

Chapter 1

Introduction



1.1 Statement of Problem

The catalyst systems used in commercial process are classified into two categories: homogeneous and heterogeneous systems. A homogeneous system is a system of which a catalyst, a substrate and a solvent are in the same phase. The catalyst and products are not easily separated from homogeneous system. The advantages of homogeneous system generally include high efficiency under mild reaction and high accessibility for substrate to reach the active site of the catalyst. However, the homogeneous system can exhibit the problems of by-products and aggregation of catalyst to form dimer or multi-nuclear clusters, leading to the loss of catalytic activity¹. An example of this system is the hydrogenation of alkenes using Wilkinson's catalyst² $\text{Rh}(\text{Cl})(\text{PPh})_3$. The other catalytic system, so called a heterogeneous system, is facile to separate the required product from the catalyst but generally the reaction rate is rather slow and often requires vigorous condition. One approach to heterogenize a catalyst is to immobilize the catalyst usually a metal complex on the support such as silica, alumina, organic polymers, or other crystalline materials. The challenge is to achieve a supported catalyst which maintains high activity and selectivity of the homogeneous counterpart. A hybrid catalyst³ which is a bridge between homogeneous and heterogeneous systems may be expected. One

potential system with these properties has been offered by the utilization of zeolites as the catalyst supports. Zeolite has well defined pore structures and can provide shape and size selectivity. The zeolite support may increase the intrinsic selectivity of the catalyst by virtue of their molecular sieving and orientating effects on a substrate molecule which must diffuse through it to the active sites. Recently, one approach area of zeolites has focused on the utilization of zeolite as catalyst support. The intrazeolite catalysts were utilized for many reactions such as acid-base reaction, hydroformylation, and oxidation of olefins. Several research groups pointed on the utilization of the zeolite catalysts in the oxidation reaction to convert low price hydrocarbons such as alkenes and alkanes to the high value compounds such as alcohols, aldehydes or ketones⁴. There are many types of catalyst prepared in zeolites but they fail to catalyze oxidation reaction⁵. This problem is due to the restrictive dimensions of the zeolite pores and may force an unusual coordination geometry or even coordinative unsaturation upon the zeolite entrapped metal catalyst. A large number of metal Schiff bases were synthesized in the cavities of zeolites⁶, characterized and studied for their potential to act as the oxidation catalyst but not so many of them were proved to be actual catalysts. Most researchers reported only the synthesis and characterization steps. For these reasons, the synthesis of a rigid bulky structure like phthalocyanine entrapped in the cavities of zeolite Y and test for its catalytic activity for oxidation of alkenes were attempted in this study.

Zeolite Y has been an important component in petroleum process technology as a catalyst itself in fluid catalytic cracking (FCC)⁷ or in hydrocracking⁸, and as catalyst supports in Fischer-Tropsch reaction⁹ and oxidation of alkenes¹⁰. The

published synthetic procedures are mostly rough recipes. Only meager information is given regarding reaction steps but the important reaction conditions are not clearly presented. Our synthetic procedure is adapted from the U.S. Patent No. 4,178,352¹¹ to provide the optimum condition for the synthesis of zeolite Y.

Zeolite Y has been chosen as the catalytic support because its attractive advantages¹² are as follows:

(i) Shape and size selectivity. Only molecules with smaller dimension than the pore aperture of the zeolite can enter the pores and reach the catalytic sites. In addition, the molecules must have shape that is appropriate to the shape of zeolite pore. For example a steric molecule, in contrast to straight chained hydrocarbon, is not stable in the narrow channels of the zeolite.

(ii) Well-defined pore structure. Zeolite Y has high ordered crystal structure which can be characterized by X-ray technique. The locations of charge balancing cations are often well identified and the sites of catalytic activity, are thus well defined. At molecular level, the pore system can potentially isolate each catalyst species apart and prevent dimerization and agglomeration of the catalyst species.

(iii) Exchangeable cation sites. The normal alkali and alkaline earth cations can be readily exchanged to transition metal cations which are the active center of catalysts.

1.2 The Conventional Immobilization Method of Organometallics in Zeolite Cavities

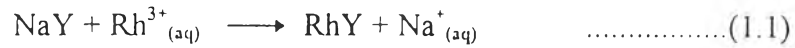
There are four methods for immobilization of metal complexes in zeolite cavities, namely, physisorption, ion exchange, anchoring, and size encapsulation.

1.2.1 Physisorption

This method is applied to volatile uncharged organometallic species such as Ni(CO)₄, Fe(CO)₅ and Mo(CO)₆¹³⁻¹⁴. The molecules can be adsorbed on the surface of zeolite by vapor deposition. The molecules loosely hold in zeolite cavities by weak Van der Waal interaction classified as physisorption or physical adsorption. This interaction cannot prevent the leaching of metal complexes from pores into solution during catalytic reaction and form oligomer which has less or does not have catalytic activity.

1.2.2 Ion Exchange

Zeolites are cation exchangeable. Metal ions and cationic complexes can occupy framework cation sites of a zeolite and exchangeable with other cations in solution. This method provides stronger coulombic interaction between the cationic species and zeolite anionic framework than the physisorption. For example¹⁵⁻¹⁸, zeolite RhY can be prepared by ion exchange of zeolite containing Na ion(s) with an aqueous solution of Rh(NO₃)₃ or RhCl₃. The reaction can be described as follows:

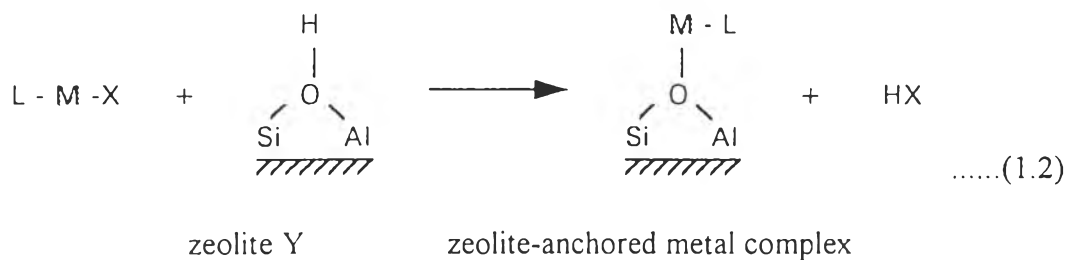


wherein

NaY	means zeolite Y having Na ⁺
RhY	means zeolite Y having Rh ³⁺
Rh ³⁺ _(aq)	means Rh ³⁺ in aqueous solution
Na ⁺ _(aq)	means Na ⁺ in aqueous solution

1.2.3 Anchoring

For this method¹⁹, the precursor must have ligands; for example methyl, allyl, alkoxide and chloride which are reactive to protons of acidic zeolite to form stable products such as methane, olefin, alcohol and hydrogen chloride, respectively. Remaining fragment of the metal species is stabilized by the coordination between the metal center and oxygen of the zeolite framework. The disadvantage of this method is the fact that, the organometallic precursors tend to be moisture and air sensitive, therefore it is difficult to prepare and handle the organometallic compounds. The reaction can be described as follows:



L-M-X	=	organometallic precursor
L	=	ligands inert to surface hydroxyl groups
X	=	reactive ligands such as alkyl, allyl and alkoxide
HX	=	by-product such as methane, olefins and alcohols

1.2.4 Size Encapsulation

This strategy is also known as “ship in the bottle” which was first used by Norman Herron²⁰⁻²¹ in 1986 to describe $\text{Ni}(\text{CO})_{n-4}\text{L}_n$ complexes entrapped in zeolite X. This method has been developed from the idea of assembling a ship in a glass bottle. Small parts of the ship were transferred into a bottle, the ship was built up from the parts within the bottle. The built ship is found too large to move out from the bottle through the bottle neck. A complex to be synthesized has all of the individual components (metal ion plus various ligands) which may easily pass in and out from the zeolite, but the final assembled coordination complex is too large and rigid to migrate out. There are two steps in preparing the size encapsulated product, ion exchange and encapsulation. First of all the metal which is a counter ion of the zeolite framework must be able to form a chelated complex. In the other word, the previous metal counter ion of the zeolite framework must be exchanged with a new-coming transition metal ion that is able to form a chelated complex.

Dioxygen binding Co^{II} complexes have been formed in zeolites using ligands like amines, cyanine, and bi- or terpyridine²². In these materials the monodispersion of the active chelates over the zeolite cages retards formation of binuclear complexes and enhances the reversibility of O_2 binding. Optimization of such systems has led to some perspectives in air separation²³⁻²⁴. A major disadvantage of most of these systems is that the number of mono- or bidentate ligands surrounding the Co^{II} cation is not easily controlled²⁴⁻²⁵. The use of polydentate ligands may solve such problems as the formed complexes were expected to be more stable and the number as well as nature of the coordinating atoms may be controlled more accurately by assembling them in a single ligand molecule.

This approach has been proposed by Herron²¹ for $[\text{Co}^{\text{II}}(\text{salen})(\text{pyridine})]$ in zeolite Y and was also followed for $[\text{Co}^{\text{II}}(\text{tetren})]^{2+}$ (tetren = tetraethylenepentamine)²⁶ in zeolite NaA. As both complexes are too large to pass through the pore opening of the zeolite cages, each of them has to be assembled *in situ* in the cage. The characteristics of the zeolite Y entrapped $[\text{Co}^{\text{II}}(\text{salen})]$ seemed to be different from those of $[\text{Co}^{\text{II}}(\text{salen})]$ in solution or $[\text{Co}^{\text{II}}(\text{salen})]$ doped in diamagnetic crystals. Indeed, planar $[\text{Co}^{\text{II}}(\text{salen})]$ or its axial base adducts were generally EPR detectable low spin complexes²⁷, but $[\text{Co}^{\text{II}}(\text{salen})]\text{NaY}$ was EPR silent, even after treatment with pyridine²¹. Anomalies were found as well in the electrochemical behavior of $[\text{Co}^{\text{II}}(\text{salen})]\text{NaY}$; cyclic voltammetry revealed a $\text{Co}^{3+}/\text{Co}^{2+}$ redox transition which is absent in solution²⁸.

Until now Schiff bases other than salen have been used for complexation with in zeolite and tested for their catalytic activity. Mn-salen²⁹, Fe-salen³⁰ and V(0)-salen³¹

encapsulated into zeolite Y were prepared³². These composites were found to be active redox catalysts. While Cu-salen was shown to be a catalyst for the selective oxidation of cyclohexanol to cyclohexanone in the presence of H₂O₂ under 80 °C²⁹. V(0)-salen encapsulated in zeolite Y was found to be an effective catalyst for the room temperature epoxidation of cyclohexene using *t*-butyl hydroperoxide (*t*-BOOH) as the oxidant³¹. While the catalyst obtained by encapsulation of heteropolyacid H₃PW₁₂O₄₀ in the supercage of faujasite was highly active and selective in isomerization and disproportionation of *m*-xylene³².

Chris Bowers, *et al.*¹⁷ found that Mn-salen⁺ which was synthesized in zeolite provided the oxidation products like epoxide, alcohol and aldehyde corresponded to their olefinic substrate. However in comparison with the catalysis by Mn-salen⁺ complexes in solution, encapsulation was found to lower the rate of reaction considerably, but provided size selectivity for oxidation of olefins.

Copper (II) complexes with N₃O₂ Schiff base ligands; for example, bis(acetylacetonate)-3-amino-bis(propylenediimine) or H₂(acac)₂trien and bis(acetylacetonate)-3-methylaminobis(propylenediimine) or H₂(acac)₂Metrien was encapsulated in the supercage of zeolite Y. The products were characterized by scanning electron microscope, X-ray photoelectron spectroscopy, bulk and surface chemical analysis, UV-VIS and FTIR spectroscopies providing evidence for the entrapment of Cu(II) complexes in the zeolite supercage³³.

The reaction in dehydrated faujasite zeolites of two different topologies charge-compensating Co^{II} cation and different Schiff base ligands were studied⁶. Tetradentate as well as pentadentate ligands were used for comparison, while the behavior of zeolite

Y, faujasite with cubic symmetry was compared to that of zeolite EMT, faujasite with hexagonal symmetry. After reaction of the Schiff bases which are shown in Figure 1.1, salen and acacen (bis(acetylaceton)ethylenediimine) with CoNaY zeolite, low spin square-planar Co^{II} was observed in low concentration in $[\text{Co}^{\text{II}}(\text{acacen})]\text{NaY}$. In $[\text{Co}^{\text{II}}(\text{salen})]\text{NaY}$, formation of planar complex was doubtful. Utilization of these tetradentate ligands for oxygen activation in zeolite Y resulted in low concentration of active oxygen-binding Co^{II} . Incorporation of a nitrogen base into these Schiff base resulted in the pentadentate ligands smdpt, (bis(salicyldehyde) methyl nitrilodipropylenediimine) and amdpt, (bis(acetylaceton)methylnitrilodipropylen diimine). Utilization of these ligands greatly raised the fraction of the Co^{II} participating in the oxygen activation. The Co^{II} form of the hexagonal faujasite NaEMT loaded with smdpt up to 25% of the total Co^{II} could reversibly bind dioxygen. Moreover, intrazeolite Co^{II} was reacted with pyren (bis(2-pyridine-carboxaldehyde) ethylenediimine). Pentadentate ligands were also more effective in withdrawing charge-compensating Co^{II} from zeolite coordination and forming encaged O_2 -binding complexes, and a hexagonal NaEMT zeolite with entrapped $[\text{Co}^{\text{II}}(\text{smdpt})]$ complex was found to be the best optimized system⁶.

The first phthalocyanine³⁴ was discovered by chance in 1928 during the course of the industrial production of phthalimide in the Grangemouth works of Messrs. Scottish Dyes, Ltd. The process consists in passing ammonia into molten phthalic anhydride in iron vessels and it was found that during certain preparations traces of a dark blue substance were formed in the molten imide. This crystalline material was

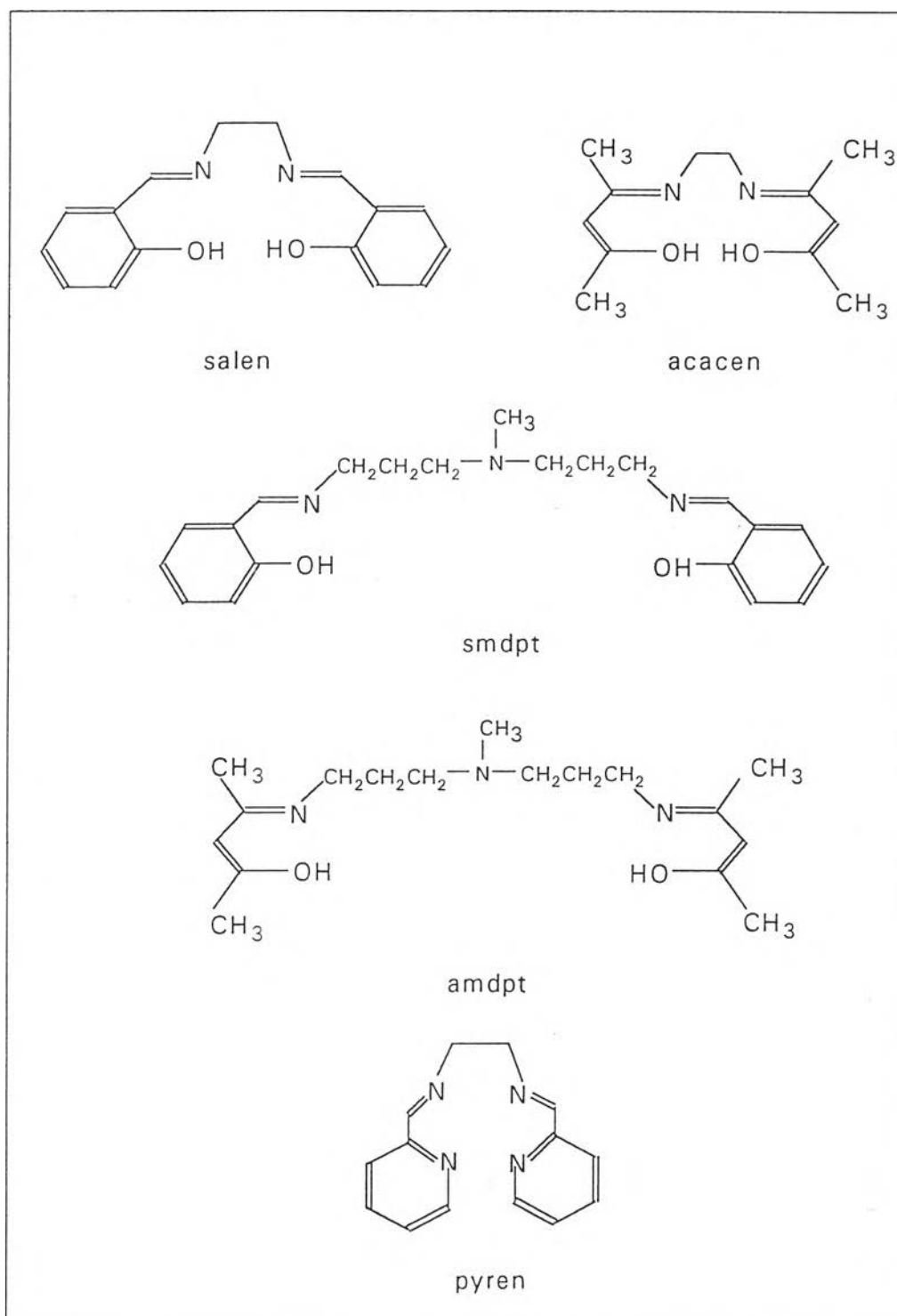
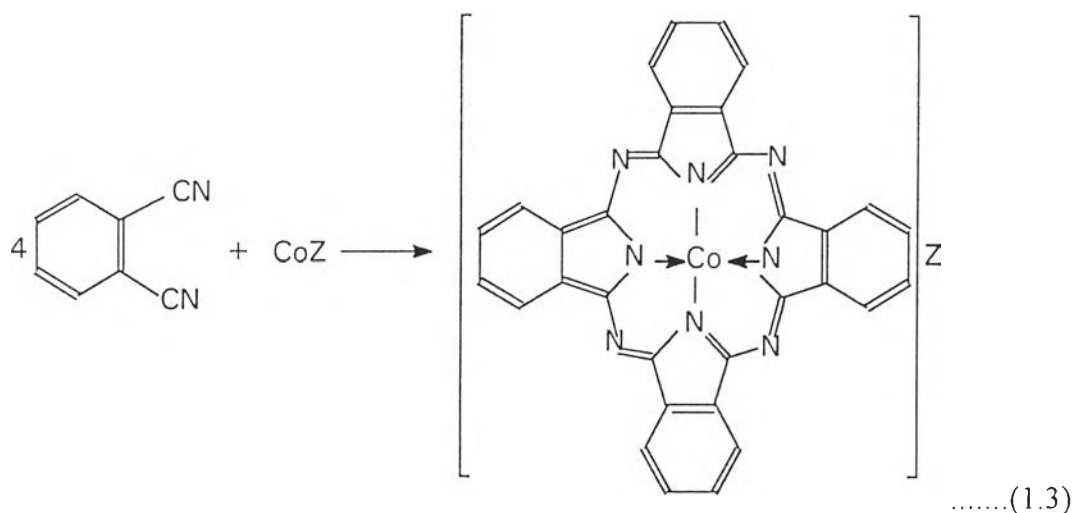


Figure 1.1 Structures of salen, acacen, smdpt, amdpt, and pyren ligands⁶

stable and contained iron which was not eliminated by treatment with concentrated sulfuric acid. As it appeared that the substance might prove of academic interest, its studies were taken up in 1929 through the kindness of Professor J. F. Thorpe, F.R.S., and the Research Committee of the Dyestuffs Group of Imperial Chemical Industries, Ltd, named this type of substance that phthalocyanines.

Metal phthalocyanines have a structure very similar to the transition-metal porphyrins. It has been known for a long time that metal porphyrins were used as the catalyst for oxidation-reduction. Transition-metal phthalocyanines as catalysts for alkene epoxidation have been published³⁵⁻³⁶. The epoxidation of alkenes catalyzed by transition-metal phthalocyanine has been studied³⁷. The transition-metal [metal = Mn (II), Fe(II), Fe(III), Co(II) and Ni(II)] phthalocyanines have catalytic properties: the manganese and iron phthalocyanines are the most effective when iodosobenzene is the oxygen donor, whereas cobalt and nickel phthalocyanine are the best under phase transfer catalysis condition with sodium hypochlorite as oxygen donor³⁷.

Cobalt phthalocyanine (CoPc) was synthesized in the cavities of zeolites Y³⁸ and in the large cages of zeolite EMT³⁹. The process of the synthesis was called thermal reaction process. The reaction of Co-zeolite with 1,2-dicyanobenzene was performed in the glass ampule in vacuum ($P < 0.3$ Pa). The ampule was heated at 200 °C. The reaction can be described as follows:



After that, the product was extracted with acetone, pyridine and again with acetone using soxhlet. The first treatment with acetone to remove 1,2-dicyanobenzene which was unreacted with zeolite. Whereas pyridine dissolved phthalocyanine and cobalt phthalocyanine from the external surface of the zeolite crystals. The final treatment with acetone removed strongly adsorbed pyridine from the previous extraction step³⁸. After extraction, the final CoPc product was characterized by elemental analysis, Fourier transform infrared spectroscopy, UV-visible spectroscopy, X-ray photoelectron spectroscopy, surface analysis, thermogravimetric analysis, X-ray diffraction and conventional transmission and high-resolution electron microscopy³⁸. The scanning electron microscopy indicated that no residual cobalt phthalocyanine was present at the external surface of the zeolite crystals after soxhlet extraction³⁹.

The X-ray diffraction patterns confirmed that in all samples of cobalt phthalocyanine in NaY zeolite, the main zeolite framework was not damaged by the reaction. The presence of nitrogen-containing organic compounds in NaY zeolite was confirmed by the characteristic band found in the IR and UV-vis spectra as shown in Figure 1.3, Table 1.1, and Figure 1.4, respectively³⁸.

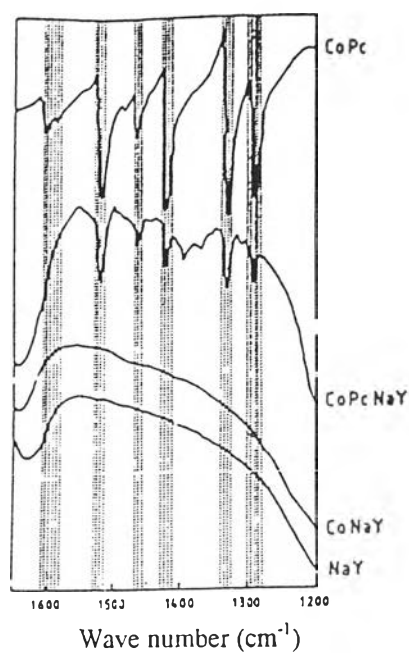


Figure 1.2 FTIR spectra of NaY, CoNaY, CoPcNaY, and CoPc in Kbr pellets³⁸

Table 1.1 FTIR bands (in cm^{-1}) for CoPc and CoPcNaY in the region of $1650 - 1200 \text{ cm}^{-1}$ ³⁸⁻³⁹

Bands for CoPc (cm^{-1})	Bands for CoPcNaY (cm^{-1})
1289	1290
1332	1334
1426	1426
1448	1451
1470	1470
1490	1492
1523	1525
1610	1616

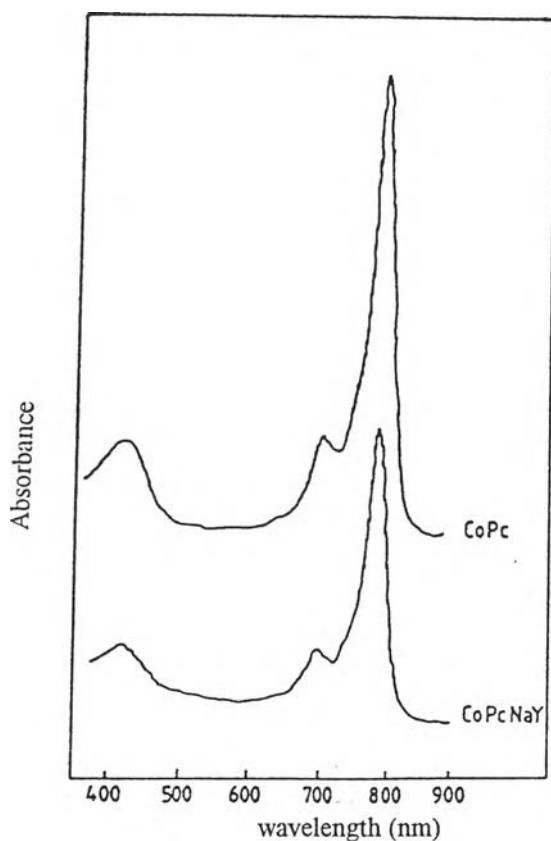


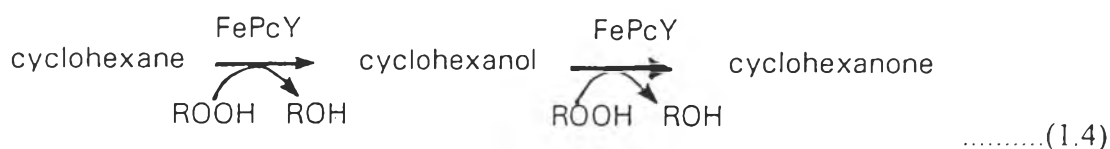
Figure 1.3 UV-visible spectra of CoPc and CoPcNaY in H_2SO_4 .³⁸

The observed C_{1s} , N_{1s} , and Co_{2p} XPS signals after encapsulation were weaker, compared to the mechanical mixtures with a similar percentage of CoPc and NaY. This could be an indication that in CoPcNaY, fewer electrons were emitted. Since, with the XPS technique, the inner structure and cavity contents of the solids were analyzed to a depth of about 50 Å, this observation implied that at least part of the CoPc must be within the cavities of the zeolite. If the phthalocyanines were deposited on the external surface of the zeolite crystals, the signal would be stronger. Moreover, the lowering of pore volume and specific surface of NaY zeolite pointed to the presence of CoPc within the cavities of the zeolite too³⁸.

The synthesized cobalt phthalocyanine in NaY zeolite was used as catalyst for oxidation of cyclohexene using iodosobenzene as oxidant in chloroform. The product was highly selective. The main product was cyclohexene oxide. The CoPcNaY catalyst was still active after 24 hours⁴⁰.

The CoPc encaged in zeolite EMT was an active catalyst³⁷ for the oxidation of ethylbenzene with molecular oxygen. Maximum turnover number (define as mol of ethylbenzene converted / mol of CoPc encaged) of ca.22,000 was observed. The sole products with the CoPcEMT-catalysts were 1-phenylethanol and acetophenone³⁹.

Iron phthalocyanine was synthesized in zeolite Y by the solid state adsorption of ferrocene on NaY by R.F. Parton, *et al*⁴¹. Subsequently, the ferrocene loaded zeolite was mixed with 1,2-dicyanobenzene (a twofold excess) and placed in a Teflon-lined autoclave and heated at 453 °K for 24 hours. The blue-green solid obtained was soxhlet extracted with acetone, dimethylformamide, and again with acetone, until a colorless extract was obtained. The extractions removed phthalocyanines from the center surface of the zeolite and unreacted reactants and intermediates from the crude catalyst. The final catalyst was air dried at 343 °K. UV-vis and IR spectra confirmed that the catalyst contained a mixture of free phthalocyanine and ion phthalocyanine complex. This iron phthalocyanine complex encapsulated in Y zeolite was tested for the catalytic activity on the oxidation of cyclohexane using tertiary butyl hydroperoxide as oxygen atom donor. The products of this reaction were cyclohexanol and cyclohexanone as the equation shown below:



Sorption measurements showed a high preference of the catalyst for polar reagents and products like acetone, cyclohexanol, cyclohexanone, and tertiary butyl hydroperoxide. Therefore, the mode of addition of peroxide and the use of solvent had a strong influence on the reaction rate. A feed-batch type set-up with slow addition of the peroxide to the reaction mixture was proven to be the best system, minimizing the decomposition reaction of the peroxide and maximizing its selective oxidation reaction. Conversion of cyclohexane with iron-phthalocyanines encapsulated in zeolite Y was relatively high (up to 25 %) with efficiencies between 40 and 10 % and high selectivity for cyclohexanone (95 %). Cyclohexanol is converted up to 70% with efficiencies around 70 %, because the alcohol moiety was more sensitive to oxidation and sorption effects favored cyclohexanol compared to cyclohexane. The iron phthalocyanines in zeolite Y were recovered for both reactions. Activities obtained by the zeolite encapsulated iron-phthalocyanines were higher than the homogeneous complexes which were oxidatively destroyed under reaction conditions and therefore not recovered. Further studies⁴² found that iron phthalocyanines on zeolite had been used for the catalysis of cyclohexanone and cyclohexane into adipic acid, by an environment friendly one-pot reaction. Heating and fine tuning of the solvent allowed high conversion and good selectivity for adipic acid.

The interest in manganese complexes as catalysts for alkene epoxidation comes mainly from their relation to the biologically relevant manganese porphyrins. Manganese porphyrins have been used as epoxidation catalysts with different oxygen sources such as⁴³ iodosylbenzene, sodium hypochlorite, molecular oxygen in the presence of an electron source, alkyl peroxides, hydroperoxide, potassium hydrogen persulfate, and oxaziridines. For example chloro(*meso*-tetraphenyl porphyrinato) manganese (III) [Mn(TPP)Cl] catalyzes epoxidation of alkenes with iodosylbenzene as oxygen donor⁴³. The first step in the reaction between Mn(TPP)Cl and iodosylbenzene is formation of an unstable and reactive oxo-Mn(TPP)Cl complex, which then epoxidizes the alkenes.

The transition-metal phthalocyanines (MPcs) are classified in the group of complexes which have been very intensively studied within many areas in chemistry. MPcs have an in-common structure very similar to the transition-metal porphyrins as shown in Figure 1.4. However, MPcs have not been studied to the same extent as catalysts in oxidation reactions and according to our knowledge, only few examples of MPcs as catalysts for alkene epoxidation have been published³⁷. This work aims to immobilize manganese phthalocyanine (MnPc) in the cavities of zeolite Y and utilize this product to catalyze the oxidation of olefins such as cyclohexene or 1-hexene.

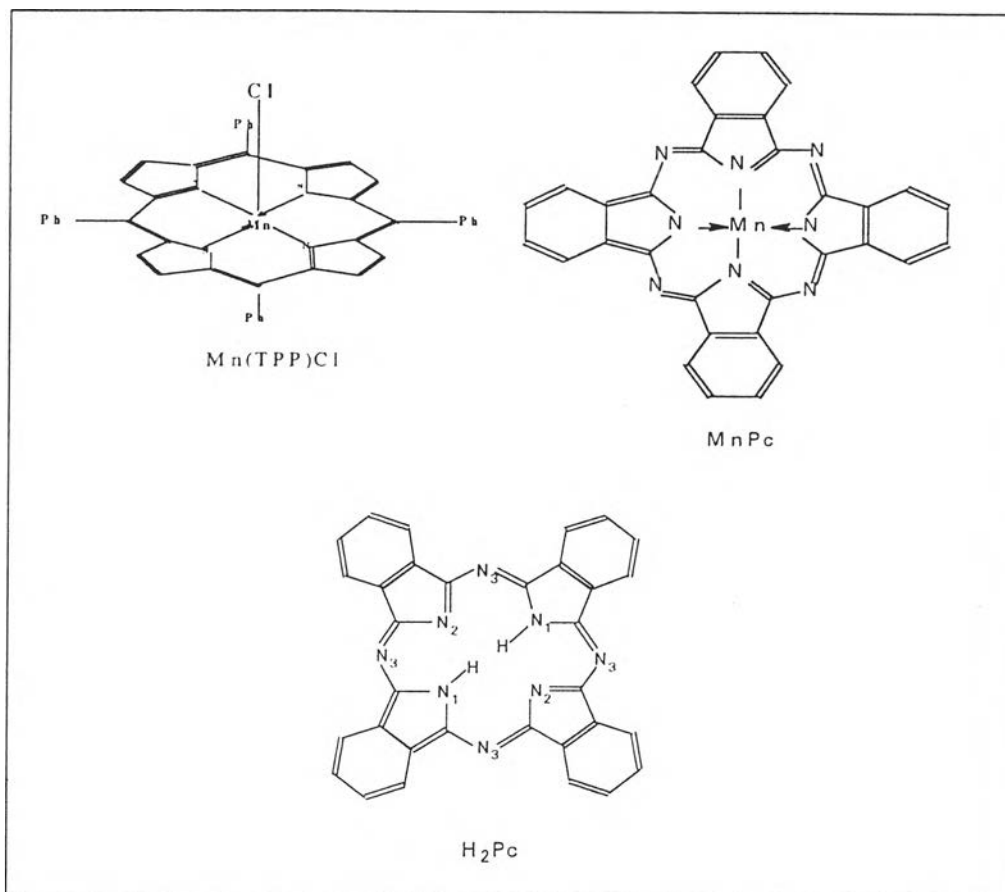


Figure 1.4 Structures of $Mn(TPP)Cl$ ⁴³, $MnPc$ ³⁷, and H_2Pc ⁴⁴

1.3 Objectives

1. To synthesize zeolite Y as catalyst host.
2. To synthesize the novel hybrid catalytic system, manganese phthalocyanine encapsulated in zeolite Y cavities.
3. To investigate the catalytic property of the intrazeolite catalyst for the oxidation of olefins: cyclohexene, and 1-hexene.