean free path is high. At pressures of 1 atm and higher, heterogeneous catalysis probably is of significance only for combinations of pressure, temperature, and gas composition close to those under which the homogeneous reaction rate of itself would be significant. That is, the catalytic reaction triggers off an incipient homogeneous reaction.

The above description is the classical form of heterogeneous, but a catalytic reaction and a homogeneous reaction may interact with each other in various subtle ways such that the net effect is not simply the sum of the two. Instead of free radicals being desorbed into the gas phase, a molecular intermediate may be formed and released instead. Its fate depends upon the relative probability of being adsorped and reacted on another site of the catalyst in contrast to reacting in a different manner in the gas phase. The overall behavior of the system may depend not only on the void fraction of a packed bed of catalyst and the amount of open volume downstream, but also on geometrical and other factors. In many catalytic oxidations the exit gas must be rapidly quenched to avoid over–oxidation or decomposition of desired product, but there is little evidence one way or the other as to whether heterogeneous catalysis contributes to these processes under practical conditions.

Homogeneous catalysts[4]

In its widest sense homogeneous catalysis occurs when the catalyst and the reactants are both in the same phase, either gas or liquid. In more recent years the term has come to be applied more specifically to the use of a solution of certain organometallic compounds in which a central metal atom is surrounded by a regular pattern of atoms or molecules, known as ligands, with which it is coordinated. Depending upon the nature of the ligands, the metal atom may be in a low-positive, zero, or low-negative state. Several different structures may exist in equilibrium in solution simultaneously, with different reactivities, but since the catalyst is dissolved in the reacting medium, each molecule of a particular structure acts like any other. In many cases the structure, although complicated, have been well characterized, and there are systematic correlations of the structure, the nature of the ligands, and the catalytic activity of the catalyst complex.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Homogeneous and heterogeneous catalysts have the advantages and disadventages as shown in Table 1.1.

Table 1.1 Comparison of homogeneous and heterogeneous catalysts

Characteristic	Homogeneous	Heterogeneous
Active centers	all metal atoms	only surface atoms
Concentration	low	high
Selectivity	high	lower
Reaction conditions	mild	severe
Modification	easy	difficult
Catalyst separation	often difficult	Relatively easy
Cost of catalyst losses	high	low

Petroleum or crude oil, occurred underground in reservoirs in porous rock in certain types of geological structures. The oil is recovered from these by drilling oil wells from which it either flows out under the reservoir pressure or is pumped out. Crude oils vary widely from region to region and from field to field. Some crudes are light-coloured, mobile liquids. Others are thick, treacly or tarry materials. Some have quite pleasant smells; others smell quite disgusting. However, all are made up mainly of three types of hydrocarbons: alkanes, cycloalkanes, and aromatics.[5] The cycloalkanes, called naphthenes in the industry, contain five and six membered ring compounds only. Uses of fractions from distillation of petroleum in petrochemical industry are indicated in Table 1.2.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 1.2 Representative fractions from distillation of petroleum

Fraction	Component range and/or Boiling point range,°C(°F)	Use
Gas	Up to C_4	Burned as fuel. Ethane may be thermally cracked to produce ethylene. propane or a mixture of propane and butane may be sold as liquified petroleum gas(LPG)
Straight-run gasoline	C_4-C_5	Blended into gasoline
Virgin naphtha	C_5-150(300)	Used as a feed to catalytic reformer or blended into gasoline
Heavy naphtha	120-200(250-400) (up to C_{15})	Jet fuel, kerosene
Light gas oil	200-310(400-600) (up to C_{20})	Used as No.2 distillate fuel oil, or blending stock for jet fuel and/or diesel fuel
Gas oil(heavy distillate)	Up to 350(650) (C_{25})	Used as a feed to catalytic cracker or sold as heavy fuel oil
Atmospheric residual	350+(650+)	Various use. May be distilled under vacuum to produce vacuum-gas oil, coked, or burned as fuel
Vacuum residual	560+(1050+) equivalent boiling point	

Cyclohexane was first obtained directly by fractional distillation of suitable crude gasoline cuts; the purity, however, was only 85%. The product quality was improved to almost 98% by the simultaneous isomerization of methylcyclopentane to cyclohexane, as first practiced in plants in the USA. Because of the markedly increasing demard for cyclohexane as a feedstock for nylon 6 and nylon 6,6[6], this covers only a small fraction of the demand for cyclohexane. The utilization of precursor as starting material in chemical industry is shown in Table 1.3.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

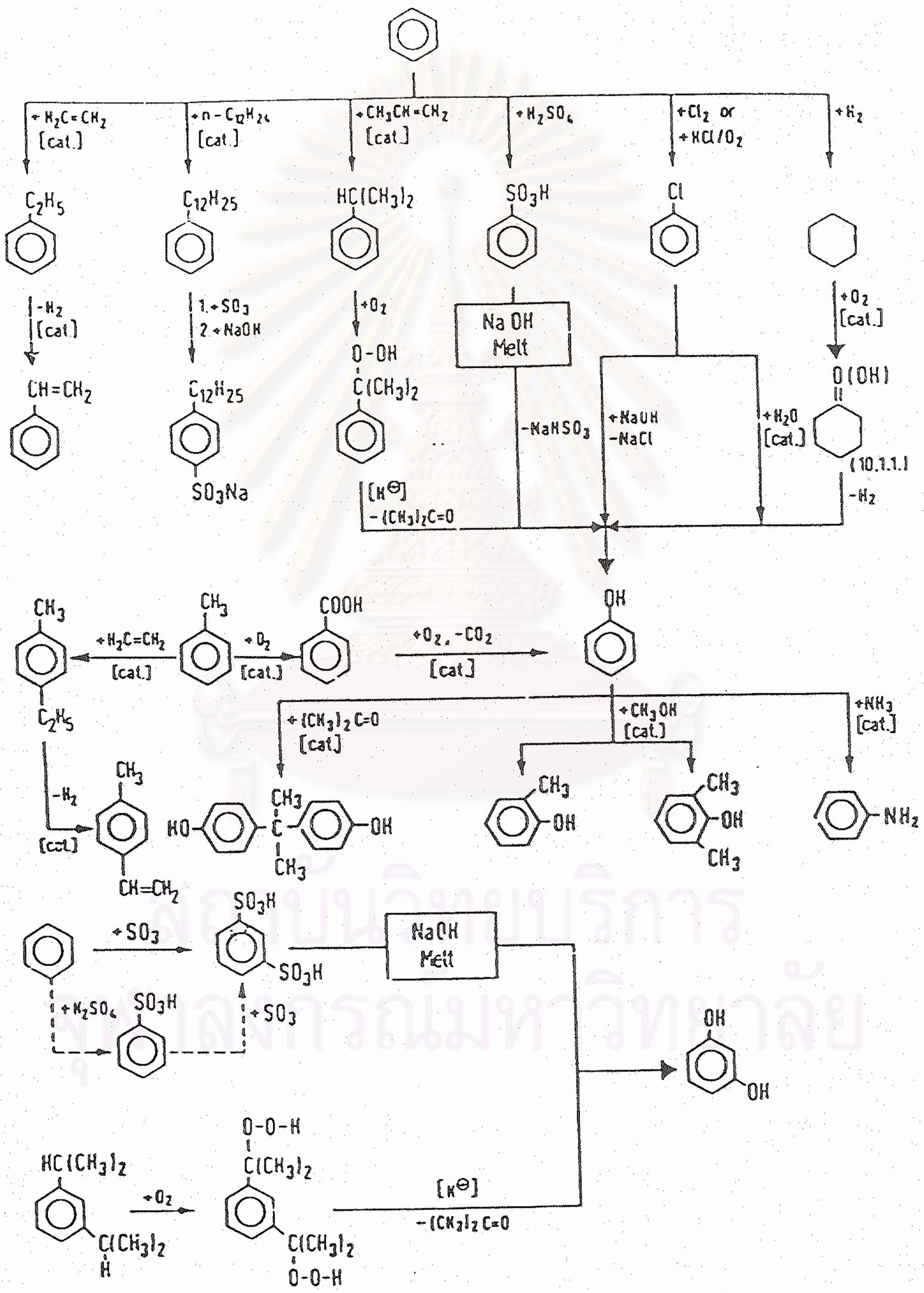
Table 1.3 Routes for manufacturing

Precursor	Intermediate	Process
Benzene	Benzenesulfonic acid	Classical
Benzene	Chlorobenzene	Dow and Bayer(alkaline hydroly Rashig-Hooker(acidic hydrolysis)
Toluene	Benzoic acid	Dow and California Research
Cyclohexane	Cyclohexanone-cyclohexanol	Scientific Design
Benzene/propene	Isopropylbenzene(cumene)	Hock

Process and product schemes of cyclohexane are listed in schemes 1.1

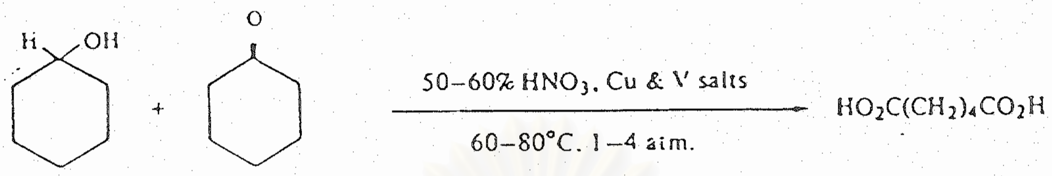
สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

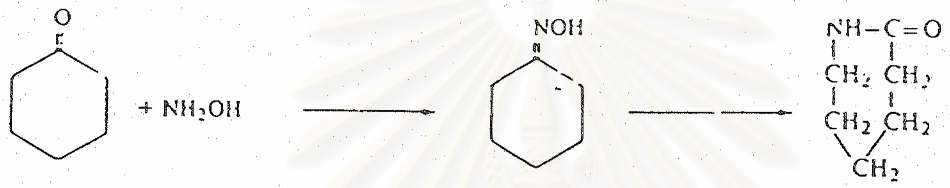
Schemes 1.1 Process and product schemes[7]



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Cyclohexanone and cyclohexanol are used for the preparation of an important intermediate in the production of nylon such as adipic acid and hexamethylene diamine for nylon 6,6 and caprolactam for nylon 6.[5]





Although saturated hydrocarbons are quite inert, previous work showed that the breaking of C-H bonds in saturated hydrocarbons usually required very expensive catalysts and severe conditions, *e.g.* high pressure, high temperature, *etc.* For example, the oxidation of cyclohexane converted to cycloxanone and cyclohexanol could proceed employing an oxidation catalyst such as cobalt complexes at 160 °C under high pressure.[8] Therefore, the development of the appropriate catalyst in the oxidation of cyclohexane under mild conditions is still being the important investigation. In this research, the mild condition for oxidation of cyclohexane to cyclohexanone and cyclohexanol using homogeneous catalyst is selected for investigation.

Organic chemists interested in electrochemical methods have been aware of a sharp contrast between the rich synthetic potentialities in the field of organic electrochemistry and the relatively slight acceptance that electrochemical techniques have actually gained in organic synthesis. There is no doubt that one of the principal reasons for this unfortunate disparity is the lack of a published treatment of electrochemical principles as they relate specifically to organic synthesis.

Voltammetry is now necessary to examine the quantitative and semiquantitative interrelationships between potential, electrochemical reaction rate,

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

and mass transport. These relationships find expression in a wide variety of voltammetric experiments commonly used to charactize the electrochemical behavior of an electroactive substance. Many chemical measurements, which involve homogeneous bulk solution, electrochemical processes take place at the electrode-solution interface.[9] Typically, the substance is fixed at the surface of electrode and electrons are transferred in the system of electrochemical cell. One advantage of electrochemical techniques is the examination of catalytic properties which could be further used for the selection of a catalyst.

Cyclic voltammetry, also called cyclic triangular-wave voltammetry, is like polarography, a relatively simple technique, capable nevertheless of providing, with relatively little experimental effort, a great deal of useful information about electrochemical behavior. Cyclic voltammetry is itself a variant on a technique known as stationary-electrode voltammetry. In the latter technique, the potential of a stationary electrode is varied linearly, as in polarography, and the resulting current is measured on a recorder. Typical stationary electrode voltammograms are illustrated in Figure 1.1.

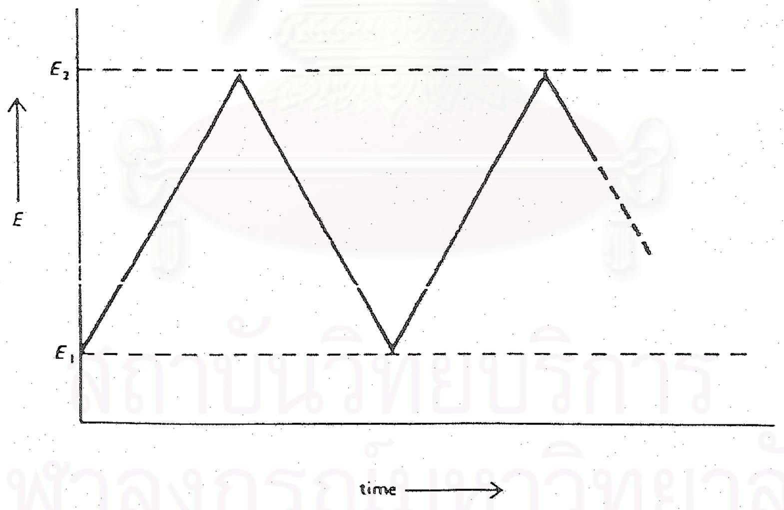


Figure 1.1 Triangular wave function

Notice that the potential may be swept either anodically or cathodically, and that unlike polarographic waves, the curves are peaked. This is a consequence of the use of stationary electrode: as the potential moves into the region where the substrate is reduced (or oxidized), the region adjacent to the electrode becomes depleted of material, and the current decreased.

The experimental feature of interest in cyclic voltammetry is this: after the stationary electrode polarogram of a substance has been measured by sweeping past the peak potential, Ep, the direction of voltage scan is reversed. This is done by causing the potential of the working electrode to vary as a cyclic triangular wave (Figure 1.1), hence the name of the technique. Either a single cycle (from E1 to E2 and back to E1) or many cycles may be carried out. Typical cyclic voltammograms are illustrated in Figure 1.3. It can be seen from the figure that cyclic voltammogram behavior can exhibit a variety of forms. The shape of the cyclic voltammogram is highly dependent on the relative rates of electron transfer, mass transport, and any chemical reactions occurring at the electrode surface; this enables one to deduce a great deal about the course of an electrode process from the cyclic voltammogram. Scan rates can be varied over a wide range (0.01-10,000 V/sec), providing, as will be seen, an extremely useful experimental parameter.[10]

In addition, cyclic voltammetry can inform the kinds of redox reactions occurred. The redox reaction can be classified into three types: reversible, quasi-reversible and irreversible. For a reversible process, the separation between the peak potentials is given by $\Delta Ep = Epc-Epa = 0.059/n$

where Epc = cathodic peak potential

Epa = anodic peak potential

n = number of electrons transferred

In addition, the ratio of the reverse-to-forward peak currents, Ipa/Ipc is unity. For quasi-reversible system, the voltammograms are more drawn out and exhibited a larger separation in peak potentials compared with a reversible system. For irreversible process, the individual peak was reduced in size and widely separated. The redox reaction can be classified into three types showed in Figure 1.2.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

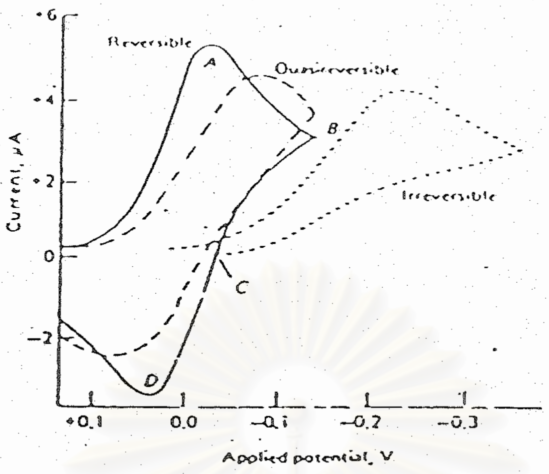


Figure 1.2 The cyclic voltammogram of three types of redox reactions

Important parameters in cyclic voltammetry are the cathodic peak potential Epc, the anodic peak potential Epa, the cathodic peak current Ipc and the anodic peak current Ipa. The relationship between the potential and the current is shown in Figure 1.3.

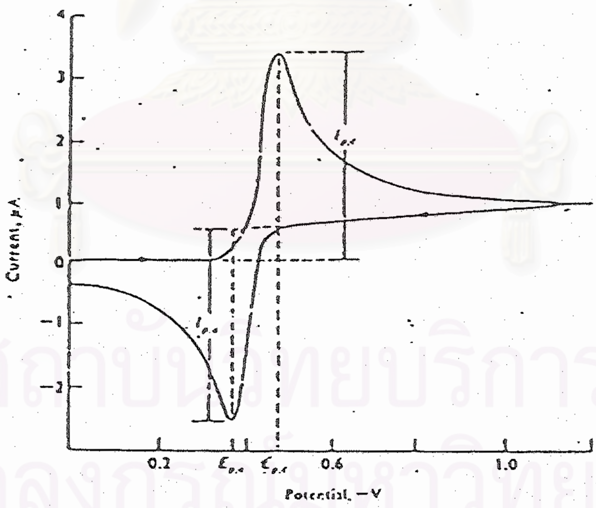


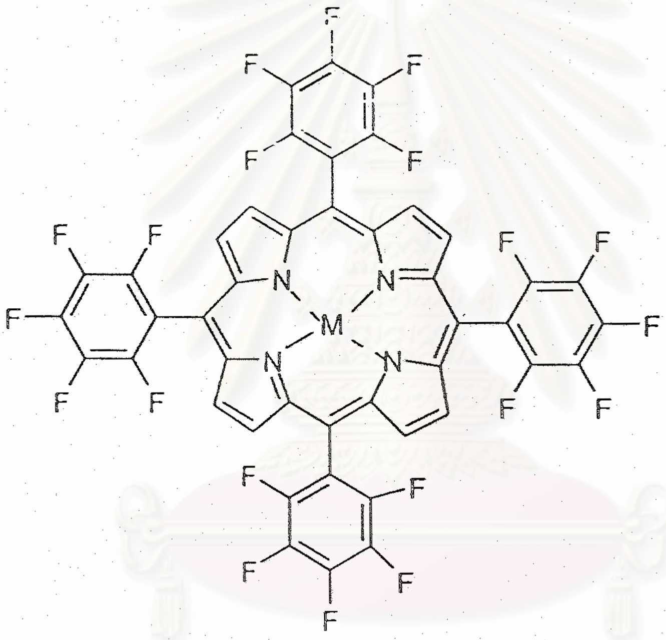
Figure 1.3 The relationship between the potential and the current

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

1.1 Literature review on transition metal complexes catalyzing oxidation of hydrocarbons

There are many systems which could selectively functionalize saturated hydrocarbons, especially using transition metal complexes as catalyst in oxidation reaction.

In 1995, Komiya and colleagues presented metalloporphyrin-catalyzed oxidation of alkanes with molular oxygen in the presence of acetaldehyde. In this system, the oxidation of cyclohexane using cobalt, manganese and ruthenium porphyrin catalysts bearing meso-pentafluorophenyl groups gave extremely high turnover numbers.[11]



meso-pentafluorophenylporphyrin

Furthermore, Ganeshpure and his colleagues reported that oxo-bridged polynuclear manganese(II) *N,N'*-1,2-cyclohexyl-1,2-dieyl-bis(salicylideneiminate) complexes was employed in the oxidation reaction of cyclohexane to cyclohexanone and cyclohexanol using *tert*-butylhydroperoxide (TBHP) or hydrogen peroxide (H_2O_2) as oxidant. Cyclohexanone was found to be a major product in good yield (72%).[12]

In 1996, Ganeshpure and colleagues reported that manganese(II) *N-N'*-ethylene bis(salicylideneaminonato) and analogous complexes were used in the oxidation reaction of cyclohexane to cyclohexanone and cyclohexanol at room temperature by TBHP as oxidant in acetronitrile. It was found that manganese(II) *N*,*N*′- ethylene bis(salicylideneaminonato) was the best catalyst. This complex provided 86% cyclohexanone and 14% cyclohexanol.[13] In the same year, Tembe and his colleagues found that the polynuclear manganese(III) Schiff base complexes were utilized in the oxidation reaction of cyclohexane at room temperature by using TBHP or H_2O_2 as oxidant in acetonitrile. These complexes provided cyclohexanone as a major product.[14]

In 1997, Punniyamurthy and colleagues reported that cobalt (II) complex derived from Schiff bases could be used as an efficient catalyst during the oxidation of wide range of organic substrates (*e.g.* alkanes and alkenes) with dioxygen in the presence of aliphatic aldehydes or ketones. These studies also demonstrate the role of ligands on cobalt in controlling the chemoselectivity of these oxidations.[15]

1.2 Literature review on iron complexes catalyzing oxidation of hydrocarbon

Examples involving the hydrocarbon oxidation catalyzed by iron complexes in recent years could be summarized as follows:

In 1986, Miyamoto and his colleagues developed iron (III) porphyrin system for the epoxidation of olefins (styrene, α-methylstyrene, cyclohexene and cyclooctane). The total yield of the product when using Mn(III) porphyrin as catalyst was similar to those employed Fe(III) porphyrin catalyst. However, in cyclohexene and cyclooctene epoxidation, the yields of these products using Fe(III) porphyrin were considerably higher than Mn(II) porphyrin.[16]

In 1989, Mansuy and co-workers reported the use of Fe(III) and Mn(III) porphyrins to catalyze cyclooctene epoxidation and cyclooctane oxidation. Effectively, cumylhydroperoxide in the presence of these metalloporphyrins has shown a poor ability to epoxidize alkenes but reacted well with alkanes to form alcohols and ketones.[17]

In 1990, Sanderson and his colleagues reported the production of ketones and alcohols by reacting an alkane with a hydroperoxide in the presence of a transition metal porphyrin catalyst. An isobutene oxidation gave better yield by using Fe(III) and Mn(III) porphyrins as catalyst.[18]

In 1994, Barton and colleagues presented a new methodology for the selective transformation of saturated hydrocarbons into ketones and alcohols. A crucial aspect of this new process is that no reaction solvent is required since the Fe(III) and Cu(II) complexes used are completely soluble in the hydrocarbon substrates. Although the reaction is slow, the addition of catalytic amounts of pyridine was found to enhance the rate of the process and affact an augmented selectivity towards the formation of ketone.[19]

In 1996, Nuntasri and Loayfakajohn showed that the iron Schiff base complexes, especially $(Fesalen)_2O$, exhibited the catalytic ability towards the oxidation of alkenes in pyridine/zinc-acetic acid system. Cyclohexane and cyclooctane could selectively be oxidized to mainly ketone at room temperature and atmospheric pressure. The efficiency of this oxidation system could be enchanced by addition of ascorbic acid or by stepwise addition of zinc powder.[20]

In 1997, Koda *et al.* presented aerobic oxidation of cyclohexane to yield cyclohexanone and cyclohexanol in the presence of Fe(III) porphyrin catalyst bearing meso-pentafluorophenyl group. The yield of products reached a maximum value at the pressure close to the critical pressure of CO_2.[21]

In 1998, Schuchardt and colleagues reported that the presence of cyclohexane soluble iron and copper catalysts, *tert*-butyl hydroperoxide selectively oxidized cyclohexane to cyclohexanone and cyclohexanol. Under 24 h, the conversions were 4 to 5% and the selectivities above 90%. Under 25 bar of oxygen at 70°C for 24 h, conversion with the iron catalysts are 9% but selectivities were below 80%, as large amounts of adipic acid are also formed. Reaction in the presence of cyclohexanone showed that the iron catalysts deactivated by complexation with the adipic acid formed by its over-oxidation.[22]

In 1999, Nam and colleagues reported that iron (III) porphyrin complexes had been used as model compounds to mimic the chemistry of cytochrome P-450 enzymes that were capable of catalyzing of cyclohexane and cyclooctane with H_2O_2 as oxidant. The iron porphyrin complex was able to oxidize cyclohexane with high product yields of cyclohexanol at –40 °C.[23]

In 2002, Machado and colleagues reported the biomimetic metalloporphyrin of Fe(III) and Mn(III) in cationic form. These compounds were characterized by several techniques, showing that metalloporphyrins molecules were adsorbed at the surface of the clay platelet crystals. The catalytic activities of the intercalated complexes for the oxidation of alkane were dependent upon the concentration of the porphyrin immobilized in the clay and factors such as the metal ion species in the porphyrins, choice of solvent, and concentration of the iodosylbenzene oxidant. Good selectivity to cyclohexanol instead of cyclohexanone was observed for the catalytic oxidation of cyclohexane by iodosylbenzene.[24]

In 2003, Guo and colleagues reported the use of simple μ-oxo-bis[tetraphenylporphinatoiron(III)] as a catalyst for the selective oxidation of cyclohexane into cyclohexanone and cyclohexanol with air. $[TPPFe^{III}]_2O$ has been used for the first time as a catalyst for the aerobic liquid phase oxidation of cyclohexane in absence of any cocatalyst or coreductants. The oxidation of cyclohexane catalyzed by a very small amount of $[TPPFe^{III}]_2O$ gave 90% selectivity to cyclohexanol and cyclohexanone at 12.55% yield and catalyst turnover number 90,000 under the conditions of 398 K and 0.6 Mpa. The oxidation of cyclohexane catalyzed by $[TPPFe^{III}]_2O$ with air had higher yield and greater turnovers.[25]

1.3 Literature review on cyclic voltammetry

Cyclic voltammetry can provide the information of the reaction and can be used to examine the electrochemical properties of complexes.

In 1993, Issa and his colleagues found that cyclic voltammetry could be used for examining the mechanism of the reduction recaction of [*N*,*N*′-1,2-phenylenebis(salicylideneiminate)] Co(II) complex and addressed that one electron of this complex was transferred in three steps.[26] In the same year, Sawyer and his colleagues reported that bis(bipyridine)copper(II) complex was used as a catalyst to activate oxygen for the dehydrogenation of alcohols. The cyclic voltammetry was employed to investigate the catalytic transformation of alcohol to aldehyde. It was found that the rate of the process of primary alcohols was faster than secondary alcohols and α-allylic alcohols.[27]

In 1994, Tsuchida and colleagues investigated deoxygenation of VO(salen) in strongly acidic non-aqueous media by cyclic voltammetry. It was found that cyclic voltammograms confirmed that the oxidation of VO(salen) by oxygen to produce VO(salen) was proved feasible in the presence of acid.[28]

In 1997, Bottcher and his colleagues investigated the spectroscopic and electrochemical properties of Co(III) (acacen) [H_2acacen = bis(acetylacetone)ethyl diiimime] and related ligand. Electronic structure calculation indicated that the adsorption between 340 and 378 nm in Co(II)(acacen) spectra was attributable to the lowest intraligand charge-transfer transition. Cyclic voltammetry of Co(II)(acacen) revealed irreversible at a potential –0.8 V and reversible process at a potential –1.6 V.[29]

In 1998, Sinclair and his collegues presented the preparation and electrochemical properties of MoO(cat)(ssp) complex by cyclic voltammetry. The result disclosed that the six-coordinate MoO^{4+} species exhibited reversible Mo(VI/V) electrochemical at potential 0.1 V.[30]

In 1999, Natiwatvittaya and Sawat synthesized metal–Schiff base complexes and reported the redox property of this complex by cyclic voltammetry technique. The complexes namely VO(salen), Cu(salophen) and Ni(salophen) displayed quasi-reversible reaction while Cu(sap), Ni(sap) and Cr(sap) displayed irreversible reaction.[31]

In 2000, Canadas and his colleagues presented that the reactions of benzilbisthiosemicarbazone(LH6) with nickel, cobalt and iron chloride and nitrate gave different complexes depending on the salts used and the working condition. Electrochemical behaviour of complexes studied by cyclic voltammetry showed metal-center reduction process for all of them. The reduction/oxidation potentials values depended on the structures of complexes. Nickel complexes exhibited waves corresponding to Ni(III)-Ni(II) process. Electrochemical response of iron complexes depended on the presence of chloride ions.[32]

In 2001, Buchmann and colleagues presented that the electrochemical oxidation of Ir(tdppcyme)(CO)Cl(*cis*,*cis*-1,3,5-tris(di-phenylphosphine)-*cis*,*cis*-1,3,5-tris (methoxy carbonyl) cyclohexane, was investigated in dichloromethane 0.1 M tetrabutylammonium hexafluorophosphate at Pt electrodes with cyclic voltammetry, chronoamperometry and chronocoulometry, as well as preparative electrolysis. While the primary one-electron oxidation to Ir(II) appeared quasi-reversible in the redox

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

reaction, the longer time scale of electrolysis allowed the formation of an insoluble product by a follow–up reaction.[33]

In 2002, Nigovic and colleagues presented that the electrochemical reduction of various aminohydroxamate complexes of iron (III), such as alanine-, serine-, lysine-, histidine-, and glutamo-γ-hydroxamate, has been investigated in aqueous solution by cyclic voltammetry on hanging mercury drop electrodes to determine the mechanism involved in the electron transfer processes. In all the studied cases, the iron(III) complexes, with the exception of histidinehydroxamate, have been found to undergo reversible reductions followed by irreversible chemical reaction. Rate constants for the irreversible dissociation of iron(II) complexes were calcurated. The typical quasi-reversible pattern for the reduction of histidinehydroxamate was attributed to the different coordination mode. The observed differences in redox potentials between the investigated complexes suggest that the electronic effort of the substituent on the carbonyl group, involvesd in the coordination to the iron center, may modify the donor properties of the oxygen atoms of the hydroxamate moiety.[34]

1.4 Literature review on the relationship of electrochemical and catalytic properties

The report on relationship of electrochemical and catalytic properties has been found recently. In 1998, Malachowski and his colleagues synthesized $[Cu-_2(tpmc)X](ClO_4)_3$ from the dinucleating octadentate ligand tetra-1,4,8,11-(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane(tpmc) (with X= F, Cl, Br or I). Catalysis of the oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylquinone using these complexes and the redox properties of these complexes was investigated. All complexes displayed reversible reaction with one–electron reductions. Electrochemical data showed a non-linear relationship between the complexes ability to oxidize 3,5-di-*tert*-butylcatechol and their reduction potentials.[35]

In 2001, Hoogenraad and his colleagues synthesized new manganese(III) complexes of Hphox(2-(2′-hydroxyphenyl)-oxazoline) and Hclphoxd(2-(5′-chloro-2-hydroxyphenyl)-oxazoline) and subjected to cyclic voltammetry examination. Cyclic voltammograms of these complexes showed quasi-reversible reaction. In addition, these complexes provided good results in the epoxidation of styrene by hydrogen peoxide.[36]

In 2002, Hoogenraad and his colleagues synthesized MnL_3(HL being 2(2′-hydroxyphenyl)oxazoline ligands) and examined the redox property. Cyclic voltammetric experiments showed the electrochemically quasi-reversible Mn-II/Mn(III) and reversible Mn(III)/Mn(IV). All complexes are active oxidation catalysts with hydrogen peroxide as the oxidant. In the oxidation of styrene, up to 220 turnover numbers were obtained towards styrene oxide.[37]

In 2003, Salimi and his colleagues reported that the sol-gel technigue was used to construct nickel pentacyanonitrosylferrate (NiPCNF) modified composite ceramic carbon electrodes. The cyclic voltammetry of the resulting surface modified CCE under optimum conditions showed a well-defined redox couple due to the [Ni^{II} FeIII/II$(CN)_5$NO] system. The electrochemical properties and stability of the modified electrode were investigated by cyclic voltammetry being about 1.1 S-1 and 0.55, respectively. Sulfite has been chosen as a model to elucidate the electrocatalytic ability of NiPCNF-modified CCE propared by one-or two–step sol-gel technique. The modified electrode showed excellent electrocatalytic activity towards the SO_3^{2-} electro oxidation in pH range 3-9 in comparison with CCE modified by homogeneous mixture of graphite powder. Sulfite was determined amporometrically at the surface of this modified electrode at pH 7. Under the optimized conditions the calibration curve is linear in the concentration range 2 μM to 2.0 mM. The detection limit and sensitive are 0.5 μM and 13.5 nA/μM. The modified carbon ceramic electrode containing nickel pentacyanonitrosylferrate displayed good repectability and short response time 90%.[38] Furthermore, Akilan and his colleagues reported that a series of new mono and binuclear copper(II) complexes $[CuL^{1a\text{-}e}H_2](ClO_4)_2$ and $[Cu_2L^{1a\text{-}e}(ClO_4)](ClO_4)$, where L is a macrobicyclic tricompartmental ligand obtained from the condensation of the precursor compound with various diamines have been synthesized. Electrochemical studies of the complexes revealed that all the mononuclear copper(II) complexes showed a single quasi-reversible one-electron transfer reduction wave (E^1pc= -0.76 to –0.84 V) and the binuclear complexes displayed two quasi-reversible one-electron transfer reduction (E^1pc= –0.86 to –1.01

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

V E^2pc = -1.11 to –1.43 V) in cathodic region. The calculated initial rate constant values for the oxidation of catechol to *o*-guinone ranges from 8.52 x10^{-3} to 3.08 x 10^{-2} min^{-1}) was higher than the mononuclear copper(II) complexes (8.52x 10^{-3}-9.67x10^{-3} min^{-1}).[39]

1.5 The research goal

The purpose of this research can be summarized as follows:

1. To synthesize Schiff base, 1,3-dicarbonyl ligands and to characterize ligands.
2. To synthesize Schiff base, 1,3-dicarbonyl, carboxylate iron complexes and to characterize iron complexes.
3. To study the cyclohexane oxidation using iron complexes.
4. To study the redox reaction using glassy carbon as a working electrode.
5. To study the relationship between electrochemical and catalytic properties of iron complexes.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER II

EXPERIMENTAL

2.1 General procedure

Melting points were determined on a Fisher-Johns melting point apparatus or Electrothermal digital melting point apparatus model IA9100 and are uncorrected. Column chromatography was carried out on silica gel (Merck Kieselgel 60, 70-230 mesh). Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck Kieselgel 60PF$_{254}$).

2.2 Instruments

The FT-IR spectra were recorded on a fourier transform infrared spectrophotometer on Nicolet model Impact 410: solid samples were mixed with potassium bromide to form pellets and liquid samples were incorporated to sodium chloride cells. The ^{1}H- and ^{13}C-NMR spectra were obtained in deuterated chloroform ($CDCl_3$) or deuterated dimethylsulfoxide (DMSO-d_6) with tetramethylsilane (TMS) as an internal reference on a Bruker model ACF 200 spectrometer. The UV-visible spectra were recorded on diode array spectrophotometer on Hewlett Packard 8452A. Gas chromatography analysis was carried out on a Shimadzu gas chromatograph GC-9A and GC-14 A instrument eguipped with flame ionization detector (FID) with N_2 as a carrier gas. The column used for chromatography was a capillary column type of DB-wax (30m x 0.250 mm) from J&W Scientific.

2.3 Chemicals

The reagents for synthesizing ligands and iron complexes were purchased from Fluka and Merck chemical companies. All solvents used in this research were purified prior to use by standard methodology except for those which were reagent grades.

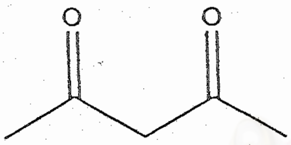
สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2.4 Syntheses of ligands

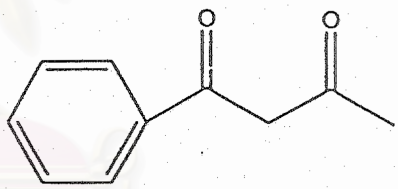
2.4.1 Syntheses of 1,3-dicarbonyl ligands[40]

Substituted acetophenone (1 mol-equiv) in dry benzene 50 mL and ethyl benzoate or ethyl benzoate derivatives (1 mol-equiv) in dry benzene 50 mL were added dropwise to a suspension of 60% NaH. The mixture was refluxed and monitored the progress of the reaction by thin layer chromatography using 30% EtOAc/hexane as an eluent. The reaction mixture was cooled down to room temperature, quenched with 10% HCl, extracted with EtOAc, washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was recrystallized from an appropriate solvent or purified by silica gel column chromatography.

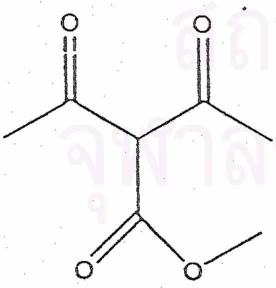
1,3-Dicarbonyl ligands namely, acetylacetone (1), benzoyl acetone (2), methyl 2-acetylacetoacetate (3), ethyl benzoylacetate (4) are depicted as shown below.



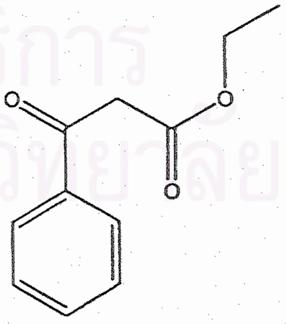
acetylacetone



benzoylacetone



methyl 2-acetylacetoacetate

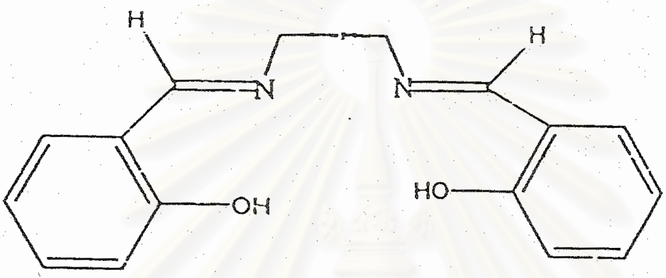


ethyl benzoylacetate

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2.4.2 Syntheses of Schiff base ligand[41]

Salicylaldehyde (2 mol –equiv) was slowly added to a solution of ethylenediamine (1 mol-equiv) in methanol. The solution was stirred at room temperature until the preciptitate occurred. The precipitate was filtered off and recrystallized by an appropriate solvent. Schiff base ligand namely salen (5) is shown below.



Salen (s)

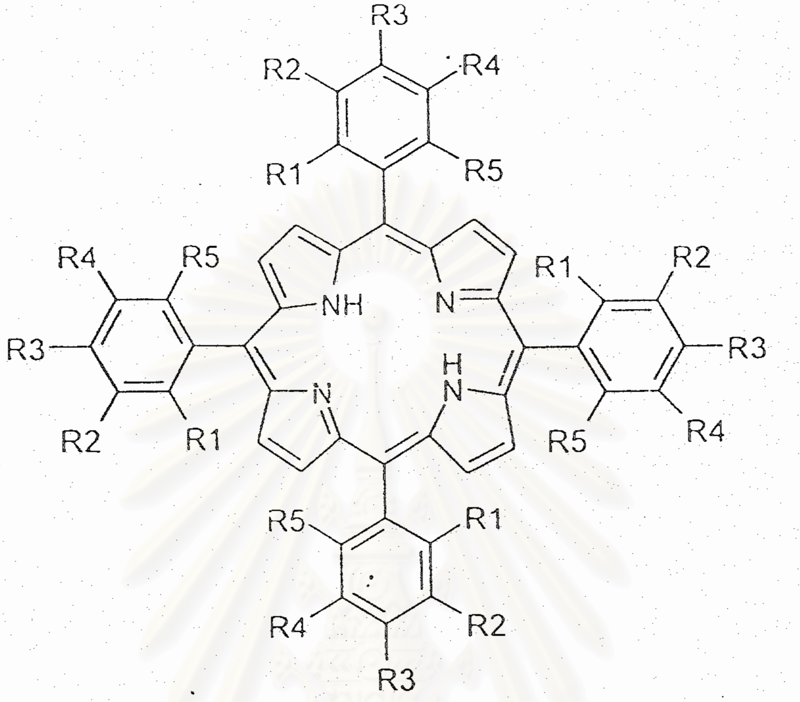
Bis(salicylaldehyde)-N,N-ethylenediimine(5)(salen)[42] : Bright yellow plate crystal (96%), m.p.125-126°C (95% ethanol), R$_f$ 0.60 (dichloromethane). IR (KBr, cm^{-1}) 3590-3270, 3070, 2950-2870, 1620, 1600, 1450, 1250 and 1180; ^{1}H-NMR (CDCl$_3$) δ (ppm): 2.37 (6H, s), 3.97 (4H, s), 6.78(2H, dt, J = 7.70, 1.28 Hz), 6.91 (2H, dd, J = 8.55, 1.28 Hz), 7.27 (2H, dt, J = 7.91, 1.28 Hz) and 7.52 (2H, dd, J = 7.91, 1.50 Hz); ^{13}C-NMR (CDCl$_3$) δ (ppm): 14.7 (2C), 117.4 (2C), 118.5 (2C), 119.4 (2C), 128.1 (2C), 132.4 (2C), 163.1 (2C) and 172.7 (2C).

2.4.3 Syntheses of porphyrin ligands[43]

Freshly distilled pyrrole 2.8 mL (0.04 mol) was added in a 250 mL round–bottom flask, along with 0.04 mol of an interested aromatic aldehyde and 150 mL of glacial acetic acid or propionic acid. The mixture was refluxed for 2-3 hours. The solution was allowed to cool to room temperature, then placed the flask in an ice bath. Dark purple crystals were formed. The crystals were removed by vacuum filtration. The collected crystals were washed with ice-cold methanol and warm distilled water.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Finally, the crystals were allowed to dry at room temperature. Porphyrin ligand is depicted as shown below.



$R_1 = H, R_2 = OCH_3, R_3 = OCH_3, R_4 = OCH_3, R_5 = H$

Porphyrin

5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)-porphyrin(6)[44]: Purple needle crystal (32%), R_f 0.30 (hexane:dichloromethane; 3:2) UV(λmax, nm) 420, IR (KBr, cm^{-1}): 3447, 3308, 2933, 1579, 1504, 1461, 1406, 1356, 1236, 1122, 1005, 925, 803 and 726; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.98 (24H, d, $J = 8.35$Hz), 4.19 (12H, s), 7.48 (8H, d, J=7.44 Hz) and 8.97 (8H, s).

2.5 Syntheses of iron complexes

2.5.1 Syntheses of 1,3-dicarbonyl iron complexes

Tris –(benzoylacetonato)-Iron(III): $Fe(BZA)_3$[45]

Ferric chloride anhydrous 0.16 g (0.99 mmol) and benzoylacetate (BZA) 0.46 g (2.80 mol) were dissolved in ethanol 50 mL. To this solution an aqueous solution (10 mL) of sodium acetate 0.15 g was added. The mixture was left

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

to stand overnight at room temperature to give dark red solid. It was collected by filtration and recrystallized from hexane.

Utilizing the above protocal, ethyl benzoylacetate (2.80 mol) and methyl-2-acetylacetoacetate (2.80 mol) were employed instead of benzoylacetone (BZA) for synthesizing Fe(ethylbenzoylacetate) and Fe(methyl-2-acethylacetoacetate), respectively.

Tris-(benzoylacetonato)-Iron (III) Fe(BZA)$_3$: Dark red solid (85%), mp 218-220°C, IR (KBr,cm^{-1}) :1590, 1542, 1451, 1374, 1298, 1000, 954 and 710.

Tris-(ethylbenzoylacetonate)-iron (III)[Fe(et)$_3$]: Brown solid (80%), m.p. >300 °C, IR (KBr, cm^{-1}): 3406, 1624, 1508, 1398 and 1072.

Tris–(methyl-2-acetylacetoacetonate)-iron(III)[Fe(met)$_3$]: Dark brown solid (85%), m.p. >300 °C , IR(KBr, cm^{-1}): 1638, 1532, 1432, 1259, 1091 and 801.

Tris-(2,4-pentanedionato)-Ferric(III): [Fe(acac)$_3$][46]

Ferric chloride anhydrous (2.00 g, 10 mmol) was dissolved in distilled water 3 mL and the mixture was heated until homogeneity. After that concentrated ammonium hydroxide 4.5 mL was dropped slowly. The solution was stirred about 15-20 min on water bath (80 °C) and brown precipitation occurred. The brown solid was filtered off and washed with distilled water until no more chloride detected. Place the precipitate in Erlenmeyer flask, acetylacetone (6 mL, 10 mmol) was dropped slowly over 35 min on water bath (80 °C) and the precipitation of red solid occurred. The products were filtered and recrystallized by 95% ethanol.

Tris-(2,4-pentanedionato)-Ferric(III) [Fe(acac)$_3$]: Red solid (90%), m.p.180-185 °C, IR (KBr, cm^{-1}):1569, 1522, 1357, 1268, 1018, 929, 722 and 662.

2.5.2 Syntheses of Schiff base iron complexes

Bis (salicylaldehyde)-N,N-ethylenediimine-Iron(II): [Fe(salen)$_2$][47]

To an aqueous ethanolic solution of Schiff base (1 mol-equiv) and $FeSO_4$ (1 mol-equiv), a solution of $CH_3COONa.3H_2O$ (16.9 mmol) was added. A crystalline solid formed immediately. The mixture was further refluxed for approximately 3 h and then cooled overnight. The solid was washed with H_2O,EtOH and Et_2O and dried *in vacuo.*

Bis(salicylaldehyde)-N,N-ethylenediimine-iron(II),Fe(salen)$_2$: Red brown fine powder (89%), m.p. 297-300 °C. IR (KBr, cm^{-1}): 3500, 3015, 2903, 1625 and 969.

μ-oxobis[Bis(salicylaldehyde)N,N –ethylenediimine] Iron(III) : (Fe salen)$_2$O [48]

Salen 2.68 g (0.01 mol) was dissolved in hot methanol 50 mL and stirred until ligand was completely dissolved. Ferric chloride 2.70 g (0.01 mol) was dissolved in methanol containing potassium hydroxide 0.56 g (0.01 mol) and added dropwise to the ligand solution. The precipitate was occurred , filtered and recrystallized with chloroform 2-3 times.

μ-oxobis[Bis(salicylaldehyde)N,N–ethylenediimine]iron(III) (Fesalen)$_2$O: Black brown powder (49%), m.p. 120 °C IR(KBr, cm^{-1}): 3040, 2930, 1629, 1600, 1450, 1311 and 1127.

2.5.3 Syntheses of Fe(porphyrin)[49]

FeSO$_4$ 1.82 mmol was dissolved in DMF. Then a solution of FeSO$_4$ was added to a solution of porphyrin ligand in 70 mL of DMF. The mixture was heated to 80 °C at least for 3 hours using an oil bath. After that, the mixture was allowed to cool down to room temperature and added an equal volume of water. The crystals were removed by vacuum filtration.

Tetra(3,4,5-trimethoxyphenyl)-porphyrin iron(II) Fe(porphyrin): purple plate solid (85%), R$_f$ 0.41 (hexane:dichloromethane; 4:1), UV (λ_{max}, nm) 422, IR(KBr, cm^{-1}): 2943, 1581, 1500, 1462, 1406, 1350, 1237, 1125, 1000, 937, 812 and 725.

2.5.4 Syntheses of Fe(salen)Cl[50]

To a solution of ferric(III) chloride anhydrous 0.10 mol in ethyleneglycol-water-methanol (1:1:3) 300 mL were added salicylaldehyde 0.20 mol and ethylene diamine 0.10 mol. After the mixture was heated at about 110° C for about 30 min sodium carbonate (0.06 mol) was added in small portions to the solution, followed by refluxing of the solution for about 3 to 4 hours on concentrating the solution a reddish brown precipitate was recrystallized from 80% ethanol to give reddish orange crystals of the desired complex 19.6 g (50% yield). The crystals are highly soluble in

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

methanol and ethanol, fairly soluble in water and almost insoluble in bezene and diethyl ether.

2.5.5 Syntheses of Fe(picolinate)$_3$, Fe(benzoate)$_3$ and Fe(4-nitrobenzoate)$_3$[51]

Carboxylic acid 22 mmol was dissolved in dilute sodium hydroxide solution (0.88 g NaOH in 20 mL distilled water) at 80°C. After stirring solution until homogeneity, Fe(III) trichloride anhydrous (1.184 g, 7.3 mmol) dissolved in 10 mL distilled water was added in one portion causing the precipitation of solid after stirring for 30 min . The precipitate was collected and dried *in vacuo.*

2.5.6 Syntheses of Fe(alanine)$_3$[52]

Alanine 2 mmol was dissolved in 5 mL of water in a small beaker. Calculate the volume of 6 M NaOH required to remove one proton from each mole of alanine, then add this volume of 6 M NaOH to the alanine solution dropwise from a faster pipet weigh 0.233 g (1 mmol) of $CrCl_3 .6H_2O$ and dissolve in to the alanine solution with swirling. When addition is complete swirl the beaker for about a minute to allow reaction to come to completion.

The complex will precipitate from solution as the ferric chloride solution is added for these the mixture may simply be filtered after swirling to remove the product. The solid may be washed 2 or 3 times with small volumes of acetone, suctioned the product dried and collected.

2.5.7 Synthese of Fe(dimethylglyoxime)[53]

Dimethylglyoxime 1 g was dissolved in 95% ethanol 100 mL. Then water 100 ml was added, stir the solution until homogeneous. Drop ammonia into the former solution until pH = 8. To those solution an aqueous solution of hydrochloric acid 1:1 was added. The mixture was heated at 70-80° C. Dimethylglyoxime 50 mL was added in solution, stir the solution until homogeneously. Drop ammonia 1:1 until pH 8.5.The mixture was left to stand overnight at room temperature. The precipitate was accurred, filtered and washed with warm water 3-4 times, 30% ethanol 1 time. The precipitate was dried at 110-130° C for 2 h and cooled in desiccator for 30-40 min.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Fe(dimethylglyoxime): Brown solid (80%) , m.p. 295-300°C, IR (KBr, cm^{-1}): 1633, 3138, 1561, 1398 and 1115.

2.5.8 Synthese of carboxylate complexes[51]

Stearic acid (6.26 g, 22 mmol) was dissolved in dilute sodium hydroxide solution (0.88 g NaOH in 20 mL distilled water) at 80°C. After the solution was stirred until homogeneity, selected transition metal salts or compounds (7.3 mmol) dissolved in 10 ml distilled water was added in one portion causing the precipitation. The mixture was allowed to stir for another 30 min, then the precipitate was collected and dried *in vacuo.*

By using this method ology, palmitic acid (22 mmol) and naphthanic acid (22mol) was employed instead of stearic acid for synthesizing of Fe(III)palmitate and Fe(III)naphthenate, respectively.

Fe(III)sterate: Orange solid (78%), m.p.94-96 °C, IR (KBr, cm^{-1}): 2912, 2846, 1705, 1583, 1461 and 723.

Fe(III)palmitate: light orange solid(81%), m.p. 98-100 °C, IR (KBr, cm^{-1}): 2905, 2847, 1703, 1573, 1458 and 721.

Fe(III)stearate: orange solid(80%), m.p. 94-96 °C, IR (KBr, cm^{-1}): 2912, 2846, 17 1583, 1461 and 723.

2.6 Oxidation of cyclohexane catalyzed by iron complexes

The oxidation reaction of cyclohexane to cyclohexanone and cyclohexanol was examined utilizing and iron complexes as a catalyst.

General procedure for the oxidation of cyclohexane[54]

Catalyst (0.25 mmol), cyclohexane (30 mmol), pyridine (14 mL), acetonitrile (14 mL) and 30% H_2O_2 (15 mmol) or 70% TBHP (15 mmol) was placed in an Erlenmeyer flask. The mixture was stirred continuously for 24 h at room temperature for H_2O_2 or at 70° C for TBHP. After the reaction was proceeded for a designed period of time, 1 mL of the reaction mixture was taken and acidified with cold 25% H_2SO_4 and extracted with diethyl ether. The combined extracts were washed with

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

saturated solution of $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4 and analyzed by GC using cyclododecane as the internal standard substance.

Injector temperature: 200 °C

Time (min)	Temperature (°C)
0	60
2	60
20	150
23	150

Detector temperature: 200 °C

Carrier gas = 1

Range = 2

At ten = 4

Speed = 4

Stop time = 23

2.7 Examination of redox reaction of iron complexes

The iron complexes were explored for redox property by cyclic voltammetry technique following the general procedure described below.

The iron complex (0.001 mol) was dissolved in 0.10 M $C_{16}H_{36}FNP$ solution. The sample solution was examined the redox reaction in electrochemical cell using glassy carbon as a working electrode, silver wire as a reference electrode and platinum wire as an auxillary electrode.

2.8 Kinetic study on the reaction rate of cyclohexane oxidation

The general oxidation procedure of cyclohexane utilizing iron complexes : *Bis* (salicylaldehyde)-N,N-ethylenediimine-Iron(II), μ-oxobis[*Bis*(salicylaldehyde)*N*,*N* –ethylenediimine]iron(III) and *Tris* –(benzoylacetonato)-iron(III) as a catalyst was carried out. At different reaction time proceeded (60, 120, 240, 360, and 480 min), an aliquot from the reaction mixture was taken and analyzed by GC or examined by cyclic voltammetry.

CHAPTER III

RESULTS AND DISCUSSION

The main purpose of this research is to study the relationship between the electrochemical and the catalytic properties of catalysts. Cyclic voltammetry, one type of electrochemical techniques, is the most widely used technique for acquiring information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide consideration information of the thermodynamics of redox processes. One advantage of cyclic voltammetry is the examination of catalytic properties which could be further used for the selection of catalyst. The iron complexes were chosen as a model to be examined by cyclic voltammetry.

3.1 Syntheses and characterization of iron complexes

According to the procedure described in section 2.3.1, sixteen ligands were synthesized. The obtained ligands were confirmed their identities by IR, ^{1}H- and ^{13}C-NMR techniques prior to use for synthesizing interested iron complexes. The comparative results of physical properties, percentage yield and IR spectroscopic data of prepared iron complexes are presented in Table 3.1.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.1 Physical properties, percentage yield and IR spectroscopic of iron complexes.

Entry	Catalyst	Color	Melting point (°C)	%yield	IR data
1	Fe(porphyrin)	Purple plate	>300	85	3447, 2931, 1598, 1461, 1409, 1344, 1296, 1235, 1104, 974, 902, 796, 742
2	Fe(salen)	Brown solid	297-300	89	3500, 3015, 2903, 1625, 969
3	$(Fesalen)_2O$	Black brown solid	120-125	49	3040, 2930, 1629, 1600, 1450, 1311, 1127
4	Fe(dimetylglyoxime)	Brown solid	295-300	80	1633,3138,1561,1398,1115
5	$Fe(acac)_3$	Red solid	180-185	90	1569,1522,1357,1268,1018,929,722, 622
6	$Fe(stearate)_3$	Orange solid	94-96	78	2912,2846,1705,1583,1461,723
7	$Fe(palmitate)_3$	Orange solid	98-100	81	2905, 2847, 1703, 1573, 1458, 721
8	$Fe(naphthenate)_3$	Orange solid	125-130	80	2828, 2638, 1683, 1583, 1473, 927
9	Fe(salen)Cl	Reddish brown	240-245	80	3436, 1629, 1445, 753
10	$Fe(alanine)_3$	Brown solid	280-285	49	3390, 1631, 467
11	$Fe(4\text{-nitrobenzoate})_3$	yellow solid	>300	83	3419, 1693, 1583, 1349, 530
12	$Fe(benzoate)_3$	Light yellow solid	290-300	98	3447, 1603, 1573, 1414, 718, 671
13	$Fe(picolinate)_3$	Light orange solid	>300	18	3523, 1678, 1559, 1468, 1320, 1243
14	$Fe(benzoylacetonate)_3$	Red solid	218-220	85	1590,1542,1451,1374,1298,1000,954,710
15	$Fe(\text{methyl 2-acetylacetoacetate})_3$	Dark brown solid	>300	85	1638,1532,1432,1259,1091,801
16	$Fe(\text{ethyl benzoylacetate})_3$	Brown solid	>300	80	3406,1624,1508,1398,1072

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Iron complexes as shown in Table 3.1 could be easily synthesized with high yield. The color of iron complexes was varied depending on type of metal and ligand. From IR spectra, iron carboxylate complexes showed a significant absorption band of carbonyl C=O around 1600-1700 cm^{-1} while the C-O band stretching vibration was observed around 1400-1450 cm^{-1}. The IR spectra of 1,3-dicarbonyl iron complexes displayed a typical characteristic carbonyl C=O absorption band around 1550-1650 cm^{-1}.

3.2 Effect of iron complexes on cyclohexane oxidation

Four iron complexes, namely $Fe(naphthenate)_3$, $Fe(alanine)_3$, $Fe(benzoate)_3$ and $Fe(benzoylacetonate)_3$ were selected as a catalyst for conducting the oxidation reaction of cyclohexane. Two common oxidants: TBHP and H_2O_2 were utilized. The results are presented in Table 3.2.

Table 3.2 The oxidation of cyclohexane catalyzed by four selected iron complexes.

Entry	Catalyst	H_2O_2		TBHP	
		-one (mmol)	-ol (mmol)	-one (mmol)	-ol (mmol)
1	$Fe(naphthenate)_3$	trace	trace	0.775	0.640
2	$Fe(alanine)_3$	0.152	0.154	0.371	0.098
3	$Fe(benzoate)_3$	0.345	0.316	0.437	0.245
4	$Fe(benzoylacetonate)_3$	0.915	0.593	1.885	1.103

Reaction conditions: cyclohexane (30 mmol), iron complex (0.25 mmol), pyridine and acetonitrile (1:1 V/V) (28 mL), H_2O_2 (15 mmol) at room temperature (30 °C) or TBHP (15 mmol) at 70 °C.

From Table 3.2, it was revealed that different iron complexes provided different amounts of the desired products. It is interesting to note that $Fe(naphthenate)_3$ and $Fe(benzoylacetonate)_3$ gave better results than other iron complexes. From recent literatures, Inpornvichitr and Tongkratok reported the use of Fe(porphyrin) and Fe(salen) as a catalyst for cyclohexane oxidation. These reactions were carried out in pyridine/acetic acid or pyridine/acetonitrile as solvents using H_2O_2 and TBHP as an oxidant at 50° C and 70°C, respectively.[55,56] It was found that the amount of the desired products derived from the reactions using TBHP as an oxidant was much superior to those employing H_2O_2 because TBHP has polarity less than H_2O_2. This outcome was similar to the results displayed in Table 3.2.

3.3 Analysis of the redox reaction utilizing iron complexes by cyclic voltammetry

Electrochemical techniques can be used for following the progress of the reaction. These processes take place at the electrode-solution interface by fitting the substrate at the surface of electrode. Cyclic voltammetry, one of the electrochemical techniques is the most effective and versatile electroanalytical technique available for the mechanistic study of redox systems. This technique can be used for studying the relationship between the current and the potential by rapidly scanned a potential. In this research the redox property of iron complexes was studied by cyclic voltammetry using a glassy carbon electrode as a working electrode, silver wire as a reference electrode and platinum wire as an auxillary electrode. Considering the results derived from previous section, the hypothesis was then arose whether the cyclic voltammetry of the iron complexes exhibiting reversible and quasi-reversible reactions would provide better yield of the desired products than those possessing irreversible reactions. From the literature review, to our best knowledge it was found that there was no report concerning with the study on the relationship between catalytic and electrochemical properties of iron complexes using cyclic voltammetry.

3.3.1 Study the redox reaction of iron complexes using a glassy carbon electrode

A glassy carbon electrode is a carbon electrode which its microstructures consist of layers of condensed, six-membered aromatic rings with sp^2-hybridized carbon atom trigonally bonded to one another. The cyclic voltammograms of six iron complexes examined using a glassy carbon electrode and voltage scan rate of 0.05 V/s are presented in Figures 3.1-3.6 and Table 3.3.

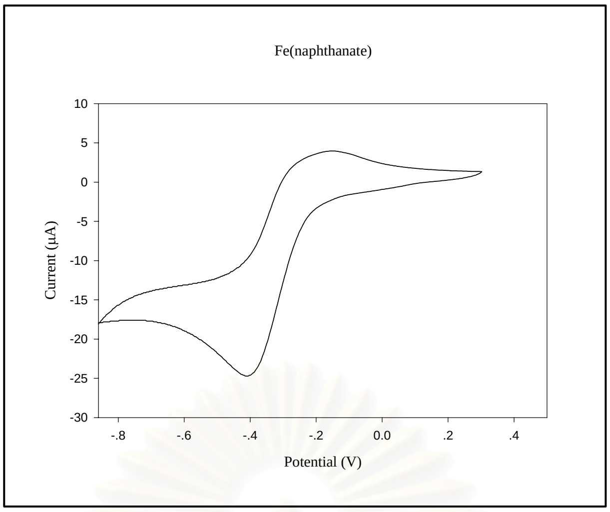
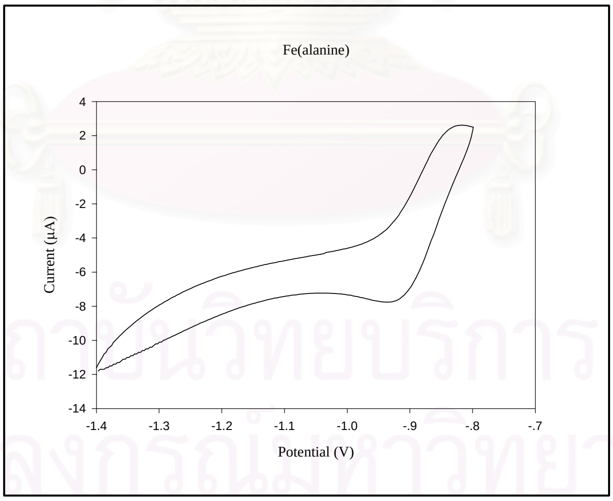


Fig 3.1 Cyclic voltammogram of 0.01 mol Fe(naphthenate)$_3$ in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.1, the cyclic voltammogram of Fe(naphthenate)$_3$ showed the peak current, Ipa of 16.432 μA and Ipc of -23.431 μA. The ratio of Ipa/Ipc = 0.700 was far less than unity and ΔEp = 0.247 V which was larger than 0.059 V anticipated for quasi-reversible one-electron transfer reduction.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Fig 3.2 Cyclic voltammogram of 0.01 mol Fe(alanine)$_3$ in 0.1 M tetrabutylammonium hexafluorophosphate solution using the glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.2, it was found that the cyclic voltammogram of Fe(alanine)$_3$ showed the peak potential, Epc of -0.939 V which was anticipated for irreversible one-electron transfer reduction.

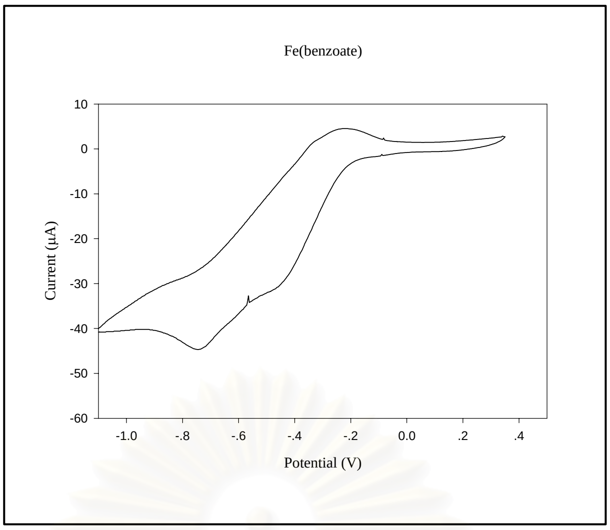


Fig 3.3 Cyclic voltammogram of 0.01 mol Fe(benzoate)$_3$ in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.3, the cyclic voltammogram of Fe(benzoate)$_3$ indicated the peak current, Ipc of -54.142 µA and Epc of -0.742 V which was anticipated for irreversible one–electron transfer reduction.

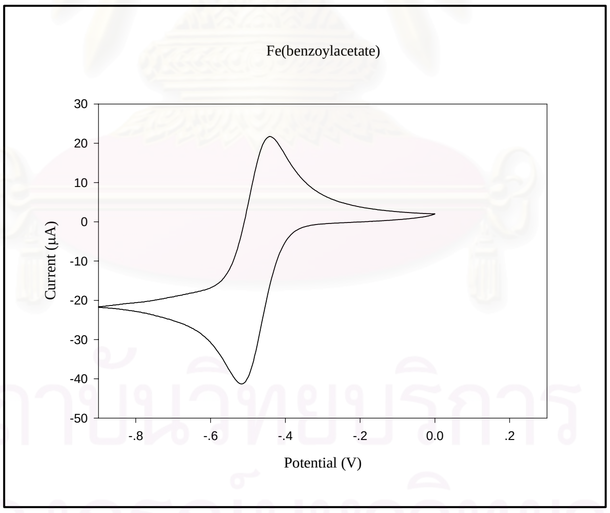


Fig 3.4 Cyclic voltammogram of 0.01 mol Fe(benzoylacetonate)$_3$ in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.4, the cyclic voltammogram of Fe(benzoylacetonate)$_3$ showed the peak current, Ipa of 33.465 µA and Ipc of -35.052 µA. The ratio of Ipa/Ipc = 0.955 which was nearly equal to unity and ΔEp = 0.070 V which was only slightly larger than 0.059 V anticipated for reversible one-electron transfer reduction.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

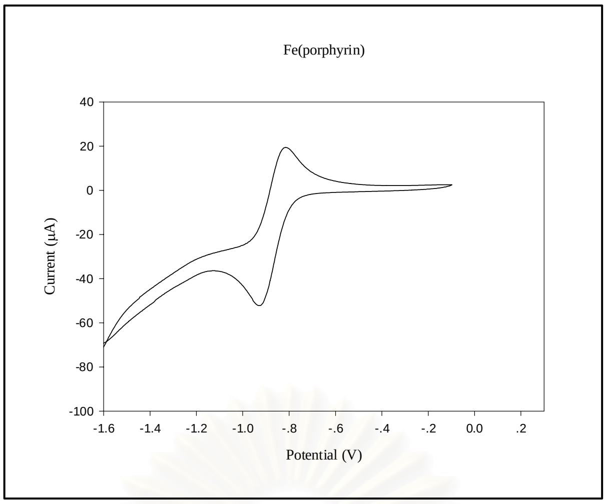


Fig 3.5 Cyclic voltammogram of 0.01 mol Fe(porphyrin) in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.5, the cyclic voltammogram of Fe(porphyrin) demonstrated the peak current, Ipa of 37.121 μA and Ipc of -34.841 μA. The ratio of Ipa/Ipc = 1.065 which was nearly equal to unity and ΔEp = 0.101 V which was larger than 0.059 V anticipated for reversible one-electron transfer reduction.

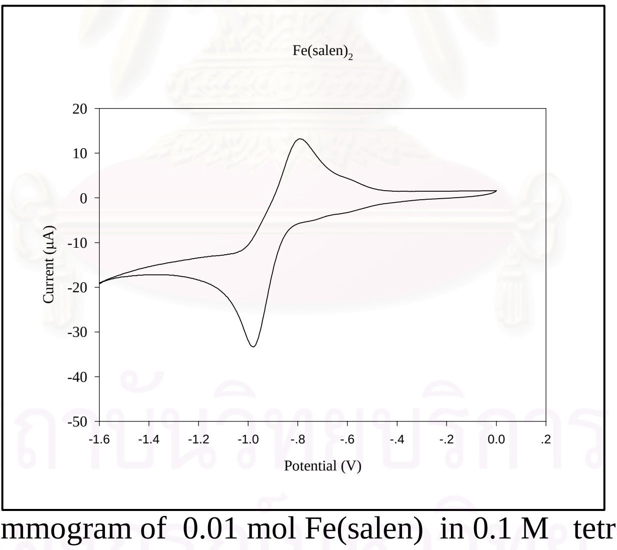


Fig 3.6 Cyclic voltammogram of 0.01 mol Fe(salen) in 0.1 M tetrabutylammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.6, Fe(salen) indicated the peak current, Ipa of 20.143 μA and Ipc of -24.132 μA. The ratio of Ipa/Ipc = 0.835 which was nearly equal to unity and ΔEp = 0.183 V which was only slightly larger than 0.059 V anticipated for quasi-reversible one-electron transfer reduction.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.3 The redox properties of iron complexes using a glassy carbon electrode

Catalyst	Epc	Ipc	Epa	Ipa	Ipa/Ipc	ΔEp	Redox reaction
Fe(naphthenate)$_3$	-0.396	-23.431	-0.149	-16.402	0.700	0.247	quasi-reversible
Fe(alanine)$_3$	-	-	-	-	-	-	-
Fe(benzoate)$_3$	-0.742	-54.142	-	-	-	-	irreversible
Fe(benzoylacetonate)$_3$	-0.516	-35.052	-0.446	33.465	0.955	0.070	reversible
Fe(porphyrin)	-0.919	-34.841	-0.818	37.121	1.065	0.101	reversible
Fe(salen)	-0.979	-24.132	-0.796	20.143	0.835	0.183	quasi-reversible

Recorded for 0.001 mol of complexes in 0.1 M tetrabutylammonium hexafluorophosphate using a glassy carbon electrode *vs* silver wire reference electrode; CV scan rate 0.05 V/s.

From Table 3.3, it was found that Fe(benzoylacetonate)$_3$ and Fe(porphyrin) exhibited the ratio of Ipa/Ipc close to unity and ΔEp value close to 0.059 V; thus it should be a reversible reaction. Both Fe(naphthenate)$_3$ and Fe(salen) revealed the ratio less than unity and ΔEp value more than 0.059 V exhibiting quasi-reversible reaction. Fe(benzoate)$_3$ and Fe(benzoylacetonate)$_3$ showed the irreversible reactions. Fe(alanine)$_3$ did not show redox reaction. In addition, it should be addressed that complexes which exhibited the reversible and quasi-reversible reactions provided the yield of product (cyclohexanone and cyclohexanol) better than other complexes shown in Table 3.2. Stemmed from these results, ten iron complexes were synthesized and subjected to determine electrochemical properties using cyclic voltammetry. From the screening for iron complexes, 1,3-dicarbonyl iron complexes and carboxylate iron complexes, Fe(acetylacetonate)$_3$ and Fe(naphthenate)$_3$, provided good results. Fe(methyl 2-acetylacetoacetate)$_3$, Fe(ethyl benzoylacetonate)$_3$, Fe(stearate)$_3$, Fe(palmitate)$_3$, Fe(alanine)$_3$, Fe(4-nitrobenzoate)$_3$, Fe(benzoate)$_3$ and Fe(picolinate)$_3$ were selected as catalysts for further study. In addition, Schiff base iron complexes such as Fe(salen) indicated very good results. Fe(salen)Cl and (Fesalen)$_2$O were thus chosen as a catalyst for this further study. In addition from literature review, it was found that no report concerning Fe(dimetylglyoxime) used as a catalyst in cyclohexane oxidation. The cyclic voltammograms of ten iron

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

complexes examined using a glassy carbon electrode and voltage scan rate of 0.05 V/s are presented in Figures 3.7-3.16 and Table 3.4.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

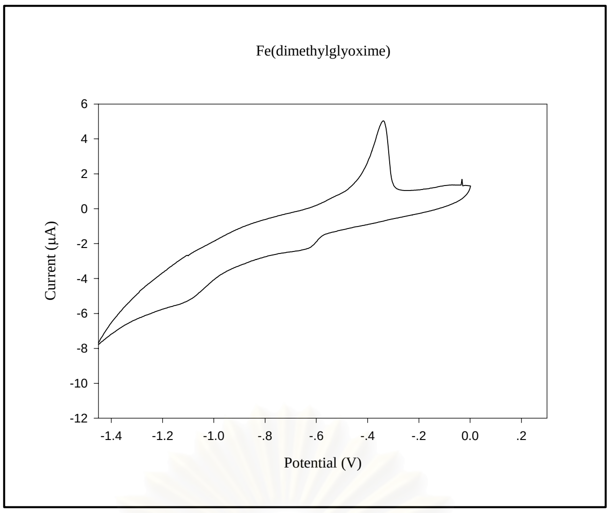


Fig 3.7 Cyclic voltammogram of 0.01 M Fe(dimethylglyoxime) in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using the glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.7, the cyclic voltammogram of Fe(dimethylglyoxime) indicated the peak current, Ipa of 4.112 µA and Epa of -0.341 V which anticipated for irreversible one-electron transfer oxidation.

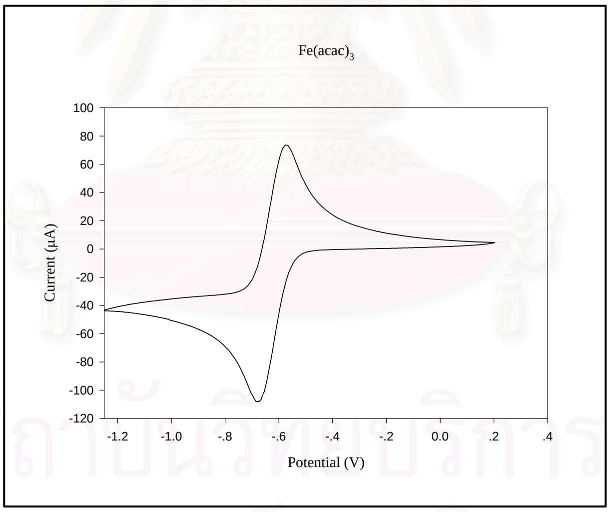


Fig 3.8 Cyclic voltammogram of 0.01 mol Fe(acetylacetonate)$_3$ in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.8, the cyclic voltammogram of Fe(acetylacetonate)$_3$ showed the peak current, Ipa of 97.342 µA and Ipc of -98.981 µA. The ratio of Ipa/Ipc = 0.983 was nearly equal to unity and ΔEp = 0.104 V which was larger than 0.059 V according to the ratio of Ipa/Ipc anticipated for reversible one-electron transfer reduction.

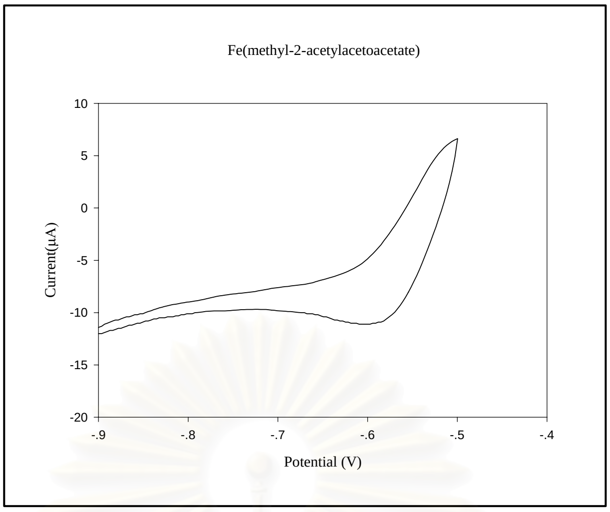
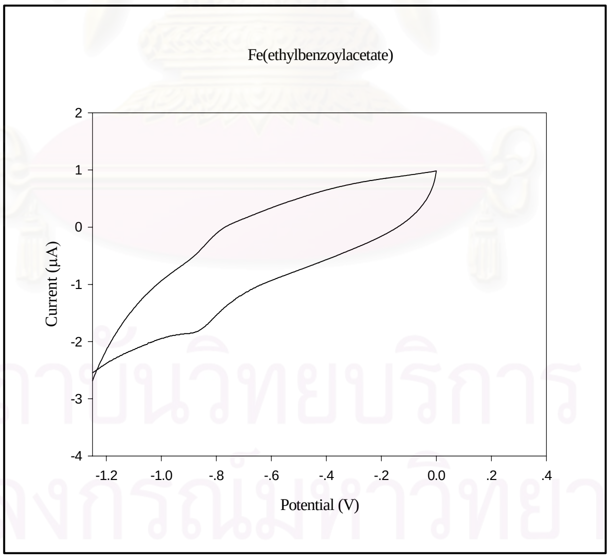


Fig 3.9 Cyclic voltammogram of 0.01 mol Fe(methyl 2-acetylacetoacetate)$_3$ in 0.1 M tetrabutylammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.9, the cyclic voltammogram of Fe(methyl-2-acetylacetoacetate)$_3$ demonstrated the peak potential, Epc of -0.606 V which was anticipated for irreversible one –electron transfer reduction.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Fig 3.10 Cyclic voltammogram of 0.01 mol Fe(etyl benzoylacetate)$_3$ in 0.1 M tetrabutylammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.10, the cyclic voltammogram of Fe(etyl benzoylacetate)$_3$ showed the peak potential, Epc of 0.881 V which was anticipated for irreversible one –electron transfer reduction.

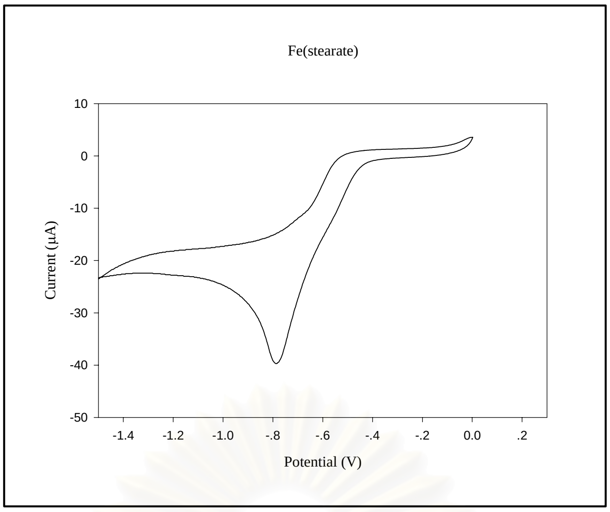
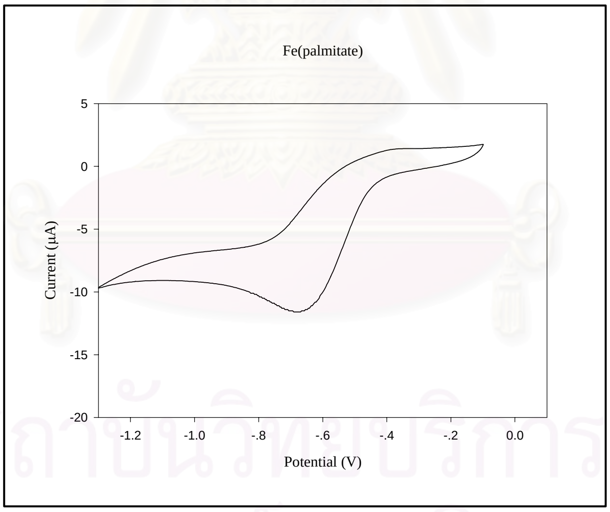


Fig 3.11 Cyclic voltammogram of 0.01 mol Fe(stearate)$_3$ in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.11, the cyclic voltammogram of Fe(stearate)$_3$ indicated the peak current, Ipc of -39.467 μA and Epc of -0.785 V which was anticipated for irreversible one–electron transfer reduction.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Fig 3.12 Cyclic voltammograms of 0.01 mol Fe(palmitate)$_3$ in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.12 , the cyclic voltammogram of Fe(pamitate)$_3$ showed the peak current, Ipc of -9.872 μA and Epc of -0.681 V which was also anticipated for irreversible one–electron transfer reduction.

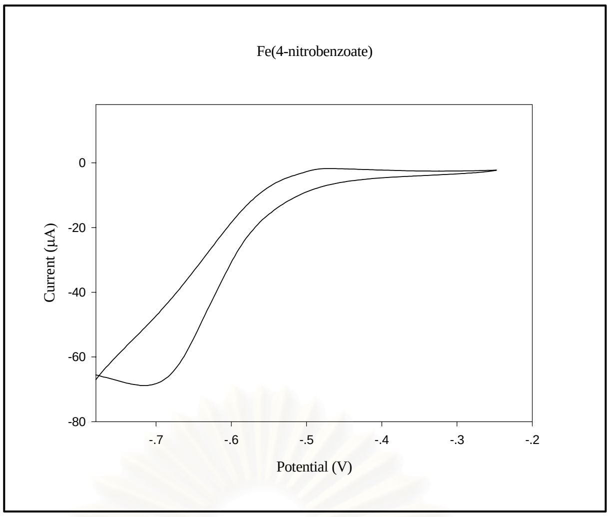


Fig 3.13 Cyclic voltammogram of 0.01 mol Fe(4-nitrobenzoate)$_3$ in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.13, the cyclic voltammogram of Fe(4-nitrobenzoate)$_3$ indicated the peak current, Ipc of -70.132 µA and Epc of -0.721 V which was anticipated for irreversible one–electron transfer reduction.

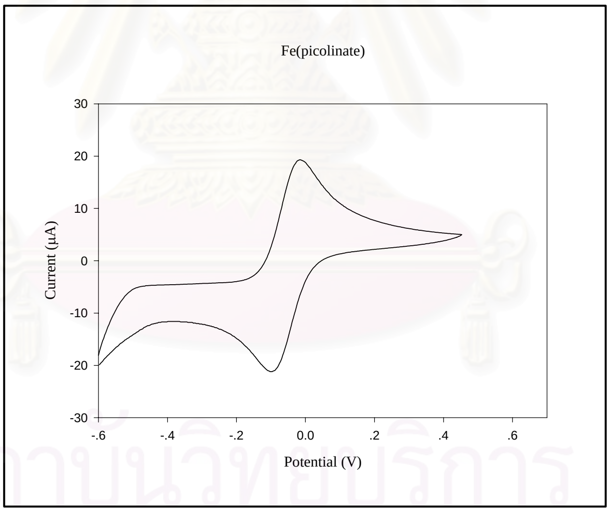


Fig 3.14 Cyclic voltammogram of 0.01 mol Fe(picolinate)$_3$ in 0.1 M tetrabutyl ammonium hexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.14, the cyclic voltammogram of Fe(picolinate)$_3$ showed the peak current, Ipa of 20.681 µA, Ipc of -17.671 µA The ratio of Ipa/Ipc = 1.171 which was nearly equal to unity and ΔEp = 0.076 V which was only slightly larger than 0.059 V anticipated for reversible one-electron transfer reduction.

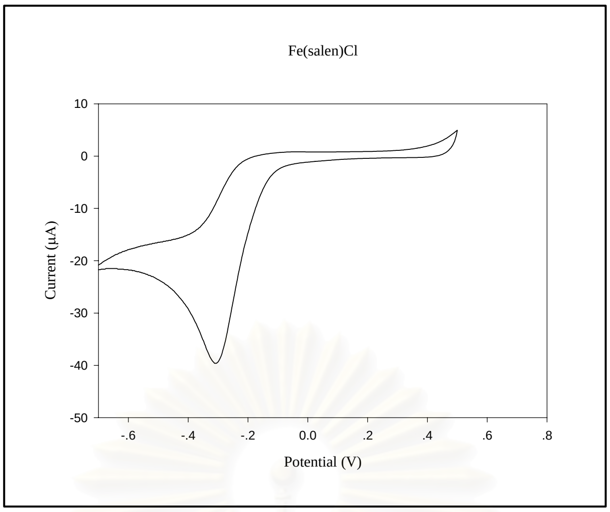


Fig 3.15 Cyclic voltammogram of 0.01 mol Fe(salen)Cl in 0.1 M tetrabutyl ammoniumhexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.15, the cyclic voltammogram of Fe(salen)Cl demonstrated the peak current, Ipc of -30.321 μA and Epc of -0.306 V which was anticipated for irreversible one–electron transfer reduction.

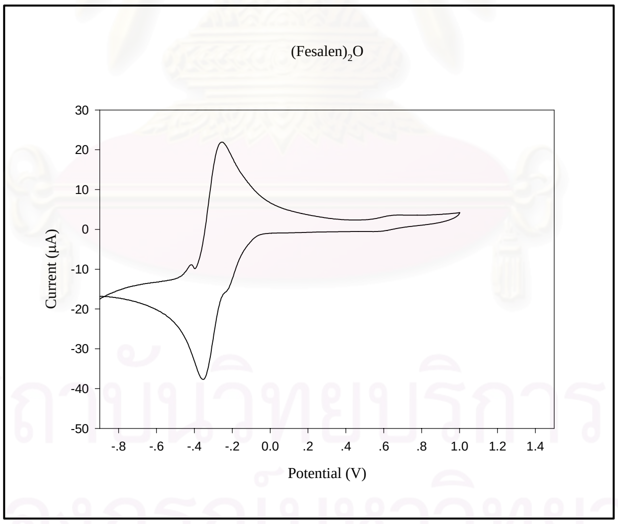


Fig 3.16 Cyclic voltammograms of 0.01 mol $(Fesalen)_2O$ in 0.1 M tetrabutyl ammoniumhexafluorophosphate solution using a glassy carbon as a working electrode, scan rate: 0.05 V/s.

From Fig 3.16, the cyclic voltammogram of $(Fesalen)_2O$ indicated the peak current, Ipa of 30.745 μA and Ipc of -24.701 μA. The ratio of Ipa/Ipc = 1.245 was a lot of large than unity and ΔEp= 0.098 V which was only slightly larger than 0.059 V anticipated for quasi-reversible one-electron transfer reduction.

Table 3.4 The redox properties of iron complexes using a glassy carbon electrode.

Catalyst	Epc	Ipc	Epa	Ipa	Ipa/Ipc	ΔEp	Redox reaction
Fe(porphyrin)	-0.919	-34.841	-0.818	37.121	1.065	0.101	reversible
Fe(salen)	-0.979	-24.132	-0.796	20.143	0.835	0.183	quasi-reversible
(Fesalen)$_2$O	-0.335	-24.701	-0.237	30.175	1.245	0.098	quasi-reversible
Fe(dimethylglyoxime)	-	-	-	-	-	-	-
Fe(acetylacetonate)$_3$	-0.676	-98.981	-0.572	97.342	0.983	0.104	reversible
Fe(stearate)$_3$	-0.785	-39.467	-	-	-	-	irreversible
Fe(palmitate)$_3$	-0.681	-9.872	-	-	-	-	irreversible
Fe(naphthenate)$_3$	-0.396	-23.431	-0.149	16.402	0.700	0.247	quasi-reversible
Fe(salen)Cl	-0.306	-30.321	-	-	-	-	irreversible
Fe(alanine)$_3$	-	-	-	-	-	-	-
Fe(4-nitrobenzoate)$_3$	-0.721	-70.132	-	-	-	-	irreversible
Fe(benzoate)$_3$	-0.357	-54.142	-	-	-	-	irreversible
Fe(picolinate)$_3$	-0.093	-17.671	-0.017	20.681	1.171	0.076	reversible
Fe(benzoylacetonate)$_3$	-0.516	-35.052	-0.446	33.465	0.955	0.070	reversible
Fe(methyl 2-acetylacetoacetate)$_3$	-	-	-	-	-	-	-
Fe(ethyl benzoylacetate)$_3$	-	-	-	-	-	-	-

Recorded for 0.001 mol of complexes in 0.1 M tetrabutylammonium hexafluorophosphate using a glassy carbon electrode *vs* silver wire reference electrode; CV scan rate 0.05 V/s.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

The cyclic voltammetry was characterized by several important parameters to inform the kinds of redox reaction. The reversible process exhibited the ratio of Ipa to Ipc about unity and the ΔEp value of complexes were close to 0.059 V. The quasi – reversible displayed the ratio of Ipa to Ipc more or less than unity and the ΔEp value of complexes was more than 0.059 V. For an irreversible process, the individual peak was reduced in size and widely separated.

From Figures 3.7-3.16 and Table 3.4, Fe(porphyrin), Fe(acetylacetonate)$_3$, Fe(picolinate)$_3$ and Fe(benzoylacetonate)$_3$ showed the ratio of Ipa/Ipc close to the unity and the ΔEp value was close to 0.059 V; thus it should be a reversible process. The iron complexes: Fe(salen), (Fesalen)$_2$O and Fe(naphthenate)$_3$ revealed more or less than the unity and the ΔEp value was more than 0.059 V because of ohmic drop occurred by the effect of the solution resistance exhibiting quasi-reversible reactions. The iron complexes: Fe(stearate)$_3$, Fe(palmitate)$_3$, Fe(salen)Cl, Fe(4-nitrobenzoate)$_3$, and Fe(benzoate)$_3$ displayed the only oxidation peak demonstrating irreversible reactions. Other iron complexes: Fe(dimethylglyoxime), Fe(alanine)$_3$, Fe(methyl 2-acetylacetoacetate)$_3$ and Fe(ethyl benzoylacetate)$_3$ were not soluble in the reaction media and thus their redox properties could not be examined.

From electrochemical properties of prepared iron complexes. Ten complexes were employed as a catalyst in cyclohexane oxidation using TBHP as an oxidant. The results are presented in Table 3.5.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.5 The oxidation of cyclohexane catalyzed by ten iron complexes.

Entry	Catalyst	Product	
		-one (mmol)	-ol (mmol)
1	Fe(dimethylglyoxime)	0.144	0.103
2	Fe(acetylacetonate)$_3$	0.818	0.531
3	Fe(methyl 2-acetylacetoacetate)$_3$	0.004	trace
4	Fe(ethyl benzoylacetonate)$_3$	0.003	trace
5	Fe(stearate)$_3$	0.424	0.288
6	Fe(palmitate)$_3$	0.088	0.082
7	Fe(4-nitrobenzoate)$_3$	0.245	0.156
8	Fe(picolinate)$_3$	0.936	0.446
9	Fe(salen)Cl	0.322	0.243
10	(Fesalen)$_2$O	0.789	0.231

Reaction conditions: cyclohexane (30 mmol), iron complexes (0.25 mmol), pyridine and acetonitrile (1:1 V/V) (28 ml), TBHP (15 mmol) at 70 °C

3.4 Effect of iron complexes on cyclohexane oxidation

Ten iron complexes, namely, Fe(naphthenate)$_3$, Fe(alanine)$_3$, Fe(benzoate)$_3$, Fe(benzoylacetonate)$_3$, Fe(salen), Fe(porphyrin), Fe(dimethylglyoxime), Fe(acetylacetonate)$_3$, Fe(methyl 2-acetylacetoacetate)$_3$, Fe(ethyl benzoylacetate)$_3$, Fe(stearate)$_3$, Fe(palmitate)$_3$, Fe(4-nitrobenzoate)$_3$, Fe(picolinate)$_3$, Fe(salen)Cl, and (Fesalen)$_2$O were utilized as a catalyst in cyclohexane oxidation. From Tables 3.3 and 3.5, it was founded that cyclohexanone was produced as a major product while cyclohexanol being a minor product. Seven iron complexes, namely, Fe(naphthenate)$_3$, Fe(benzoylactonate)$_3$, Fe(salen), Fe(porphyrin), Fe(acetylacetonate)$_3$, Fe(picolinate)$_3$ and (Fesalen)$_2$O that comprised donating group provided good results in cyclohexane oxidation. In addition, four Fe(III)-1,3-

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

dicarbonyl complexes, respectively. It was found that Fe(benzoylacetate)$_3$ gave superior amount of the oxidation product. This was clearly observed that the electron donating groups that were able to donate electron to iron make possible form the appropiate iron complex and activate cyclohexane oxidation much faster.

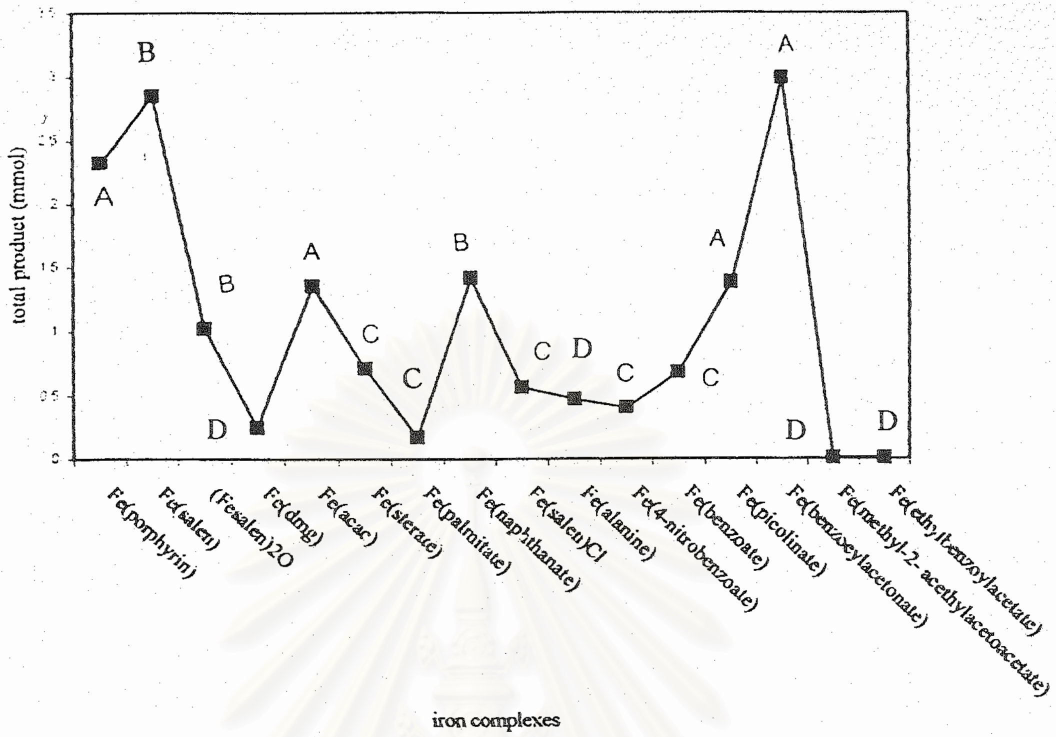
3.5 Comparative study on redox and catalytic properties of iron complexes

Sixteen iron complexes were chosen to study the relationship between electrochemical and catalytic properties. The outcome from this study would be a benefit database for determining the appropriate catalysts. The results of catalytic and redox properties are presented in Table 3.6 and Figure 3.17.

Table 3.6 The catalytic and redox properties of the iron complexes.

Catalyst	Product (mmol)		Redox reaction
	-one	-ol	
Fe(porphyrin)	1.679	0.644	reversible
Fe(salen)	2.527	0.321	quasi-reversible
(Fesalen)$_2$O	0.789	0.231	quasi-reversible
Fe(dimethylglyoxime)	0.144	0.103	-
Fe(acetylacetonate)$_3$	0.818	0.531	reversible
Fe(stearate)$_3$	0.424	0.288	irreversible
Fe(palmitate)$_3$	0.088	0.082	irreversible
Fe(naphthenate)$_3$	0.775	0.641	quasi-reversible
Fe(salen)Cl	0.322	0.243	irreversible
Fe(alanine)$_3$	0.371	0.098	-
Fe(4-nitrobenzoate)$_3$	0.245	0.156	irreversible
Fe(benzoate)$_3$	0.437	0.245	irreversible
Fe(picolinate)$_3$	0.936	0.446	reversible
Fe(benzoylacetate)$_3$	1.885	1.103	reversible
Fe(metyl 2- acetylacetoacetate)$_3$	0.004	trace	-
Fe(ethyl benzoylacetate)$_3$	0.003	trace	-

Recorded 0.001 mol of complexes in 0.1 M. tetrabutylammonium hexafluorophosphate using a glassy carbon electrode *vs* silver wire reference electrode; CV sweep rate 0.05 V/s.



A = reversible B = quasi-reversible C = irreversible D = no redox reaction

Figure 3.17 Catalytic and redox properties of the iron complexes

From Table 3.6 and Figure 3.17, it was found that Fe(porphyrin), Fe(salen), Fe(acetylacetonate)$_3$, Fe(picolinate)$_3$, Fe(benzoylacetonate)$_3$, (Fesalen)$_2$O and Fe(naphthenate)$_3$ provided better yield of the desired product than other complexes. These complexes exhibited the reversible and quasi–reversible, reactions. While iron complexes: Fe(dmg), Fe(stearate)$_3$, Fe(palmitate)$_3$, Fe(salen)Cl, Fe(alanine)$_3$, Fe(4-nitrobenzoate)$_3$, Fe(benzoate)$_3$, Fe(methyl 2-acethylacetoacetate)$_3$ and Fe(ethyl benzoylacetate)$_3$ which gave trace amount of desired product displayed an irreversible reaction. Therefore, it could clearly be seen that iron complexes gave the catalytic properties resulting in concomitant with that of redox properties.

3.6 Kinetic study on the reaction rate of cyclohexane oxidation.

Various recent catalytic models that mimic enzymatic systems had an attempt to develop the reactions to be of a capability to proceed at room temperature and atmospheric pressure. Nevertheless, the rates of these reactions are generally slow and need to spend more time to complete the reaction. Therefore, the catalytic systems that consume less time to complete the reaction should be explicitly needed. The rate of cyclohexane oxidation catalyzed by Fe(salen), $(Fesalen)_2O$ and $Fe(benzoylacetonate)_3$ using TBHP as an oxidant was studied. The kinetic analysis results are presented in Figure 3.18.

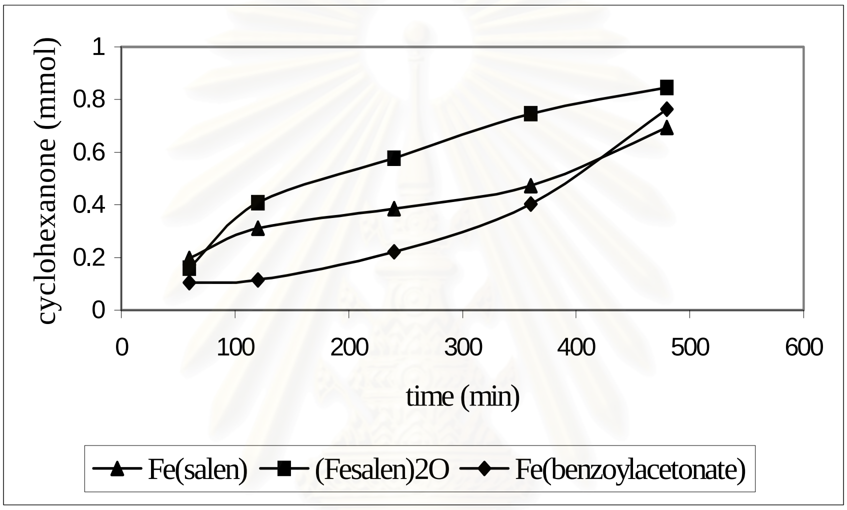


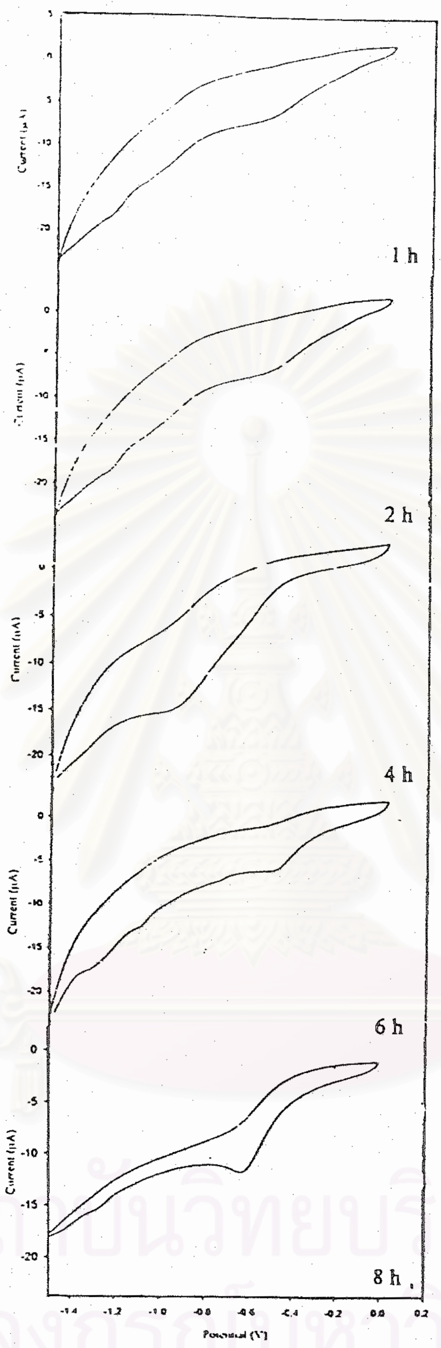
Figure 3.18. Kinetic study on cyclohexane oxidation catalyzed by various catalysts

From Figure 3.18, it was found that the rates of the reaction employing $(Fesalen)_2O$ and Fe(salen) were significantly better than that utilized $Fe(benzoylacetonate)_3$. The desired product was taken place when the reaction time was about 60 minutes by using Fe(salen), $(Fesalen)_2O$ and $Fe(benzoylacetate)_3$. From this result, it could be observed that under this particular system, the reaction with $(Fesalen)_2O$ and Fe(salen) catalysts proceeded the oxidation reaction very fast. Moreover, cyclohexane oxidation using the series of iron complex catalysts reinforced the concept of the importance of ligand around metal iron. The appropriate ligands may assist the reaction to take place with satisfied rates and in some cases may elevate the selectivity of reactions as required.

3.7 Kinetic study of cyclohexane oxidation examined by cyclic voltammetry

The kinetic study of cyclohexane oxidation using Fe(salen), $(Fesalen)_2O$ and $Fe(benzoylacetonate)_3$ as catalysts and TBHP as an oxidant was examined by cyclic voltammetry. The kinetic study of reaction using cyclic voltammetry was performed to compare with the kinetic study on the reaction rate of cyclohexane oxidation. The kinetic voltammogram results are presented in Figures 3.19-3.21.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Fig 3.19 Kinetic cyclic voltammogram of cyclohexane oxidation catalyzed by Fe(salen)

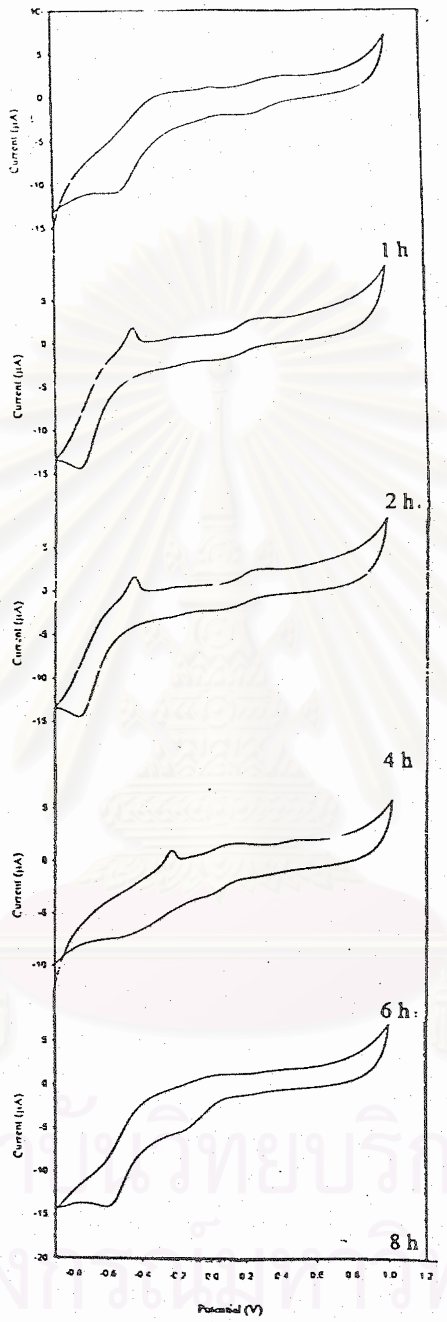


Fig 3.20 Kinetic cyclic voltammogram of cyclohexane oxidation catalyzed by (Fesalen)$_2$O

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

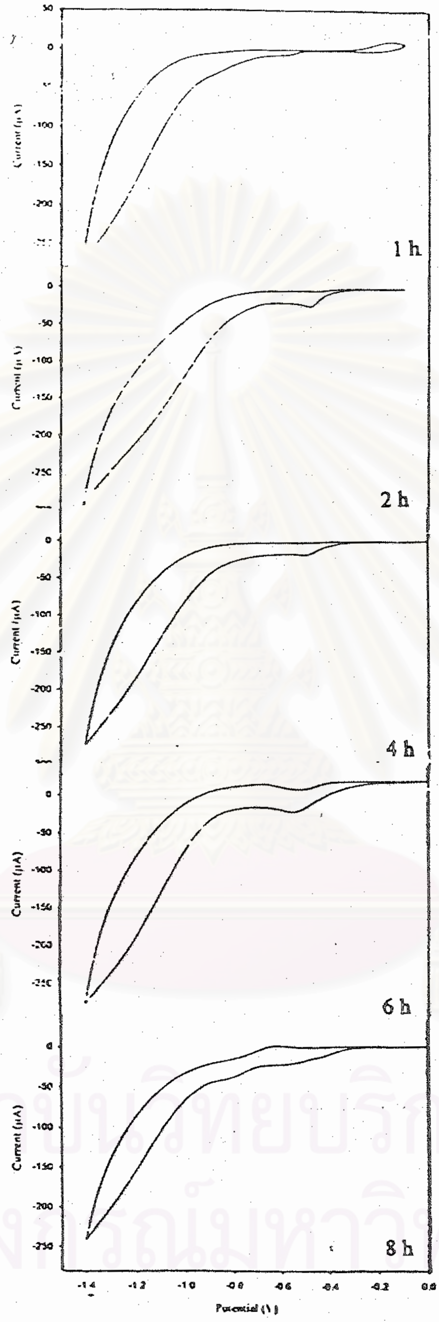


Fig 3.21 Kinetic cyclic voltammogram of cyclohexane oxidation catalyzed by Fe(benzoylacetonate)$_3$

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.7 The redox properties of Fe(salen) using a glassy carbon electrode.

Time (h)	Epc	Ipc	Epa	Ipa	Ipa/Ipc	ΔEp	Redox reaction
1	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
6	-0.485	-4.783	-	-	-	-	irreversible
8	-0.632	-9.652	-	-	-	-	irreversible

Table 3.8 The redox properties of $(Fesalen)_2O$ using a glassy carbon electrode.

Time (h)	Epc	Ipc	Epa	Ipa	Ipa/Ipc	ΔEp	Redox reaction
1	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
6	-0.598	-6.872	-	-	-	-	irreversible
8	-0.612	-14.371	-	-	-	-	irreversible

From Figure 3.19-3.21 and Table 3.6-3.7, it was found that Fe(salen) and $(Fesalen)_2O$ did not show redox reaction during 1-6 h, but showed an irreversible reaction at 8 h while $Fe(benzoylacetonate)_3$ did not reveal a redox reaction during 1-8 h. This result could be implied that Fe(salen) and $(Fesalen)_2O$ had an interaction with TBHP to gain a high valent oxidizing agent (LM^{III}-$OO^{t}Bu$) during 1-6 h; thus these complexes did not show a redox reaction during this period of time. At 8 h, the oxidation of cyclohexane was nearly completed; thus Fe(salen) and $(Fesalen)_2O$ displayed an irreversible reaction. The cyclohexane oxidation catalyzed by $Fe(benzoylacetonate)_3$ did not complete during 8 h. This $Fe(benzoylacetonate)_3$ may be in the form of (LM^{III}-$OO^{t}Bu$). Thus, $Fe(benzoylacetonate)_3$ did not display redox reaction during 1 to 8 h.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Considering the results derived from this study, the cyclic voltammetry of the iron complexes exhibiting reversible and quasi-reversible reactions would provide better yield of the desired products than those possessing irreversible reactions. The kinetic study of cyclohexane oxidation was found in good agreement with the cyclic voltammograms that gained from cyclic voltammetry.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER IV

CONCLUSION AND SUGGESTION FOR FURTHER WORK

Oxidation of cyclohexane to cyclohexanone and cyclohexanol catalyzed by iron complexes using H_2O_2 at room temperature and TBHP at 70 °C as an oxidizing agent in a mixture of pyridine-acetonitrile (1:1 v/v) was investigated. The oxidation of cyclohexane produced mainly cyclohexanone and small amount of cyclohexanol. In addition, the use of TBHP as an oxidizing agent gave better yield than H_2O_2. Cyclic voltammetry was employed for examination redox reaction of iron complexes using glassy carbon as working electrode, silver wire as reference electrode and platinum wire as auxillary electrode. The cyclic voltammograms of sixteen iron complexes revealed that Fe(porphyrin), Fe(benzoylacetonate)$_3$, Fe(acetylacetonate)$_3$ and Fe(picolinate)$_3$ showed reversible reactions while Fe(salen), (Fesalen)$_2$O and Fe(naphthenate)$_3$ displayed quasi-reversible reactions and Fe(benzoate)$_3$, Fe(stearate)$_3$, Fe(palmitate)$_3$, Fe(salen)Cl and Fe(4-nitrobenzoate)$_3$ showed irreversible reactions. Fe(dimethylglyoxime), Fe(alanine)$_3$, Fe(methyl 2-acetylacetoacetate)$_3$ and Fe(ethyl benzoylacetate)$_3$ did not show redox reactions. From electrochemical properties of iron complexes, Sixteen complexes were employed as a catalyst in cyclohexane oxidation using TBHP as an oxidant. The results were presented that Fe(porphyrin), Fe(benzoylacetonate)$_3$, Fe(acetylacetonate)$_3$, Fe(picolinate)$_3$, Fe(salen), (Fesalen)$_2$O and Fe(naphthenate)$_3$ provided a better yield than other iron complexes. These complexes exhibited the reversible reaction and quasi–reversible, respectively. While complexes of Fe(dimetylglyoxime), Fe(stearate)$_3$, Fe(palmitate)$_3$, Fe(salen)Cl, Fe(alanine)$_3$, Fe(4-nitrobenzoate)$_3$, Fe(benzoate)$_3$, Fe(methyl-2-acethylacetoacetate)$_3$ and Fe(ethylbenzoylacetate)$_3$ gave trace amount of desired product displayed an irreversible reaction. Therefore, it could clearly be seen that iron complexes gave the catalytic properties results in concomitant with that of redox properties.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

In the term of kinetic study, using Fe(salen) and $(Fesalen)_2O$, the oxidation reaction rate was faster than using Fe(benzoylacetonate). Considering, the kinetic of cyclohexane oxidation, iron complexes Fe(salen) and $(Fesalen)_2O$ showed irreversible reaction at 6 h and 8 h while $Fe(benzoylacetonate)_3$ did not show redox reaction. The kinetic study of cyclohexane oxidation was found in good agreement with the cyclic voltammograms that gained from cyclic voltammetry.

Suggestion of further work

The study of redox properties to investigate the relationship between electrochemical and catalytic properties in other catalysts such as Cr-catalysts is interesting. Other electrochemical techniques can be used to examine the mechanism of the electrochemical reactions such as preparative electrolysis. This method can be performed to find the number of electron transfers. Simulated voltammetry is one of methods which is interesting for determination of rate constant, for the further work.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

REFERENCES

1. Balandin, A. A. *Advanced Catalyst*. New York : Wiley-VCH Publishing, **1980**.
2. Roginskii, S. Z. *Scientific Selection of Catalysts*. New York: Keter Pub. House, **1986**.
3. Satterfield, C. N. *Heterogeneous Catalysis in Practice*. New York: McGraw-Hill Company, **1980**.
4. Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*. New York: John Wiley & Son Plishing, **1992**.
5. Wiseman, P. *Petrochemicals*. New York: Ellis Horwood Limited, **1986,** 15.
6. Richardson, D.; Xu, C.; Abboud, K. and Weakley, G. K. *Catalytic Oxidation of Hydrocarbon,* U.S. Pat. No 6, **2001**, 307,100.
7. Lindley, C. R. *Industrial Organic Chemistry*. New York: VCH Publishers, Inc, **1997**, 348.
8. Ingold, K. U. *At the Organic Chemistry Bioscience Interface: Rate Processes in Complex System, Aldrichimica Acta*, **1989**, *22*, 69-73.
9. Braun, R. D. *Introduction to Instrumental Analysis*. New York: McGRAW-HILL International editions, **1987**, 785.
10. Fry, A. J. *Synthetic Organic Electrochemistry*: New York: Happer & Row Publishers, **1972**, 26.
11. Murahashi, S.; Naota, T. and Komiya, N. *Metalloporphyrin-Catalyzed Oxidation of Alkanes with Molecular Oxygen in the Presence of Acetaldehyde, Tetrahedron Lett.*, **1995**, *36*, 8059-8062.
12. Ganeshpure, P.; Tembe, G.; Satish, S., *Oxyfunctionalization of Cyclohexane Catalyzed by Oxo-bridged Manganese Schiff Base Complexes, Tetrahedron Lett.*, **1995**, *36*, 8861-8864.
13. Ganeshpure, P.; Tembe, G.; Satish, S., *Oxidation of cyclohexane by Tert-Butylhydroperoxide Catalyzed by Manganese(II) Catalyzed by N,N′-ethylene bis(salicylideneaminato) and Analogous Complexes, J. Mol. Cat A-Chem.*, **1996**, *113*, L423-L425.
14. Tembe, G.; Ganeshpure, P.; Satish, S., *Oxidation of Alkanes by Tert*

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Butylhydroperoxide Catalyzed by Polynuclear Manganese Schiff Base Complexes, J. Mol. Cat A-Chem., **1996**, *121*, 17-23.

15. Panniyamurthy, T.; Bhatia, B., Reddy, M., Maikap, G., Iqbal, J., *A Versatile Cobalt(II)-Schiff base Catalyzed Oxidation of Organic Substrates with Dioxygen: Scope and Mechanism, Tetrahedron Lett*., **1997**, *53*, 7649-7670.
16. Takagi, S.; Takahashi, E. and Miyamoto, T. K., *A New Iron (III) Porphyrin System for Olefin Epoxidation Catalysts, Chem. Lett*., **1986**, 1275-1278.
17. Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M. and Mansuy, D. *Monooxygenese-like Oxidation of Hydrocarbons by H_2O_2 Catalyzed by Manganese Porphyrins and Imidazole: Selection of the Best Catalytic System and Nature of the Active Oxygen Species, J. Am. Chem. Soc.*, **1988**, 8462-8470.
18. Sanderson, J.R.; Marquis, E. T. and Payton, H. F. *Production of Detergent Range Alcohols and Ketones Using Porphyrin Catalysts, U. S. Pat*. No. 4, 978, 799, **1990.**
19. Barton, D. H. R.; Beviere, S. D. and Hill, D. R. *The Functionalization of the saturated hydrocarbons Part XXIX. Application of tert-Butylhydroperoxide and Dioxygen Using Soluble Fe(III) and Cu(III) Chelates., Tetrahedron*, **1994**, *50*, 2665-2670.
20. Nuntasri, D.; Loayfakajohn, S. *The Oxidation of Saturated Hydrocarbons Catalyzed by Some Transition Metal-Schiff Base Complexes, Senior Project,* Department of Chemistry, Chulalongkorn University, **1996**.
21. Wu, X.; Oshima, Y. and Koda, S. *Aerobic Oxidation of Cyclohexane Catalyzed* by *Fe(III)(5,10,15,20-tetrakis(pentafluorophenyl)porphyrin)Cl in Sub- and Super-Critical CO_2, Chem.Lett*., **1997**, 1045-1046.
22. Schuchardt, U.; Pereira, R. and Rufo, M. *Iron(III) and Copper(II) Catalysed Cyclohexane Oxidation by Molecular Oxygen in the Presence of tert-butylhydroperoxide, J. Mol. Cat A-Chem*, **1998**, *135*, 257-262.
23. Nam, W.; Goh, Y. M.; Lee, Y.J.; Lim, M. H. and Kim, C. *Biomimic Alkane Hydroxylation by an Iron(III) Porphyrin Complex with H_2O_2 and by a High-Valent Iron(IV) Oxo Porphyrin Cation Radical Complex, Inorg. Chem*., **1999,** *38*, 3238-3240.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

24. Machado, A.M.; Wypych F.; Drechsel, S.M. and Nakagaki, S. *Study of the Catalytic Beheavior of Montmorillonite/Iron(III) and Mn(III) Cationic Porphyrins, J. Colliod*., **2002,** *254*, 158-164.

25. Guo, C.C .; Liu X.; Liu Y.; Liu q.; Chu M. and Zhang, X. *Studies of Simple μ-oxo-bisiron(III) porphyrin as Catalyst of Cyclohexane Oxidation with Air in Absence of Cocatalysts or Coreductants, J. Mol. Cat A-Chem,* **2003**, *192*, 289-294.

26. Isse, A.; Gennaro, A.; Vianelo, E. *The Electrochemical Reduction-Mechanism of [N,N′-1,2-phenyllene bis(salicylideneiminato)] Cobalt(II), J. Chem. Soc.-Dal. Trans*., **1993,** *14*, 2091-2096.

27. Sawyer, D. T.; Liu, X.; Qiu, A. *The Bis(bipyridine)copper(II)-Induced Activation of Dioxygen for the Catalytic Dehydrogenation of Alcohols, J. Chem. Soc.,* **1993**, *115*, 3239-3243.

28. Tshchida, E.; Yamamoto, K.; Qyaizu, K. Iwasaki, N.; Anson F.C.*Electrochemical Investigations of the Complexes Resulting from the Acid-Promoted Deoxygenation and Dimerization of (N,N′-Ethylenebis(salicylideneiminato)) oxovanadium(IV), Inorg. Chem*., **1994**, *33*, 1056-1063.

29. Bottcher, A.; Takeuchi, T.; Hardcastle, K.I.; Meade, T.J.; Gray, H.B.*Spectroscopy and Electrochemistry of Cobalt(III) Schiff base Complexes, Inorg. Chem.,* **1997**, *36*, 2498-2504.

30. Sinclair, L.; Mondal, J. U.; Uhrhammer, D.; Schultz, F. A. *Preparation and Electrochemical of Six- Coordinate Monooxomolybdenum(VI) Complexes Containing Bidentate Catecholate and Tridentate NOS-Donor Schiff base Ligand, Inorg. Chem. Acta*, **1998**, *278*, 1-5.

31. Natiwatvittaya, T.; Sawat, A. *Electrochemical Reaction Study of transition Metal Schiff Base Complexes, Senior Project, Department of Chemistry,* Chulalongkorn University, **2000.**

32. Canadas, M.; Torres, E. L.; Arias, A. M.; Mendiola, M. A. and Sevilla, M. T. *Spectroscopic and Electrochemical properties of Nickel(II), Iron(III) and Cobalt(II) Complexes with Benzilbisthiosemicarbazone Importance of Working Conditions and the Metal Salt Used in the Final Complex, Polyhedron*, **2000**, *19*, 2059-2068.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

33. Buchmann, S.; Mayer, H. A.; Speiser, B.; Seiler, M.; Bertagnolli, H. and Steinbrecher, S. *Electrochemical of Transition Metal Complex Catalysts Part 8. One –electron Oxidation of an Iridium Complex with a Cyclohexane-derived Tripod Phosphine Ligand –Cyclic Voltammetry and Preparative electrolysis, Electrochimica Acta*, **2001**, *46*, 3207-3217.
34. Nigovic, B. and Kujundzic, N. *Electrochemical Behavior of Iron(III)Complexes with Aminohydroxanic acids*, **2002**, *21*, 1661-1666.
35. Malachowski, M. R.; Dorsey, B. T.; Parker, M. J.; Adams, M.E. and Kelly, R. S. *Probing the Catalytic properties of Copper(II) Complexes of Appended Cyclams: Correlations between Catalysis and Stability constants or Electrochemical properties*, **1997**, *97*, 1289-1294.
36. Hoogenraad, M.; Ramkisoensing, K.; Driessen, W. L.; Kooijman, H.; Spek, A.L.; Bouwman, E.; Haasnoot, J. G.; Reedijk, J. *Catalytic and Electrochemical properties of New Manganese(II) Compounds of 2-2′-hydroxyphenyl)-oxazoline(Hphox or Helphox). Molecular structures of [Mn)Clphox)(2)(MEOH)(2) (ClO_4) and [Mn(phox)(2)(MEOH)(2)][Mn(phox)(2)(MEOH)(2)(H_2O_2)(2), Inorg. Chem. Acta*, **2001**, *320*, 117-126.
37. Hoogenraad, M.; Ramkisoensing, K.; Gorther, S.; Drieessen, W.L.; Bouwman, E.; Haasnooet, J. G.; Reedijk, J.; Mahabiersing, T.; Hartl, F. *Electrochemical and Catalytic properties of Novel Manganese(III) complexes with Substituted2-(2′-oxozolinyl)phenolato] Manganese(III) and Tris[5-chloride-2-(2′-oxozolinyl)phenol] Manganese(III), E. J. Inorg. Chem.*, **2002**, *2*, 377-387.
38. Salimi, A.; Abdi, K. and Khayatiyan, G. R. *Preparation and Electrocatalytic oxidation properties of a Nickel pentacyanonitrosylferrate modified Carbon Composite Electrode by Two-step sol-gel Technique: Improvement of the Catalytic activity*, **2003**, *22*, 3483-3492.
39. Akilan, P.; Trirumavalavan, M. and Kandaswamy, M. *Synthesis of Mono and Binuclear Copper(II) Complexes using New Macrobicyclic Tricompartmental unsymmetrical Ligands Magnetic, Electrochemical and Catalytic studied*, **2003**, *22*, 3483-3492.
40. Swamer, F. W. and Harser, C.*R. Claisen Acylations and Carbethoxylations of*

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Ketone and Esters by Means of Sodium Hydride, *J. Am. Chem. Soc*., **1950**, 72, 1352-1356.

41. Wilkinson. G.; Gillard, R. D.; Mcclerverty, J. *A. Comprehension Coordination Chemistry.*Vol 2. New York: Pergamon Press Publishing, **1981**, 120, 1252-1259.
42. Sebin, J.; Manning, H.R.; Cessac, G. Ligation *Effects in Vanadyl Complexes, J. Inorg. Nucl.Chem*, **1963**, *25*, 1253-1258.
43. Falvo, R.E.; Mink, L. M. and Marsh, D.F. *Microscale Synthesis and* ^{1}*H NMR Analysis of Tetraphenylporphyrins, J.Chem Ed*., **1999**, *76*, 237-239.
44. Nian, J.L.; Min, L. and Kong, H. *A. Syntheses and Characterization of Some Porphyrin and Metalloporphyrins, Inorg. Chim. Acta*, **1990,** *178*, 59-65.
45. Furness, S.; Hanoford, J.; Smith, G. and Tachell, R. *Vogel's Textbook of Practical Organic Chemistry,* 5th ed., **1980**, 1077.
46. Takai, T.; Hata, E.; Yamada, T. and Mukaiyama, T . *Aerobic Epoxidation of Olefinic Compounds Catalyzed by Tris(1,3-dikitonate)iron(III), Bull.Chem. Soc. Jpn*., **1991**, 64, 2513-2518.
47. Mazzanti, M.; Gambarotta, S.; Floriani, C. *Vanadium(III) – Schiff base Complexes a Synthetic and Structural Study, Inorg. Chem*, **1986**, *25*, 2308-2314.
48. Lewis , J.; Mabbs, F. E. and Richards, *A. The Preparation and Magnetic Properties of Some Oxy-bridged Binuclear Iron(II) Schiff-base Complexes, J. Chem. Soc. (A),* **1967**, 1014.
49. Harada, A.; Shiotsuki, K.; Fukushima, H.; Yamaguchi, H. and Kamachi, M. *Supramolecular Assembly of Porphyrins and Monoclonal Antibodies, Inorg.Chem*, **1995**, *34*, 1070-1076.
50. Hughes, D. L.; Kleinkes, U.; Leidgh, G. J.; Maiwald, M. and Sanders, J.R., *The Preparation and Structure of* $[VI_2(salen)].CH_2Cl_2$ *[salen = N,N′ -ethylenebis(salicylideneiminate)(2-)] and of Some Homologues of Related Schiff Bases, J. Chem. Soc.,* Dalton Trans., **1993,** 3093-3096.
51. Kirk-othmer, *Encyclopedia of Chemical Technology*, 2nd ed, **1968**, 473-496.
52. Menage, S.; *Reaction of copper ion with an amino acid* .http:www.wpi.edu /Academics/ Depts/ Chemistry/ Courses/ CH1010/ Stream1.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

53. Chaitheumwon S, Analysis Chemistry, **1993,** 100-103.

54. Barton, D. H. R.; Lee, K. W.; Mehl, W.; Zhang, L. *Functionalization of Saturated Hydrocarbons. Part XVIII. Reactivity of Carbon-carbon Double Bond, Tetrahedron Letts,* **1990,** *46*, 3753-3768.

55. Inpornvichitr, T. *Oxidation of Saturated Hydrocarbons catalyzed by metal porphyrin complexes, thesis*, Program of Petrochemistry and Polymer Science, **2001**.

56. Tongkratok, S. *Electrochemical and Catalytic Properties of transition metal-Schiff base complexes, thesis*, Program of Petrochemistry and Polymer Science, **2001**.

57. Chavez, F. A.; Mascharak, P. K. *Co(III)-Alklyperoxo Complexes: Syntheses, Structure- Reactivity Correlations, and Use in the Oxidation of Hydrocarbons. Acc. Chem. Res*., **2000**, *33*, 539-545.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

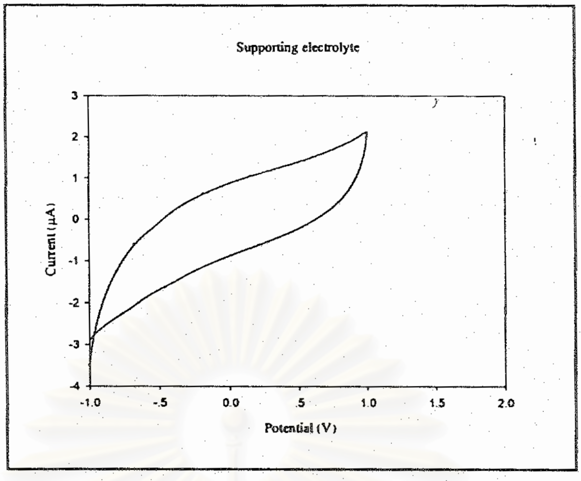


Figure 1 Cyclic voltammogram of 0.1 M tetrabutylammonium hexafluorophosphateusing a glassy carbon as a working electrode, scan rate 0.05 V/s

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

VITAE

Miss Teeraporn Timthong was born on April 3, 1979 in Bangkok, Thailand. She received a Bachelor Degree of Science, majoring in Chemistry from Chulalongkorn University in 2000, she has been a graduate student studying in the Program of Petrochemistry and Polymer Science of Chulalongkorn University, she was supported by a research grant for her Master degree′s thesis from the Graduate School, Chulalongkorn University. She graduated with Master Degree of Science in 2003.

Her present address is 63/29 Teparak Road, Bangmeungmai, Meung, Samutprakan, Thailand 10270, Tel. 02-7530475.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย