

# CHAPTER 1

## INTRODUCTION



Catalysis is the main factor for chemical transformations. Most industrial syntheses require catalysts in process of production for increasing the desired product and decreasing capital. The catalysts can also influence the selectivity of chemical reactions. The important role of catalyst is the reduction of the activation energy of the reaction process. Catalyst can generally be classified into two groups: heterogeneous and homogeneous catalysts. Heterogeneous catalyst exists as another phase in the reaction medium, typically as a solid in the presence of a liquid or gaseous solution of reactants. Homogeneous catalyst is dissolved in the reaction medium along with the reactants. Both of them have the advantage and disadvantage as shown in Table 1.1.<sup>1</sup>

**Table 1.1** Comparison of homogeneous and heterogeneous catalysts

Features	Homogeneous	Heterogeneous
Active site	All metal atoms	Only atoms on the surface
Concentration	Low	High
Selectivity	High	Low
Reaction condition	Mild (50-200 °C)	Severe (often >250 °C)
Separation	Complicated	Simple

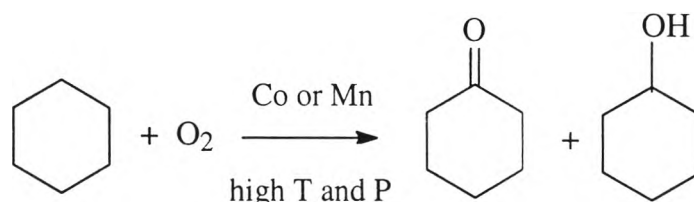
Homogeneous catalysts have a higher degree of dispersion in the reaction media than that of heterogeneous catalysts. Theoretically, in homogeneous catalysts each individual atom can be catalytically active, whereas heterogeneous catalysts have only the surface atoms active. Homogeneous catalysts exhibit a high activity per unit mass of metal more than heterogeneous catalysts. The high mobility of the molecules in the reaction mixture results in more collisions with substrate molecules. Thus, homogeneous catalysts are used in the lower amount and milder reaction conditions.

The largest scale application of homogeneous catalysis is the oxidation of hydrocarbons by molecular oxygen. Oxidation processes and their uses are listed in Table 1.2.<sup>2</sup>

**Table 1.2** Major industrial oxidation of hydrocarbons

Hydrocarbons	Oxidation Products	Applications
Cyclohexane	Cyclohexanol and cyclohexanone	Converted to adipic acid and caprolactam (polyamide precursors)
Cyclododecane	C <sub>12</sub> H <sub>23</sub> OH and C <sub>12</sub> H <sub>22</sub> O	Oxidized to dodecanedioic acid and lauryl lactam (polyamide precursors)
Butane	Acetic acid	Solvent, vinyl acetate polymers
Toluene	Benzoic acid	Caprolactam (polyamide precursors), phenol and food preservative
	Benzaldehyde	Agrochemical, flavorings and fragrances
<i>m</i> -Xylene	Isophthalic acid	Polymers and plasticizers
<i>p</i> -Xylene	Terephthalic acid	Polyester fibers, films and plastics,
	Terephthalate esters	plasticizers

In petrochemical industries, hydrocarbons are the largest component derived from petroleum refining. Saturated hydrocarbons are the largest composition in total hydrocarbons.<sup>3</sup> Consequently, they are used solely as an energy supplier or as a fuel source and generally are not expensive. Thus, the functionalization of saturated hydrocarbons to valuable products is the important process. In this study, the functionalization of cyclohexane using homogeneous catalyst is selected for investigation. Generally, cyclohexane is oxidized to cyclohexanone and cyclohexanol by utilizing cobalt or manganese complexes as catalyst between 120-250 °C at high pressure of oxygen.<sup>4</sup>



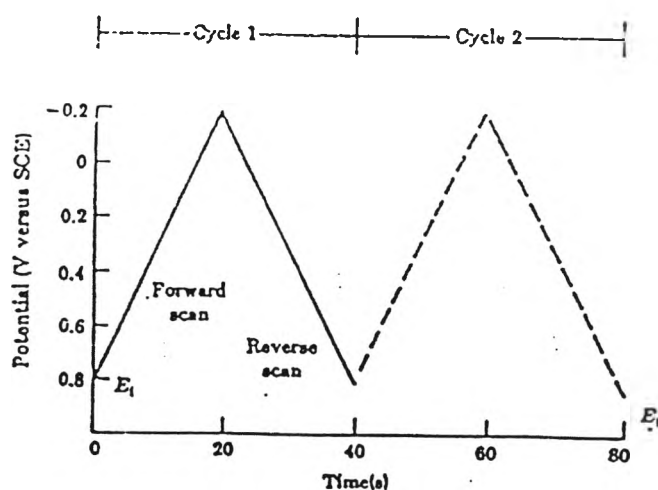
Cyclohexanone and cyclohexanol are used for the preparation of an important intermediate in the production of nylon such as adipic acid and hexamethylene diamine for nylon 66 and caprolactam for nylon 6.<sup>5</sup> Therefore, the development of the appropriate catalyst in oxidation of cyclohexane under mild conditions is still being the important investigation.

Electrochemical techniques are concerned with the interplay between electricity and chemistry. These techniques are the important methodology for following up the reaction. Many chemical measurements, which involve homogeneous bulk solution, electrochemical processes take place at the electrode-solution interface. Typically, the substance is fixed at the surface of electrode and electrons are transferred in 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.

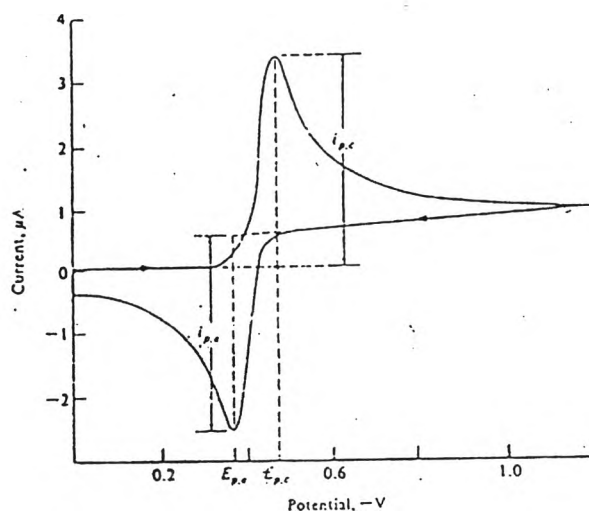
Cyclic voltammetry, one type of electrochemical techniques, is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process.

Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode, using a triangular potential wave-form as shown in Fig 1.1.<sup>6</sup>



**Fig.1.1** Potential-time excitation signal in cyclic voltammetric experiment.

During the potential sweep, the potentiostat measures the current resulting from the applied potential. The relationship between the potential applied and the current obtained is called cyclic voltammogram as shown in Fig 1.2.<sup>7</sup>



$i_{pa}$  = anodic peak current

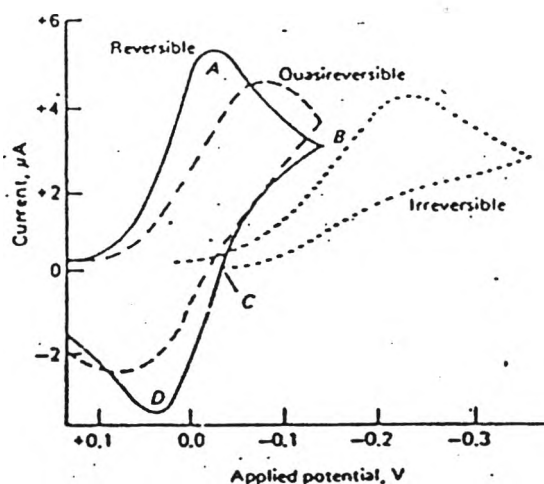
$i_{pc}$  = cathodic peak current

$E_{pa}$  = anodic peak potential

$E_{pc}$  = cathodic peak potential

**Fig 1.2** The relationship between the potential and the current

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 showed in Fig 1.3, which gives the information in a system.



**Fig 1.3** The cyclic voltammogram of three types of redox reactions

For a reversible process, the separation between the peak potentials is given

by

$$\Delta E_p = E_{pc} - E_{pa} = 0.059/n$$

where  $E_{pc}$  = cathodic peak potential

$E_{pa}$  = anodic peak potential

$n$  = number of electrons transferred

In addition, the ratio of the reverse-to-forward peak currents,  $i_{pa}/i_{pc}$ , 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.<sup>8</sup>

### 1.1 Literature review on metal Schiff base-catalyzed oxidation of cyclohexane

The process of the functionalization of cyclohexane to cyclohexanone and cyclohexanol must work under hard conditions and the selectivity of reaction is normally low. Schiff base complexes have been reported to be employed as catalyst in the functionalization of cyclohexane under mild conditions and the selectivity of reaction is generally high.

In 1995, Ganeshpure and his colleagues reported that oxo-bridged polynuclear manganese(II) *N,N'*-1,2-cyclohexyl-1,2-diyil-bis(salicylideneiminate) complexes was employed in the oxidation reaction of cyclohexane to cyclohexanone and cyclohexanol using *tert* – butylhydroperoxide (TBHP) or hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as oxidant. Cyclohexanone was found to be a major product in good yield (72%).<sup>9</sup>

In 1996, Ganeshpure and colleagues reported that the manganese(II) *N,N'*-ethylene bis(salicylideneamionato) and analogous complexes were used in oxidation reaction of cyclohexane to cyclohexanone and cyclohexanol at room temperature by TBHP as oxidant in acetonitrile. It was found that manganese(II) *N,N'*-ethylene bis(salicylideneamionato) was the best catalyst. This complex provided 86% cyclohexanone and 14% cyclohexanol.<sup>10</sup> In the same year, Tembe and his colleagues found that the polynuclear manganese(III) Schiff base complexes was utilized in oxidation reaction of cyclohexane at room temperature by using TBHP or  $\text{H}_2\text{O}_2$  as oxidant in acetonitrile. These complexes provided cyclohexanone as a major product (~ 80%).<sup>11</sup> Furthermore, Nuntasri and Loayfakajohn showed that the iron Schiff base complexes, especially  $(\text{Fesalen})_2\text{O}$ , 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 enhanced by the addition of ascorbic acid or by stepwise addition of zinc powder.<sup>12</sup>

## 1.2 Literature review on cyclic voltammetry

Cyclic voltammetry can provide the information of the reaction and examine the catalytic properties of complexes. In 1993, Issa and his colleagues found that cyclic voltammetry could be used for examining the mechanism of the reduction reaction of  $[N,N'-1,2\text{-phenylenebis(salicylideneimine)}]Co(II)$  complex and addressed that one electron of this complex was transferred in three steps.<sup>13</sup> In the same year, Sawyer and his colleagues reported that bis(bipyridine)copper(II) complex was used as a catalyst to activate oxygen ( $O_2$ ) 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  $\alpha$ -allylic alcohols.<sup>14</sup>

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 the oxidation of VO(salen) by oxygen to produce VO(salen)<sup>+</sup> proved feasible in the presence of acid.<sup>15</sup> In 1996, Kimihisa and his colleagues synthesized  $[(\text{salen})VOV(\text{salen})](I_3)$ ,  $[(\text{salen})VOVO(\text{salen})](I_3)$ ,  $[(\text{salen})VOVO(\text{salen})](ClO_4)$  and utilized in the reduction of oxygen as catalyst and studied the mechanism of the reduction of oxygen by cyclic voltammetry technique.<sup>16</sup>

In 1997, Bottcher and his colleagues investigated the spectroscopic and electrochemical properties of Co(III) (acacen) [ $H_2acacen = \text{bis(acetylacetonate) ethylenediimine}$ ] and related ligand. Electronic structure calculations indicated that the absorption between 340 and 378 nm in Co(III) (acacen) spectra was attributable to the lowest intraligand charge-transfer transition. Cyclic voltammogram of Co(III) (acacen)



revealed irreversible reduction at a potential  $-0.8$  V and reversible process at a potential  $-1.6$  V.<sup>17</sup>

In 1998, Sinclair and his colleagues presented the preparation and electrochemical properties of MoO(cat)(ssp) complex by cyclic voltammetry. The result disclosed that the six-coordinate MoO<sup>4+</sup> species exhibited reversible Mo(VI/V) electrochemistry at a potential  $0.1$  V.<sup>18</sup>

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(salophen), VO(hean) and VO(sap) exhibited reversible reaction, while VO(salen), Cu(salophen) and Ni(salophen) displayed quasi-reversible reaction and Cu(sap), Ni(sap) and Cr(sap) displayed irreversible reaction.<sup>19</sup>

### **1.3 Literature review on 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<sub>4</sub>)(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 were investigated. All complexes displayed reversible reaction with two 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.<sup>20</sup>

In 2001, Hoogenraad and his colleagues synthesized new manganese(III) complexes of Hphox (2-(2'-hydroxyphenyl)-oxazoline) and HClphox(2-(5'-chloro-2'-hydroxyphenyl)-oxazoline) and were examined by cyclic voltammetry. It was found that cyclic voltammogram of these complexes showed quasi-reversible reaction and these complexes provided good results in the epoxidation of styrene by hydrogen peroxide.<sup>21</sup>

In 2002, Hoogenraad and his colleagues synthesized  $MnL_3$  (HL being 2(2'-hydroxyphenyl)oxazoline ligands) and was examined the redox property. Cyclic voltammetry experiments show that the electrochemically quasi-reversible Mn-II/Mn-III and reversible Mn-III/Mn-IV. All complexes are active oxidation catalysts with dihydrogen peroxide as the oxidant. In the oxidation of styrene, up to 220 turnover numbers were obtained towards styrene oxide.<sup>22</sup>

#### **1.4 The goal of this research**

The purpose of this research can be summarized as follows:

1. To synthesize Schiff base ligands
2. To synthesize metal Schiff base complexes
3. To study the relationship between electrochemical and catalytic properties of metal Schiff base complexes