

CHAPTER I

INTRODUCTION

During the last decade, petrochemical industries have been developed rapidly in Thailand. Petroleum is a mixture of thousands of different hydrocarbon compounds. All of them can be burned, which is why petroleum is such a wonderful source of fuel. Petrochemical industry provides a huge range of useful products, such as plastics, rubbers, fibers, detergents, and solvents, and supplies raw materials for the manufacture of many other chemicals.¹ The largest component in petroleum products is found to be saturated hydrocarbons. However, functionalization of saturated hydrocarbons to other organic compounds have not been widely reported. Because of their high bond dissociation energy, they are mostly used as fuel source or as solvent.² 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 cyclohexanone and cyclohexanol could proceed employing an oxidation catalyst such as cobalt complexes at 160⁰C and under high pressure.³ Due to these conditions, the chemical reaction is unselective and many products are invariably produced, such as succinic, glutaric and caproic acids.⁴

Previously, it was reported that several biological systems particularly those found in mammals, for example, cytochrome P-450 enzyme system and peroxidase, can hydroxylate saturated hydrocarbons under mild condition.⁵ Working towards the

main aim to carry on the reaction at lower temperature is very promising idea because it can reduce the capital cost that is the main objective in petrochemical industries.

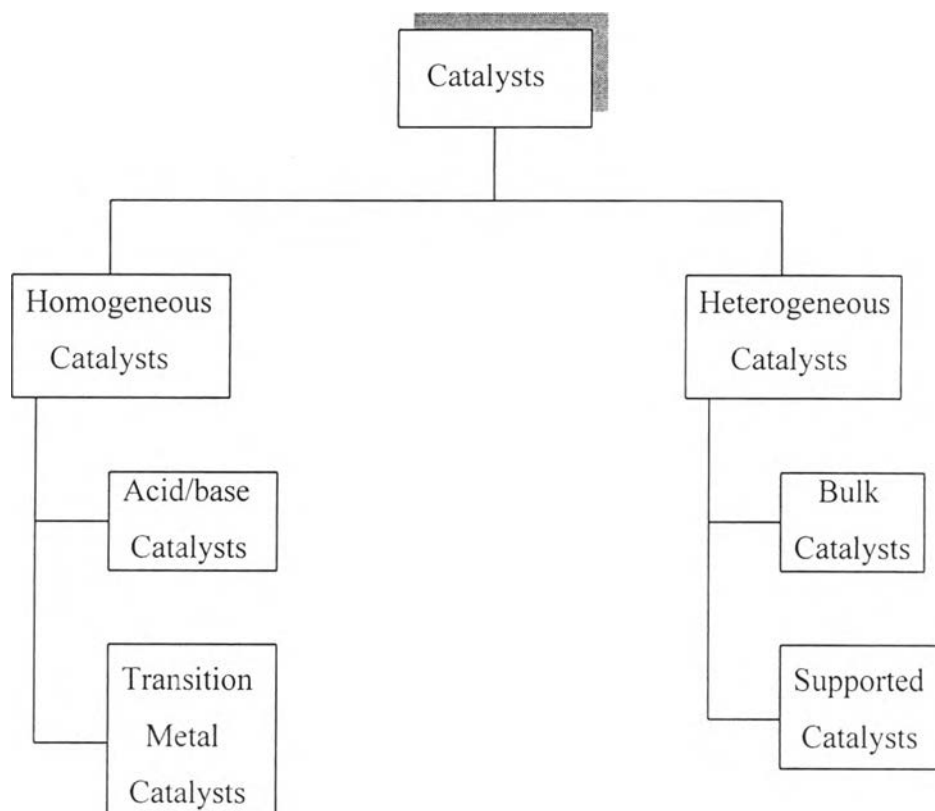
In this research, the oxidation of cyclohexane to cyclohexanone and cyclohexanol, one of the most important oxidation process in industry, was chosen to examine. Both products show the important role as intermediates for the conversion into adipic acid and caprolactam and hence to nylon, which has enormous commercial applications.⁶ However, in industry, oxidation of saturated hydrocarbons proceeded under severe conditions. Thus, the mild condition for the oxidation of saturated hydrocarbons catalyzed by metal porphyrin complexes were investigated. Due to this mild condition, undesired side products were not occurred. In addition, the suitable conditions for the oxidation reactions were explored, for example, temperature, oxidant and additive.

Catalysts have been successfully used in the chemical industry for hundreds of years, and many large-scale industrial processes can only be carried out with the aid of catalysis. Catalysis is the key to chemical transformations. Most industrial syntheses and nearly all biological reactions require catalysts.

Apart from accelerating reactions, catalysts have another important property. They can influence the selectivity of chemical reactions. This means that completely different products can be obtained from a given starting material by using different catalyst systems.

Catalysts can be gases, liquids or solids. But most of industrial catalysts are liquids or solids. The importance of catalysis in the chemical industry is shown by the fact that 75 % of all chemicals are produced with the aid of catalysts. In nearly developed processes, the figure is over 90 %.⁷

The numerous catalysts known today can be classified into two large groups: heterogeneous and homogeneous catalysts.



Most of the processes involved in crude-oil processing and petrochemistry, such as purification, stages, refining and chemical transformation, require catalysts. Oxidation of saturated hydrocarbons also requires catalysts. Catalysts in this research are transition metal complexes, which are homogeneous catalysts.

In homogeneous catalysis, catalyst, starting materials and products are present in the same phase. Homogeneous catalysts have a higher degree of dispersion than heterogeneous catalysts since in theory each individual atom can be catalytically active. In heterogeneous catalysts only the surface atoms are active.⁸

Moreover, the most prominent feature of homogeneous transition metal catalysts is the high selectivities that can be achieved. The major disadvantage of

homogeneous transition metal catalysts is the difficulty of separating the catalyst from the product. In this case, more complicated processes such as distillation, liquid-liquid extraction and ion exchange must often be used.

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

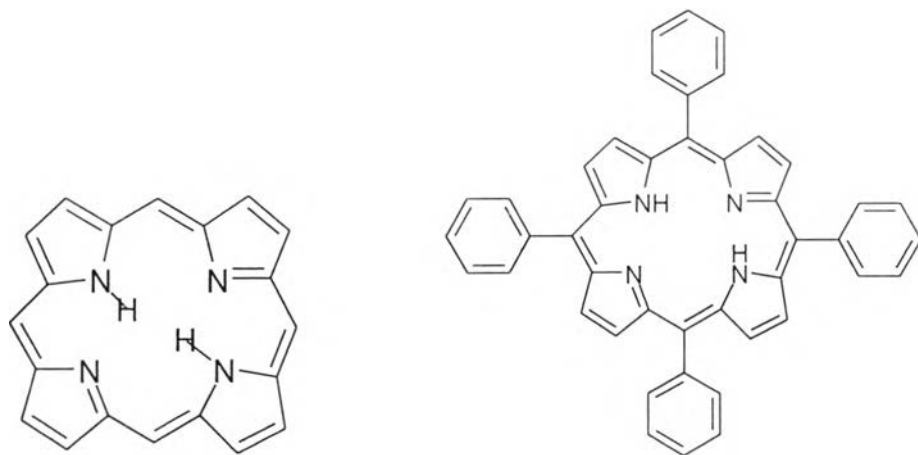
C-H bond activation has been one of the most challenging problems in catalysis because of its difficulty to functionalize and because alkanes are the most abundant source of starting materials.⁹ Cytochromes P-450 can functionalize C-H bond at ambient temperature with product specificity. This ability shows importance in porphyrin-based biomimetic systems.¹⁰ Among these processes, oxidation of saturated hydrocarbons has attracted the most attention for high selectivity and effectiveness. So, the metalloporphyrins play an important role among the metal complexes utilized as catalysts in the oxidation of organic compounds, as they can be considered good models of heme-containing enzymes, which are able to catalyze

various oxidation reactions. Furthermore, the search for a suitable model metalloporphyrin to act as a best catalyst is the main target in this research.

Porphyrin is a macrocyclic compound containing four pyrrole units which are connected by methylene bridges. Most of the metalloporphyrins used as oxidation catalysts are based on the *meso*-tetraphenylporphyrin ligand family.¹¹ These porphyrins are accessible in a one-step reaction from substituted benzaldehyde and pyrrole.¹² As would be expected for such an extended system of conjugation, the porphyrins are intensely colored.

The porphyrins find important roles in biology. These include transporting oxygen from air to the cells, acting as intermediates in the transfer of electrons from oxidizing to reducing agents within a cell, converting light into chemical energy in photosynthesis, and playing a number of roles in biosynthetic pathways.¹³

The basic structure of porphyrin is shown below.



Porphyrin

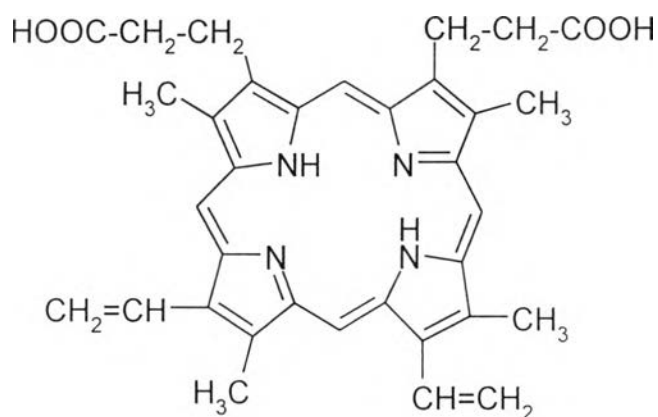
Meso-tetraphenylporphyrin

Porphyrin and *Meso*-tetraphenylporphyrin

Important porphyrins such as chlorophyll and heme are derivatives of the basic porphyrin molecule.

Heme

Throughout the animal kingdom, substances are required capability of binding oxygen from the air and transporting it to the cells, where it can be utilized in metabolism. The most common oxygen-transporting substances are proteins, hemoglobin and myoglobin. Hemoglobin and myoglobin possess groups that consist of a porphyrin containing an iron atom bonded to four nitrogens of the central cavity. This iron porphyrin is known as heme. The basic skeleton structure of heme is depicted as shown below.



Heme

The protein myoglobin contains one heme group. It acts to store oxygen in muscle tissue and to promote the transfer of oxygen to the mitochondria of muscle cells. Hemoglobin, which binds oxygen from the air and transports it through the blood to the cells, contains four heme groups. Hemoglobin therefore can be considered a tetramer of myoglobin.

The cytochromes are also proteins that contain iron porphyrins. The cytochromes play important roles in a biological electron-transport chain. They act as intermediates in the transfer of electrons from reducing agents to oxidizing agents in the cell. There are several types of cytochromes, and they play different roles in electron transport. They all possess a heme unit or a derivative of heme.¹⁴

Iron porphyrin complexes are very stable, and the reaction of free Fe(II) porphyrin complexes with O₂ provides a highly significant contrast with those of hemoglobin. These complexes do not act as oxygen carriers but instead undergo so-called "autoxidation". According to this interesting oxidation reaction, all of the oxidation of saturated hydrocarbons in this research were proceeded by using metal porphyrin complexed as catalyst.

Catalytic oxidation with molecular oxygen has been investigated extensively in the last several decades as the most prospective conversion to introduce functional group into inactive hydrocarbons for the utilization of cheaper organic carbon resources.¹⁵ Recently, not only the direct activation of dioxygen with catalyst but also indirect activation, especially the activation of dioxygen in the presence of reducing agents have been investigated extensively and these new type activations of dioxygen have been widely employed in the functionalization of inert hydrocarbon.

D.H.R. Barton established an aerobic oxidation using zinc powder as the reducing agent in acidic conditions. The reaction system is composed of an iron complex, pyridine, acetic acid and Zn powder so-called Gif system, which can oxidize saturated hydrocarbon to ketone and alcohol at ambient temperature.¹⁶ This research have also demonstrated an aerobic oxidation with zinc by mimicking cytochrome P 450 catalyzed oxidation reaction.

1.1 Literature review on the activation of saturated C-H bonds

Previously, most hydrocarbons derived from crude oil are unfortunately burned to carbon dioxide and water. In the near future, saturated hydrocarbons should mainly be used as raw materials for the manufacturing of chemicals. However, the direct activation of saturated hydrocarbons by classical methods usually requires severe conditions, affording mixtures of products derived from overoxidation. Therefore, the oxidation under mild conditions of the most abundant and cheapest class of organic compounds is an important aim of this research.

1.1.1 Industrial process for the homogeneous, metal-catalyzed oxidation of saturated hydrocarbons

The manufacturing of cyclohexanone and cyclohexanol is the first step 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 6.¹⁷ Petrochemical process of cyclohexane from petrochemical feedstock is shown in Fig 1.1 and the utilization of cyclohexane as starting material in chemical industry is shown in Table 1.2.

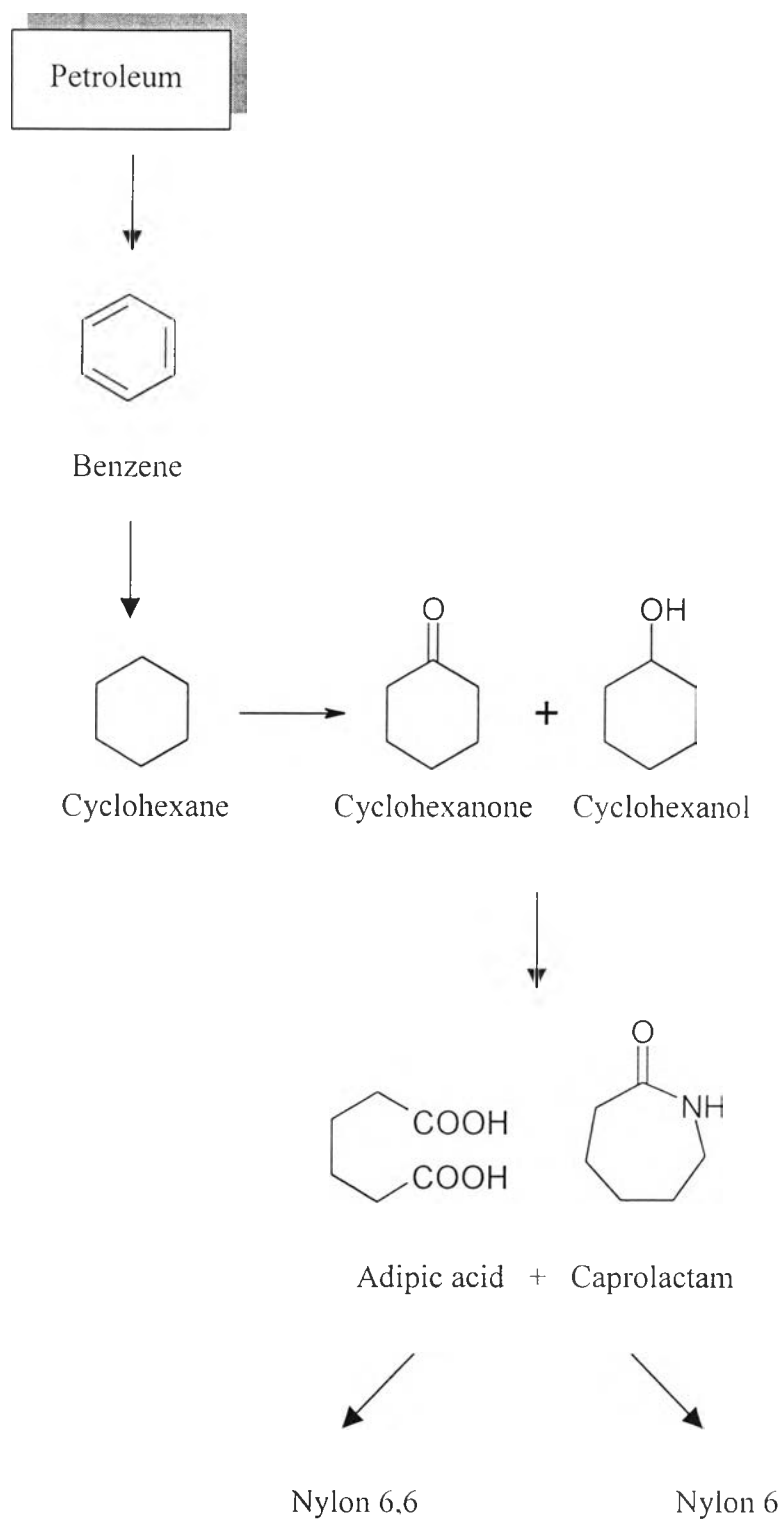


Fig 1.1 Petrochemical process from benzene to nylons

Table 1.2 Uses of cyclohexane

Products	Usage
Adipic acid	55 %
Caprolactam	26 %
Miscellaneous	19 %

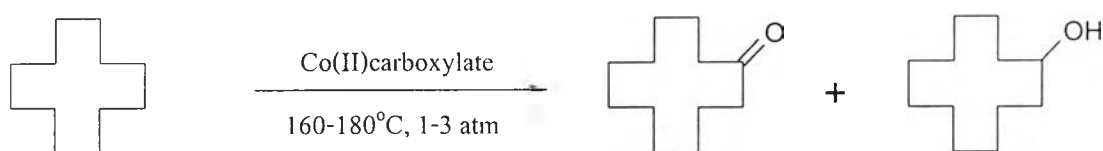
Adipic acid is a very important chemical that is used all over the world to produce various daily products. The process of producing adipic acid can be done by using different reactions. The main reaction is made by oxidizing cyclohexanol/cyclohexanone mixture with nitric acid. Yields of 92% to 96% are obtained with complete conversion. The adipic acid is purified by recrystallization from water. Nylon 6,6 is the largest outlet for adipic acid. More than 90% of adipic acid is consumed in the manufacture of nylon 6,6. Adipic acid is also used as a food ingredient in gelatins, desserts and other foods that require acidulation.¹⁸ Nylon is used for everyday applications such as electrical connectors, cable tires, fishing line, fabrics, carpeting and many other useful products.¹⁹ Uses of adipic acid in petrochemical industry are indicated in Table 1.3.

Table 1.3 Uses of adipic acid

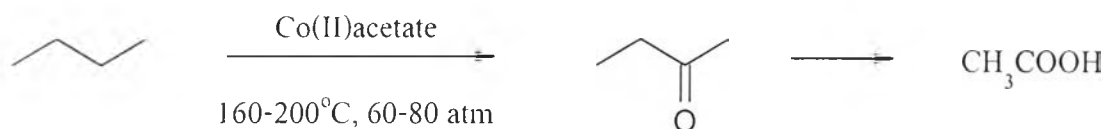
Products	Usage
Nylon 6,6 fibers	72 %
Nylon 6,6 resins	18 %
Polyurethanes	5 %
Plasticizer	3 %
Miscellaneous	2 %

Most caprolactam is made from cyclohexanone. Originally the cyclohexanone was made by hydrogenating phenol, but material prepared from cyclohexanol/cyclohexanone mixtures is now also commonly used. Nylon 6 is made by polymerizing caprolactam in the presence of a catalytic amount of water, under conditions similar to those used in nylon 6,6 manufacture. The properties of nylon 6 are very similar to those of nylon 6,6, and the two are virtually interchangeable in their applications.

Another major industrial application utilizing alkane is the synthesis of cyclododecanone and cyclododecanol from cyclododecane. These compounds are done by process very similar to that of cyclohexane: cobalt (II) carboxylates are used as catalysts, at 160-180 °C and 1-3 atm pressure.



Another example, butane is oxidized by air, in acidic solution, catalyzed by cobalt (II) acetate. Reaction conditions are 160-200 °C and 60-80 atm pressure. The by-products are propionic acid, butyric acid and 2-butanone.²⁰



1.1.2 Literature review on the oxidation of saturated hydrocarbons

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

In 1994, Barton and colleagues²¹ 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 affect an augmented selectivity towards the formation of ketone.

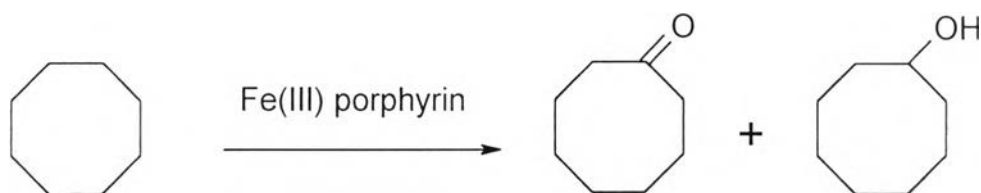
In 1999, Kyu-Wan Lee and his colleagues²² reported cyclohexane oxidation using metal oxides such as Fe₂O₃, FeO as a catalyst. They found that the selectivity ratio of cyclohexanone to cyclohexanol were greatly affected by the acidity of metal oxides. When metal oxide has more acidic property, the reactivity on oxidation is increased and the formation of cyclohexanone is more favored.

1.1.3 Literature review on the functionalization of hydrocarbon catalyzed by metal porphyrin complexes

Metalloporphyrins were found to act as good catalysts for the formation of epoxides from alkenes and ketones and alcohols from alkanes for a long time.

In 1986, Miyamoto and his colleagues²³ had developed iron (III) porphyrin system in the epoxidation of olefins (styrene, α -methylstyrene, cyclohexene and cyclooctene). They found that the total yield of the product when using Mn (III) porphyrin as catalyst was similar to those of Fe (III) porphyrin. However, in cyclohexene and cyclooctene epoxidation, the yields of these products using Fe (III) porphyrin were considerably higher than Mn (III) porphyrin.

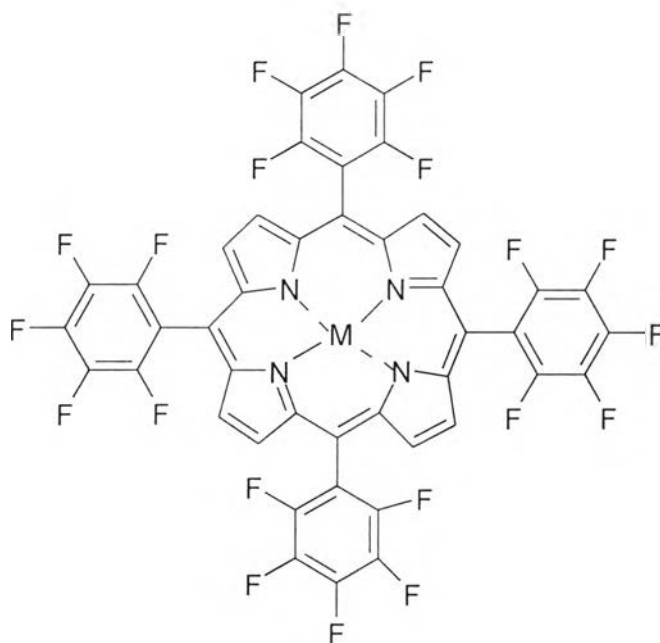
In 1989, Mansuy and co-workers²⁴ reported the use of Fe (III) and Mn (III) porphyrins to catalyze cyclooctene epoxidation and cyclooctane oxidation. Effectively, cumylhydroperoxide in the presence of these metalloporphyrins has shown a poor ability to epoxidize alkenes but reacted well with alkanes with formation of alcohols and ketones.



In 1990, Sanderson and his colleagues²⁵ reported the production of ketones and alcohols by reacting an alkane with a hydroperoxide in the presence of a transition metal porphyrin catalyst. They found that an isobutane oxidation gave high yield by using Fe (III) and Mn (III) porphyrin as catalyst.

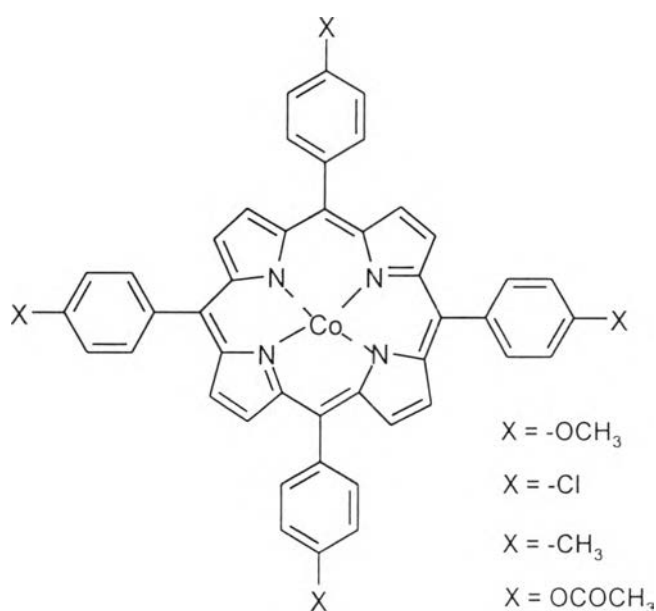
In 1994, Mansuy and colleagues²⁶ found that an oxidation system comprising of Mn (III) porphyrin catalyst and ammonium acetate cocatalyst oxidized alkanes with yields of 45-87%. In this reaction, H₂O₂ appeared to be a particularly interesting oxygen atom donor as it is inexpensive, readily available oxidant which should give H₂O as the only by-product.

In 1995, Komiya and colleagues²⁷ presented metalloporphyrin-catalyzed oxidation of alkanes with molecular 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.



meso-pentafluorophenylporphyrin

In 1996, Iqbal and co-workers²⁸ reported the use of cobalt (II) porphyrin as catalyst for the oxidation of wide range of organic substrates at ambient condition by using a combination of molecular oxygen and 2-methyl propanal. The observations suggest that substituents in the *para* position of aromatic ring in porphyrin play quite an effective role during the oxidations and as indicated methoxy group appears to enhance the catalytic activity of the oxidations.

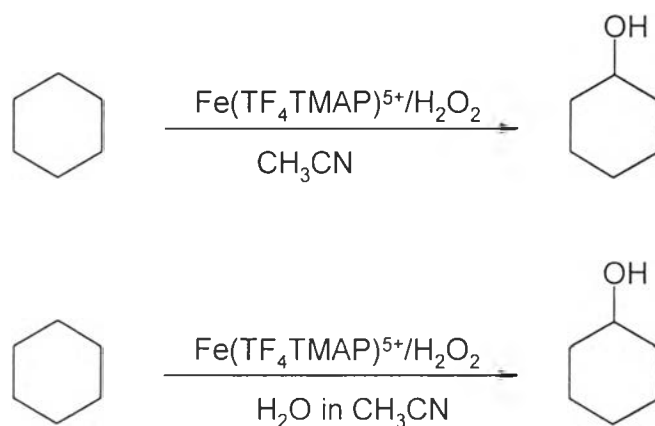


Variation of *para*- substituent in *meso*-tetraphenylporphyrin

In 1997, Koda et al.²⁹ presented aerobic oxidation of cyclohexane to yield cyclohexanone and cyclohexanol in the presence of Fe (III) porphyrin catalyst bearing *meso*-pentafluorophenyl group. They found that the yield of products reached a maximum value at the pressure close to the critical pressure of CO₂.

In 1999, Nam and colleagues³⁰ reported that iron (III) porphyrin complexes had been used as model compounds to mimic the chemistry of cytochrome P-450

enzymes that are capable of catalyzing oxidation of cyclohexane and cyclooctane with H_2O_2 as oxidant. The iron porphyrin complex is able to oxidize cyclohexane with high product yields of cyclohexanol at $-40\text{ }^\circ\text{C}$.



1.2 The goal of this research

The purposes of this research can be summarized as follows :

1. To synthesize tetraphenylporphyrin ligands
2. To synthesize metalloporphyrins
3. To study the optimum conditions for cycloalkanes oxidation by using metal porphyrin complexes
4. To study the regio- and chemoselectivity of this developed oxidation system