# CHAPTER I

INTRODUCTION

Saturated hydrocarbons account for one of the largest sources of natural feedstock materials which traditionally have been used as fuels, lubricants, and solvents [1]. During the past few decades, there has been an increase in interest in the oxidation of inexpensive saturated hydrocarbons by transition metal salt (or complexes) to more commercially valuable products related to pharmaceuticals, flavors, fragrances, plasticizers, and polymer precursors. Generally, the oxidation reaction of this class of compounds, required vigorous conditions such as high temperature or high pressure and employed cobalt or manganese complexes as catalyst. Development of metal-based catalyst which carries out these oxidation processes under mild conditions and with inexpensive and environmentally benign oxidant such as O_2, H_2O_2, and $ROOH$ has for some time been a sought after goal for both industry and academia. In this research, the oxidation of saturated hydrocarbons was developed by using soluble metal stearate complexes as catalyst under mild conditions was used in the system [2].

1.1 Classification of catalysts [3]

Numerous catalysts known today can be classified according to various criteria: structure, composition, area of application, or state of aggregation. According to the state of aggregation in which they act, three large groups of catalysts can be divided: heterogeneous catalysts (solid-state catalysts), heterogenized homogeneous catalysts and homogenous catalysts (Scheme1.1). There are also intermediate forms such as homogeneous catalysts attached to solids (supported catalysts), also known as immobilized catalysts. The well-known biocatalysts (enzymes) also belong to this class.
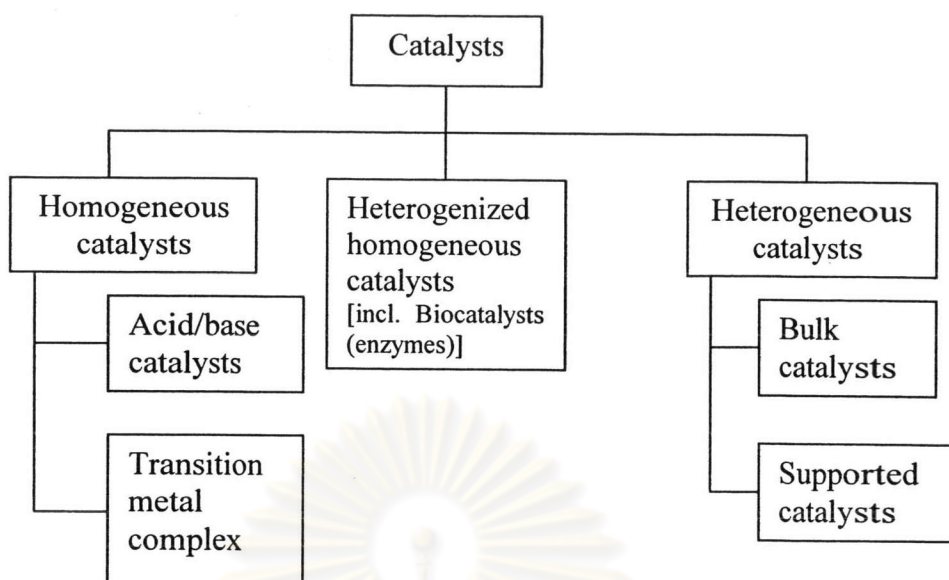
Scheme 1.1 Classification of catalysts.

1.1.1 Comparison of homogeneous and heterogeneous catalysts

Whereas for heterogeneous catalysts, phase boundaries are always present between the catalyst and reactants, in homogeneous catalysis, catalysts, starting materials, and products are present in the same phase. Homogenous catalysts have a higher degree of dispersion than heterogeneous catalysts which only the surface atoms are active.

Due to their high degree of dispersion, homogeneous catalysts exhibit a higher activity per unit mass of metal than heterogeneous catalysts. The high mobility of the molecules in the reaction mixture results in more collisions with substrate molecules. The reactants can approach the catalytically active center from any direction, and a reaction at an active center does not block the neighboring centers. This allows the use of lower catalyst concentrations and milder reaction conditions.

The most prominent feature of homogeneous transition metal catalysts are the high selectivity that can be achieved. Homogeneously catalyzed reactions are controlled mainly by kinetics and less by material transport, because diffusion of the reactants to the catalyst can occur more readily. Due to the well-defined reaction site, the mechanism of homogeneous catalysis is relatively well understood. Mechanistic investigations can readily be carried out under reaction conditions by means of

spectroscopic methods. In contrast, processes occurring in heterogeneous catalysis are often obscure.

Owing to the thermal stability of organometallic complexes in the liquid phase, industrially realizable homogeneous catalysis is limited to temperature below 200°C. In this temperature range, homogenous catalysts can readily be stabilized or modified by addition of ligands; considerable solvent effects also occur.

In industrial use, both types of catalysts are subjected to deactivation as a result of chemical or physical processes. Table 1.1 summarizes the advantages and disadvantages of the two classes of catalysts.

Table 1.1 Comparison of homogeneous and heterogeneous catalysts

	Homogeneous	Heterogeneous
Effectivity		
Active centers	all metal atoms	only surface atoms
Concentration	low	high
Selectivity	high	lower
Diffusion problems	practically absent	present
Reaction conditions	mild (50-200°C)	severe (often>250°C)
Applicability	limited	wide
Activity loss	irreversible reaction with products (cluster formation); poisoning	sintering of the metal crystallites; poisoning
Catalyst properties		
Structure/stoichiometry	defined	undefined
Modification possibilities	high	low
Thermal stability	low	high
Catalyst separation	sometimes laborious (chemical decomposition, distillation, extraction)	fixed-bed: necessary suspension: filtration
Catalyst recycling	possible	unnecessary (fixed-bed) or easy (suspension)
Cost of catalyst losses	high	low

The major disadvantage of homogeneous transition metal catalysts is the difficulty of separating the catalyst from the product. Heterogeneous catalysts are either automatically removed in the process, or they can be separated by simple methods such as filtration or centrifugation. In the case of homogeneous catalysts, more complicated processes such as distillation, liquid-liquid extraction, and ion exchange must often be used.

1.1.2 The oxidation of alkanes in the presence of metal compounds [4]

Metal complexes may participate in the oxidation of hydrocarbons, including alkanes, in reactions of three main types:

1. Direct oxidation under the reaction of a metal complex in high oxidation state (without the participation of dioxygen).
2. Oxidation by dioxygen, peroxide and other oxidants with a metal compound playing the role of an initiator or a catalyst.
3. Coupled oxidation where a metal complex in low oxidation state induces stoichiometric hydrocarbons oxidation when being oxidized.

The mechanisms of these three reaction types often have much in common; moreover, one type of oxidation may change to another. For example, in the presence of an additional electron donor, stoichiometric oxidation of hydrocarbons of type 3 might become a catalytic oxidation coupled with the oxidation of the donor if the transition metal complex involved in the oxidation-reduction cycle.

As for the elementary mechanism of hydrocarbon reactions in the oxidation of all three types, the metal complex may interact with the hydrocarbon molecule directly, or by forming active species (*e.g.*, free radical) which would react with the hydrocarbon independently.

1.1.3 Participation of transition metal ions and complexes in the oxidation of hydrocarbons by molecular oxygen

The oxidation of hydrocarbons by molecular oxygen includes very important chemical processes known for very long time. Their importance is connected with the necessity of rational use of hydrocarbons from coal, oil and natural gas. Despite the great amount of work devoted to this problem, it is far from being completely solved.

At present its significance, in terms of the urgent necessity of more economical consumption of natural resources, is increasing with time.

The use of salts and complexes of transition metals creates great possibilities for solving problems of selective oxidation, as has been demonstrated for a number of important processes.

1.2 Chain mechanisms of oxidation of alkanes

To explain the molecular oxygen interaction with organic compounds, Bach and Engler proposed the so-called peroxide theory at the end of the 19th century. In accordance with this theory the initial reaction products are peroxides, which are later transformed into more stable products.

Further investigations have conformed the intermediate formation of peroxide. However, a real mechanism of autoxidation involving hydrocarbons was elucidated only with the discovery of chain reactions and the formation, mainly by Semenov and his co-workers, of the theory of branched chain processes.

A detailed study of liquid phase oxidation including that of alkanes for the last several decades has led to considerable understanding of the reaction mechanism.
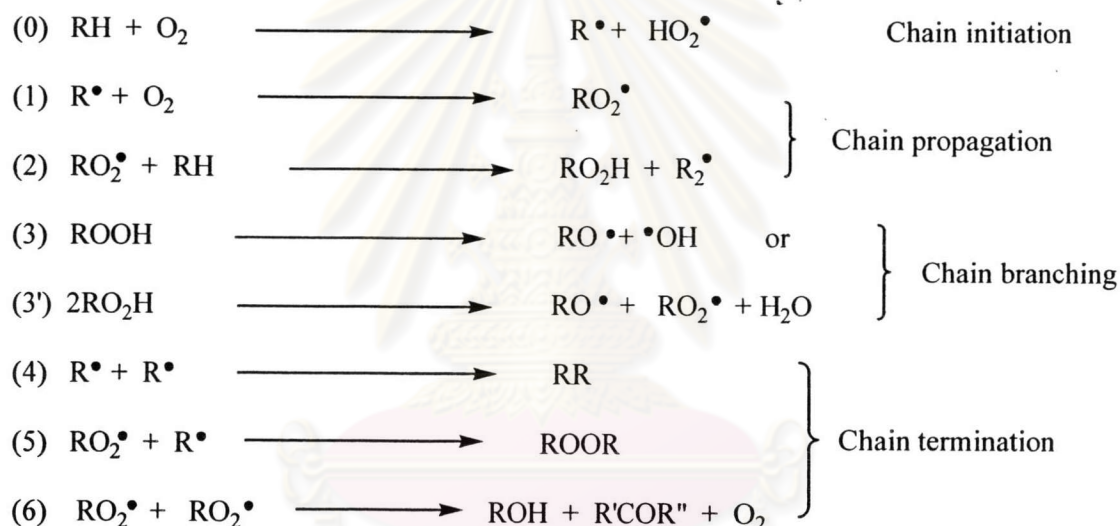
Catalytic and non-catalytic autoxidation of hydrocarbons (including alkanes) is usually a branched chain process with a so-called 'degenerate' chain branching. This means that branching of each chain happens much later than its termination (as distinct from non-degenerate branching which occurs virtually simultaneously with chain propagation) and causes by the formation of a rather stable intermediate which is nevertheless chemically more active than the initial hydrocarbon and can form free radicals at a greater rate than that of the chain initiation process. Hydroperoxides turn out to be the intermediates in liquid phase oxidation, thus confirming the peroxide theory. The comparatively low energy of the O-O bond in hydroperoxide brings with formation of free radicals.

The study of ROOH hydroperoxide produced from hydrocarbons has shown the structure of R in ROOH to be the same as in the initial RH, which confirms that a hydroperoxide is formed in the interaction of $RO_2\cdot$ radicals with the molecule of the initial hydrocarbon.

$$RO_2^\bullet + RH \longrightarrow ROOH + R\bullet$$

The evidence for the chain mechanism of hydrocarbon oxidation is primarily based on the observation of the enhancing effect of light. Ionizing radiation and small additions of various initiators easily decomposing into free radicals, as well readily react with free radicals. For some oxidation reactions, $RO_2\cdot$ radicals involved in the chain propagation were directly observed by EPR.

The following classical scheme presents a typical mechanism of liquid-phase hydrocarbon oxidation for the early stages when the effect of reaction products may be neglected.

(0) $RH + O_2 \longrightarrow R^\bullet + HO_2^\bullet$ Chain initiation

(1) $R^\bullet + O_2 \longrightarrow RO_2^\bullet$

(2) $RO_2^\bullet + RH \longrightarrow RO_2H + R_2^\bullet$ Chain propagation

(3) $ROOH \longrightarrow RO^\bullet + {}^\bullet OH$ or

(3') $2RO_2H \longrightarrow RO^\bullet + RO_2^\bullet + H_2O$ Chain branching

(4) $R^\bullet + R^\bullet \longrightarrow RR$

(5) $RO_2^\bullet + R^\bullet \longrightarrow ROOR$ Chain termination

(6) $RO_2^\bullet + RO_2^\bullet \longrightarrow ROH + R'COR'' + O_2$

Each specific hydrocarbon has its own characteristics. However, in principle, the branching chain mechanism has some general features.

1.3 Cyclohexane oxidation [5]

Adipic acid, an important intermediate in the production of nylon, is made by oxidation of cyclohexanone and cyclohexanol. These intermediates, in turn, come from the oxidation of cyclohexane. They are also intermediate in the production of caprolactam, which can be polymerized to form 6-nylon directly. In the simplest model, cyclohexane is converted to cyclohexyl hydroperoxide and some or all of

hydroperoxide is decomposed to the observed products, cyclohexanol, and cyclohexanone:
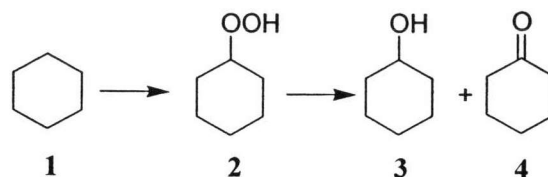

Oxidative attack on the C-H bonds of cyclohexane **1** is slow and requires vigorous reaction conditions. In contrast, the hydroperoxide **2**, alcohol **3**, and ketone **4** are easily oxidized. As a result, the reaction is generally run with low conversions of cyclohexane to avoid degradation of the desired products.

A typical industrial oxidation may be carried out by reacting air with a cyclohexane solution of a soluble cobalt(II) salt at about 140-165°C and 10 atmospheres in a continuous process. The residence time in the reactor is limited to achieve up to 10% conversion of the cyclohexane. Liquid reaction mixture is withdrawn continuously and distilled; unreacted cyclohexane is recycled to the oxidation reactor. Cyclohexanol and cyclohexanone are sent to another oxidation unit for conversion to adipic acid as described below or to caprolactam. Combined yields of alcohol and ketone are 60-70% if conversion is limited to 6-9%. An alternative strategy involves maximizing the peroxide is then composed under conditions which maximize the yield of cyclohexanone and cyclohexanol from the peroxide. In a process developed by Halcon, considerably higher yields can be attained at 10-12% conversion if boric acid is added to stabilize the cyclohexanol as it is formed. The borate is believed to react with the peroxide **2** to form a peroxylborate which subsequently decompose to the borate ester of cyclohexanol from subsequent oxidation, thereby allowing the higher conversions. The improved yields are partially offset by the added investment and operating costs for boric acid recycle, but this technology is used by several major adipic acid products.
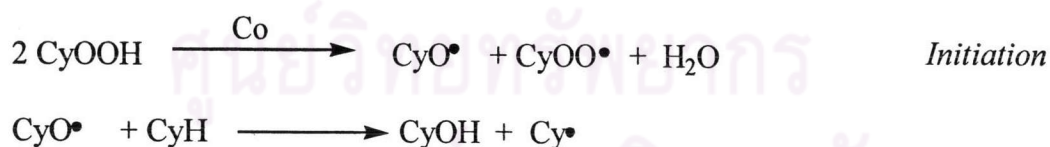
The metal ions probably have no direct part in the conversion of cyclohexane to cyclohexyl hydroperoxide because this oxidation is a simple radical chain process. However, the metal ions have a role in controlling the conversion of the hydroperoxide to cyclohexanol and cyclohexanone. In addition, metal catalyzed hydroperoxide reactions supply the free-radicals necessary to initiate and maintain the

oxidation. The metal ion concentration provides some control of the overall reaction rate. Cobalt and manganese ion catalysts produce both cyclohexanol and cyclohexanone. Chromium favors the production of cyclohexanone.

The attack of a radical, **X•**, on cyclohexane initiates the oxidation process by abstracting a hydrogen atom from cyclohexane. The resulting cyclohexyl radical rapidly combines with O_2 to form a cyclohexylperoxy radical. When the latter encounters a cyclohexane molecule, it abstracts hydrogen from a C-H bond in an endothermic but nonetheless important, equilibrium reaction. The transfer of H from C to O produces a primary product, cyclohexyl hydroperoxide, and regenerates a cyclohexyl radical. The cyclohexyl radical is immediately trapped by oxygen, shifting the equilibrium and starting another reaction cycle.
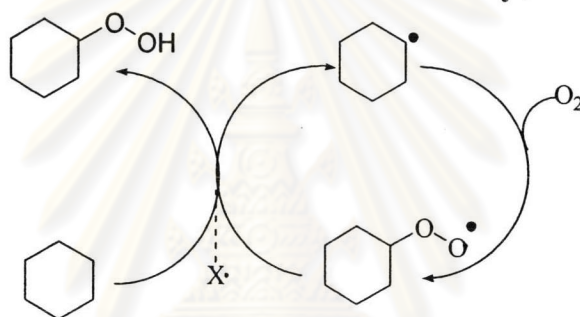

Once oxidation begins, the process is a typical radical chain process consisting of initiation, propagation, and termination reactions. Initiation is primarily a result of the Haber-Weiss cycle decomposition of cyclohexyl hydroperoxide.

$$2\ CyOOH \xrightarrow{\text{Co}} CyO^\bullet + CyOO^\bullet + H_2O \qquad \textit{Initiation}$$

$$CyO^\bullet + CyH \longrightarrow CyOH + Cy^\bullet$$

The highly energetic cyclohexyloxy radical abstracts any available hydrogen atom, primarily from the cyclohexane, which is in large excess, to give cyclohexanol.

The longer-lived cyclohexylperoxy radical is capable of abstracting a hydrogen atom from cyclohexane despite the endothermic nature of the reaction because the resulting cyclohexyl radical rapidly combines with an oxygen molecule to form a more stable cyclohexylperoxy radical combines with an oxygen molecule thereby driving the equilibrium to the right.

$$CyOO^{\bullet} + CyH \rightleftharpoons CyOOH + Cy \qquad \textit{Propagation}$$

$$Cy^{\bullet} + O_2 \longrightarrow CyOO^{\bullet}$$
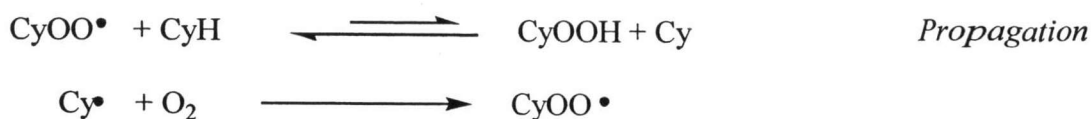
This cycle provides the chain mechanism which accounts for several cyclohexylhydroperoxide molecules for each initiating event.

The major termination in cyclohexane oxidations at low conversion is the bimolecular combination of two cyclohexylperoxy radicals.
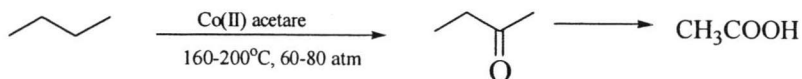
Termination
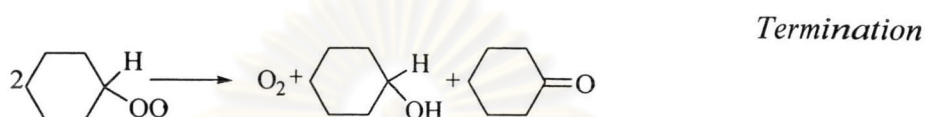
The reaction occurs with little or no activation .energy and is essentially independent of temperature. It is thought to proceed through a transitory tetroxide which undergoes intramolecular H-atom transfer to give one cyclohexanone and one cyclohexanol. The probability of this bimolecular reaction is enhanced by the relative stability of the CyOO· radical and by coordination to manganese or cobalt. The ketone is formed in a triplet state, resulting in the chemiluminescence observed during cyclohexane oxidation or cyclohexylhydroperoxide decomposition.

Because the reaction is typically run in a continuous manner at steady state, the initiation and termination reactions must occur at equal rates. The initiation gives one molecule of cyclohexanol, whereas termination gives one cyclohexanol and one cyclohexanone. This balance explains the observed cyclohexanone to cyclohexanol ratio of approximately 0.5 in cobalt catalyzed reactions.

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.
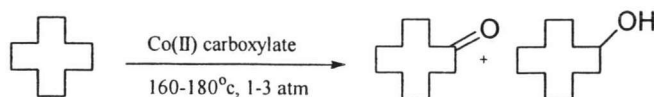
In another example, butane is oxidized by air, in acid solution, catalyzed by Co(II) acetate. Reaction conditions are 160-200°C and 60-80 atm. The by-products are propionic acid, butyric acid and 2-butanone [6].

$$\text{(butane)} \xrightarrow[\text{160-200}^{\circ}\text{C, 60-80 atm}]{\text{Co(II) acetare}} \text{(2-butanone)} \longrightarrow CH_3COOH$$

1.4 Product Selectivity

Regioselectivity

A regioselective reaction is one in which one direction of bond making or breaking occurs preferentially over all other possible directions. Reactions are termed completely (100%) regioselective if the discrimination is complete, or partially (χ%), if the product of the reaction at one site predominates over the product of reaction at other sites. The discrimination may also semi-quantitatively be referred to as high or low regioselectivity.

In the past, the term 'regiospecificity' was proposed for 100% regioselectivity. This terminology is not recommended owing to inconsistency with the terms stereoselectivity and stereospecificity.

Stereoselectivity

The preferential formation in a chemical reaction of one stereoisomer over another when the stereoisomers are enantiomer, the phenomenon is called enantioselectivity and is quantitatively expressed by the enantiomer excess; when they are diastereoisomers, it is called diastereoselectivity and is quantitatively expressed by the diastereoisomer excess.

Chemoselectivity

Chemoselectivity is the preferential reaction of a chemical reagent with one of two or more different functional groups. A reagent has a high chemoselectivity if reaction occurs with only a limited number of different functional groups. For example, sodium tetrahydroborate is a more chemoselective reducing agent than lithium tetrahydroaluminate. The term is also applied to reacting molecules or intermediates which exhibit selectivity toward chemically different reagents.

1.5 Literature review on the oxidation of saturated hydrocarbons

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

For instance, in 1988, Geletii and his colleagues reported cyclohexane oxidation using Cu(II) and Fe(III) perchlorate as catalysts. Hydrogen peroxide was used as an oxidant in pyridine solution. The main product was the ketone, the usual alcohol / ketone ratio being *ca.* 0.05-0.15 [7].

In 1991, Sarneski and his colleagues presented that the new cluster $[Mn_3O_4(dipy)_4(OH_2)_2](ClO_4)_4$ was particularly active for the oxidation of alkanes, alkenes, and alkylated arenas with alkyl hydroperoxides in CH_3CN. The oxidants used were TBHP or $PhCMe_2OOH$. These systems could work well even at low temperature (0^oC). Though turnover/h of product was high, the selectivity (ketone/alcohol) was not good [8].

In 1992, Mario and his co-workers addressed the use of ruthenium catalysts catalyzed the oxidation of saturated hydrocarbons. Two ruthenium catalysts: $K_2[Ru(H_2O)PW_{11}O_{39}]$ and *cis*-$[Ru(H_2O)_2(dmso)_4](BF_4)_2$ were used to catalylze the oxidation reaction of various substrates such as adamantane, cyclooctane, cyclohexane, hexane and heptane. Various oxidants were namely TBHP and hypochloride. The mechanism proposed was involved free radical pathway [9].

In 1993, Muzart reported the use of Cr(VI) complexes to catalyze the oxidation reaction of adamantane to 1-adamantanol and 2-adamantanone by using TBHP as an oxidant in benzene. The selectivity ratio of C_2/C_3 was 0.23-0.54 [10].

In 1994, Barton and his colleagues presented a new methodology for the selective transformation of saturated hydrocarbons to ketones and alcohols. A crucial aspect of this new process was that no reaction solvent was required since the Fe(III) and Cu(II) complexes used were completely soluble in hydrocarbon substrate. Although the rate of the oxidation reaction was slow, the addition of catalytic amount of pyridine was found to enhance the rate of process and affected an augmented selectivity towards the formation of ketone [11].

In 1996, Pralhad and his co-workers reported the use of manganese(II) *N,N'*-ethylene bis (salicylideneaminato) and analogous manganese(II) complexes catalyzed

oxyfunctionalization of cyclohexane. TBHP was employed as an oxidant. It was observed that cyclohexane was transformed to cyclohexanol and cyclohexanone in high yield at room temperature in CH_3CN. A pathway involving oxomanganese intermediate was suggested for the reaction [12].

In 1998, Motowo and his colleagues found the new mixed ligand chlororuthenium(II) complexes $[RuCl(L)(tpy)]Cl_n$ and $[RuCl(L)(tpm)]Cl_n$ (L= bpy, dmpa or dmgly; n=0 or 1) were prepared, and the catalytic activity for alkanes oxidation using m-chloroperbenzoic acid was examined. Alcohol was the main product: oxidation of adamantane, cyclooctane or ethylbenzene gave hydroxylated products, 1-adamantanol (66%), cyclooctanol (22%) or 1-phenylethanol (48%), respectively [13].

In 1999, Ullf and his co-workers reported the use of Fe(III) and Cu(II) complexes to catalyze the oxidation reaction of cyclohexane to cyclohexanone and cyclohexanol. TBHP was used as an oxidant. Under reflux for 24 h, it was observed that the copper catalyst gave high selectivity under this conditions [14].

In 1999, Lee and his colleagues reported cyclohexane oxidation using metal oxide such as Fe_2O_3 and FeO as catalysts. It was observed that the selectivity ratio of cyclohexane to cyclohexanol were greatly affected by the acidity of metal oxide when metal oxide was more acidic property, the reactivity on oxidation is increased and the formation of cyclohexanone is more favored [15].

In 1999, Jame reported the use of diacetatopalladium(II) to catalyze adamantane oxidation in trifluoroacetic acid. It was observed that adamantane was transformed to alcohol and ketone in low yield. In addition, the use of potassium persulfate as an oxidant was found to increase the yield of the reaction; however, the selectivity was still low [16].

In 1999, Masahiro and his co-workers found that the oxidation reaction of alkanes by TBHP in the presence of titanium alkoxides produced the corresponding alcohols and ketones. The feature of this reaction was different from titanosilicate, although tetra-alkoxide structure of titanium alkoxides was similar to titanosilicate. Other titanium complexes with titanyl or peroxo-titanium groups were not effective. This oxidation reaction proceeded in radical mechanism. t-Butoxyl radical formed from TBHP and titanium alkoxide started the radical reaction. The evolution of

oxygen (the decomposition of peroxide) and the abstraction of hydrogen from alkane to form alkyl radical occurred [17].

In 2000, Hui and his co-worker discovered that cobalt(II) porphyrin complexes catalyzed the oxidation of alkanes by oxygen in a mixture of trifluoroacetic acid and water. Carbon monoxide was required as a coreductant for the oxidations to proceed. While the turnover rates were slow, the system displays unusual selectivity in the primary C-H bonds are more reactive than the weaker secondary C-H bonds or C-H bonds $\propto$ to an alcohol functionality [18].

According to previous literatures, a number of reports concerning the selectivities of functionalization of hydrocarbons have been addressed. However, no report was mainly dealth with the selectivity of various types of saturated hydrocarbons. Therefore, this work focuses on the systematic study on the selectivity of the oxidation of saturated hydrocarbons using metal stearate as catalysts.

1.6 The goal of this research

The purpose of this research can be summarized as follows:

1. To synthesize metal stearate complexes
2. To study the regioselectivity and chemoselectivity of this developed oxidation system
3. To study this oxidation system in the large scale