ตัวเร่งปฏิกิริยาโคบอลต์ชิฟเบสรองรับบนพอลิสไตรีน
สำหรับไฮโดรจิเนชันของไซโคลออกทีน

นางสาว วรางคณา กันจินะ

POLYSTYRENE SUPPORTED COBALT SCHIFF BASE CATALYSTS FOR HYDROGENATION OF CYCLOOCTENE
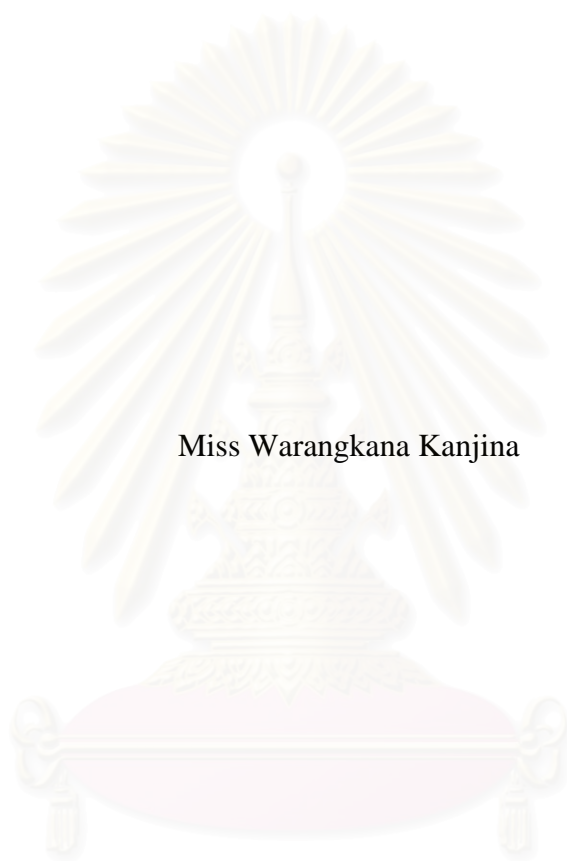
Miss Warangkana Kanjina

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 2004

Thesis Title	POLYSTYRENE SUPPORTED COBALT SCHIFF BASE CATALYSTS FOR HYDROGENATION OF CYCLOOCTENE
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Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Wimonrat Trakarnpruk, Ph.D.

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วรางคณา กันจินะ : ตัวเร่งปฏิกิริยาโคบอลต์ชิฟเบสรองรับบนพอลิสไตรีนสำหรับไฮโดร
จิเนชันของไซโคลออกทีน (POLYSTYRENE SUPPORTED COBALT SCHIFF BASE
CATALYSTS FOR HYDROGENATION OF CYCLOOCTENE) อาจารย์ที่ปรึกษา:
รศ. ดร. วิมลรัตน์ ตระการพฤกษ์; 88 หน้า. ISBN: 974-17-5958-4

ในงานวิจัยนี้ได้เตรียมตัวเร่งปฏิกิริยาโคบอลต์บนตัวรองรับชนิด พอลิ(สไตรีน-โค-ไดไวนิล
เบนซิน-โค-ไวนิลเบนซิลคลอไรด์) 5% เชื่อมขวาง ทำปฏิกิริยากับชิฟเบส กับนอนซิฟเบสไบเดน
เทต และไทรเดนเทตลิแกนด์ ซึ่งประกอบด้วยไนโตรเจน และออกซิเจนเป็นอะตอมที่ให้อิเลคตรอน
ตรวจพิสูจน์เอกลักษณ์ของสารเชิงซ้อนโคบอลต์ที่รองรับบนพอลิสไตรีนเหล่านี้ด้วยเทคนิค FT-IR,
XRF, AAS และ TGA และสารเหล่านี้ใช้เป็นตัวเร่งปฏิกิริยาสำหรับไฮโดรจิเนชันของไซโคลออกทีน
ได้ศึกษาถึงผลของพารามิเตอร์ต่าง ๆ ได้แก่ อุณหภูมิ ความดันของแก๊สไฮโดรเจน ปริมาณของ
ตัวเร่งปฏิกิริยา ปริมาณของสารตั้งต้น เวลา ชนิดของตัวทำละลาย ชนิดของสารประกอบโลหะ
โคบอลต์ และชนิดของลิแกนด์ พบว่าตัวเร่งปฏิกิริยาที่เตรียมขึ้นทั้งหมดสามารถเร่งปฏิกิริยาไฮโดร
จิเนชันของไซโคลออกทีนให้ไซโคลออกเทนในปริมาณที่สูง (>69 %) ที่อุณหภูมิ 60 องศาเซลเซียส
ความดันของแก๊สไฮโดรเจน 9 บรรยากาศ ในเวลา 3 ชั่วโมง ตัวเร่งปฏิกิริยารองรับบนพอลิสไตรีนมี
เสถียรภาพทางความร้อนสูง และสามารถนำกลับมาใช้ซ้ำได้ โดยแอกติวิตีลดลงเล็กน้อย และมี
การหลุดของโคบอลต์จากตัวรองรับพอลิสไตรีนเพียงเล็กน้อย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต.................................
ปีการศึกษา 2547 ลายมือชื่ออาจารย์ที่ปรึกษา......................

4572646923: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: COBALT / HYDROGENATION / POLYMER SUPPORTED

WARANGKANA KANJINA : POLYSTYRENE SUPPORTED COBALT SCHIFF BASE CATALYSTS FOR HYDROGENATION OF CYCLOOCTENE. THESIS ADVISOR : ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph. D., 88 pp. ISBN: 974-17-5958-4

In this work, cobalt complexes supported on 5% crosslink poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) Schiff base, non Schiff base bidentate and tridentate ligands, in which N and O are donor atom, were prepared. These polystyrene supported cobalt complexes were characterized by FT-IR, XRF, AAS and TGA techniques and used as catalyst for cyclooctene hydrogenation. The influence of various parameters such as temperature, hydrogen pressure, amount of catalyst, amount of substrate, reaction time, types of solvent, type of cobalt compounds and ligand types, were studied. It was found that all prepared catalysts were efficient, giving high yield of cyclooctane (>69%) at 60°C, 9 atm in 3 h. The polystyrene supported catalysts have high thermal stability and can be reused successfully with only slight loss of activity and little leaching of metal from the polystyrene support.

Field of Study Petrochemistry and Polymer Science Student's signature ....
Academic year 2004 Advisor's signature ....

ACKNOWLEDGEMENTS

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atm	atmosphere
rpm	Round per minute
h	hour (s)
GC	gas chromatography
cm^{-1}	unit of wavenumber
st.	stretching
ml	milliliter (s)
min	minute (s)
g	gram (s)
°C	degree Celsius
TGA	Thermogravimetric analysis
^{13}C NMR	Carbon nuclear magnetic resonance
FT-IR	Fourier transform infrared spectroscpy
TON	Turn over number
ee.	Enantiomeric excess
nm.	nanometer
CH_3COO^-	acetate
CS	crosslink polystyrene
DVB	divinylbenzene
AcAc	acetylacetonate
PE	polyethylene
PS	polystyrene
kPa.	Kilo Pascal
mmol	millimole

CHAPTER I

INTRODUCTION

Many different groups of products such as pharmaceuticals, dye, food additives, cosmetics, vitamins, and photochemicals are classified as fine chemicals. Many products and intermediates are produced by catalytic hydrogenation under mild condition. The starting materials often have complex structures and high molecular masses and are temperature sensitive. In a world of rapidly shrinking resources the so-called "green" chemistry becomes more and more important. Homogeneous catalysts are the showcase materials being studied in this direction for many decades, and they are still improved following different strategies: they are tailored according to the needs of the catalytic reaction, and are made more and more efficient, also by combination two different catalysts.[1] The tailoring of support metal catalyst consists of the 'heterogenization' of homogeneous catalyst by anchoring the catalyst on a solid support, i.e. an inorganic material or organic polymer. Soluble homogeneous catalysts offer high selectivity under mild operating conditions but are not enviro-economical. On the other hand heterogenenization of homogeneous catalysts presents a rapidly expanding research area providing advantages such as simple handling and product separation, and catalyst recovery. [2-4]

The choice of the polymer is crucial: a large swelling with the reaction solvent is very necessary. The choice between the two ways to the synthesis of functionalized polymers depends mainly on the required chemical and physical properties of the support for a specific application. Usually the requirements of the individual system must be throughly examined in order to take full advantage of each of the preparative techniques.[5]

Although many polymer types, including both aliphatic and aromatic organic as well as inorganic polymers, have been employed as a carrier for the functional group, the most widely used as support is the polystyrene matrix. The uses of polymers other than polystyrene have met with limited success for reasons such as lack of reactivity, degradation of the polymer chain, or other unsuitable physical

properties of the finished polymer. The polystyrene are used in variety of industrial purposed, for example, in the manufacture of resins for gel permeation chromatography, polymeric supports for size exclusion chromatography, ion exchange resin, polymer supported catalyst, absorbent in chemical, medical, and agricultural applications.[5]

Since the hydrogenation of various functional groups is among the most common and useful organic reactions, a great deal of effort has been invested in the development of improved catalysts and part of that effort has involved polymer bound transition metal catalysts. Cobalt is a very active element in different fields of catalysis. Organometallic cobalt complexes are known since many years as excellent homogeneous catalysts for hydroformylation and different carbonylation, hydrogenation and isomerization reactions.[6]

1.1 The objectives of the thesis

1.1.1   To prepare polystyrene supported cobalt catalysts.

1.1.2   To test the catalytic activity of the polystyrene supported cobalt catalyst in hydrogenation of cyclooctene.

1.2 To scopes of the thesis

The experiments were divided into following:

1.2.1   Preparation of functionalized polystyrene support by anchoring ligands.

1.2.2   Preparation of polymer supported cobalt catalysts.

1.2.3   Hydrogenation of cyclooctene with the prepared catalysts.

1.2.4   Recycling catalyst for hydrogenation of cyclooctene.

1.2.5   Test of catalyst leaching from polystyrene supports.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Hydrogenation of alkene

A attempt to improve the potential of catalysts for hydrogenation which act by add molecular of hydrogen to C=C group of alkene to give an alkane is still a challenge. The driving force for the introduction of new processes is economic considerations, which are largely influenced by the production costs. Since the starting materials often have several reactive groups, hydrogenation can give rise to various products, only one of which is usually desired. Careful adjustment of all experimental parameters, including type and amount of catalyst, solvent, temperature, pressure, and degree of mixing (e.g., stirring speed), is necessary to maximize the yield of the desired product.

2.2 Homogeneous catalysts

Homogeneous catalysts are often organotransition metal complexes; it is relatively easy to modify these compounds in order to increase selectivity. Selectivity is becoming the decisive factor in industrial processes. But homogeneous catalysts are often much less thermal stable than their heterogeneous catalysts and difficult to remove from the product.

2.3 Heterogeneous catalysts

In heterogeneous catalysis the reaction occurs on the interphase boundary. Adsorption of reagents on the catalyst surface is followed by their activation. However all these centers locate on the catalyst surface are not equivalent. It is possible that only one of the set is capable of catalyzing the desired reaction, while others are inactive and even responsible for some side reactions. It should be noted that there is also evidence of a primary role for the individual active center in heterogeneous catalysis but not of collective electronic properties of the surface.

Heterogeneous catalyst is the reaction which contains catalyst in another phase of the reaction medium such as solid catalyst in liquid or aqueous solution. The number of phase combinations can then occur, as shown in Table 2.1.

Table 2.1 Phase combinations for heterogeneous catalysis[7]

Catalyst	Reactant	Example
Liquid	Gas	Polymerization of alkenes catalyzed by phosphoric acid
Solid	Liquid	Decomposition of hydrogen peroxide catalyzed by gold
Solid	Gas	Ammonia synthesis catalyzed by iron
Solid	Liquid + Gas	Hydrogenation of nitrobenzene to aniline catalyzed by palladium

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.

According to the thermal stability of organometallic complexes in the liquid phase, industrially realizable homogeneous catalysis is limited to temperatures below 200°C. In this temperature range, homogeneous catalysts can readily be stabilized or modified by addition of ligands; considerable solvent effects also occur. Table 2.2 summarized the advantages and disadvantages of two classes of catalyst.

Table 2.2 Differences between homogeneous and heterogeneous catalysts.[3]

Characteristic	Homogeneous catalyst	Heterogeneous catalyst
1.Catalyst composition and nature of active site	Discrete molecules with well-defined active site	Nondiscrete molecular entities: active site not well-defined
2. Determination of reaction mechanism	Relatively straightforward using standard techniques	Very difficult
3. Catalyst properties	Easily modified, often highly selective, poor thermal stability and mild conditions	Difficult to modify, relatively unselective, thermally robust and vigorous reaction condition
4.Separation from product	Often difficult	Relatively easy
5.Cost of catalyst losses	High	Low

2.4   Support materials[4]

The choice of the appropriate catalyst support for a particular active component is important because in many reactions the support can significantly influence the reaction rate and the course of the reaction. The following materials have been used as supports:

1. Linear, non-crosslinked polymers and, more recently, also better defined dendrimers are soluble in suitable solvents and give catalysts with high mobility and good mass transport properties, However, separation is not trivial (precipitation or ultrafiltration).

2. Swellable, slightly crosslinked polymers such as polystyrene crosslinked with 0.5-3% 1,4-divinylbenzene, can easily be separated by filtration or sedimentation. To allow good mass transport, these polymers have to be used in solvents in which they swell.

3. Highly crosslinked polymer (e.g. macroreticular polystyrenes or polyacrylates) and inorganic supports (metal oxides, e.g. silica gel) hardly swell and can be used in a large variety of different solvents without changes of texture or mass transport properties.

4. For immobilization via entrapment or intercalation, materials such as zeolites or clays with defined pores and cavities have to be used to affect reliable confinement of the metal complex catalysts.

2.5   Polymer supports[4]

Although many polymer types, including both aliphatic and aromatic organic as well as inorganic polymers. Typical organic support include polystyrene, poly(amino acid), polyaniline, acrylic polymers, and crosslinked dextrans. The most widely used as support is the polystyrene. The uses of polymers other than polystyrene have met with limited success for reasons such as lack of reactivity, degradation of the polymer chain, or other unsuitable physical properties of the finished polymer.

In principle, polystyrene fulfils the major requirements for a solid support because it has many advantages over other resins.

1. It undergoes facial functionalization through the aromatic ring by electrophilic substitution.

2. Compatibility: styrenic polymers are compatible with most organic solvents and so functional groups are easily accessible to the reagents and solvents.

3. Chemical stability: the aliphatic hydrocarbon backbone is resistant to attack by most reagents. Hence the polymer chains are not susceptible to degradative scission by most chemical reagents under ordinary conditions.

4. Mechanical stability: styrenic polymers are mechanically stable to the physical handling required in sequential synthesis.

5. Crosslinking: since the degree of crosslinking in the polymer influences its swelling nature and the pore dimension, the type and degree of crosslinking can easily be controlled during manufacture by regulating the concentration of divinylbenzene.

6. Polystyrene is readily available commercially.

Polystyrene, chloromethylated polystyrene and ring-lithiated polystyrene are used in the chemical modification of styrene resins for the preparation of new functional polymers because they provide a method of attaching a wide variety of both electrophilic and nucleophilic. The ability of a substance to act as a catalyst in a specified system depends on its chemical nature. Heterogeneous catalysis is concerned with the specific chemical properties of the surface of the chosen substance.

2.6   Immobilized and functionalized homogeneous catalysts[5]

Homogeneous catalysts which are soluble catalysts are more difficult to separate and to handle than the technically well established heterogeneous catalysts. One promising strategy to combine the best properties of the two catalyst types is the heterogenization or immobilization of active metal complexes on supports or carriers. This may be separated by filtration or precipitation. Another strategy is the functionalization of ligands to allow separation from the product solution. In order to be generally useful the chosen ligand must be readily available, be relatively inexpensive, be able to bind to a large variety of transition-metal species, be able to bound to the polymer support smoothly and be efficiently, and be chemically inert under a wide variety of potential reaction condition.

The most important approaches to immobilize or heterogenize soluble catalysts can be summarizde in Figure 2.1.

Figure 2.1 Schematic view and important properties of immobilized complexes.[5]

2.6.1 Immobilization via covalently bound ligands

Covalent binding, by far the most frequently used strategy, can be effected either by copolymerization of functionalized ligands with a suitable monomer or by grafting functionalized ligands or metal complexes with reactive groups of a pre-formed support. The catalysts are much more complex than their homogeneous counterparts, and many additional parameters such as type of support, solvent, spacer length and flexibility, degree of surface coverage have to be optimized to obtain an acceptable catalytic performance.

The highest activities and productivities and very good e.e.'s have so far been obtained in hydrogenations with chiral Rh- and Ir-diphosphines that were immobilized on solid inorganic supports or on soluble polymers. These catalysts were built up using a modular system combining functionalized ligands with different supports and linkers. Excellent enantioselectivities and practically unchanged activities have been obtained with enantioselective hydroformylation catalysts. Polymer and silica gel supported Co-salen complexes exhibited excellent performance for the hydrolytic kinetic resolution of terminal epoxides, e.g. epichlorohydrin.

2.6.2 Immobilization via adsorption and ion-pair formation

This approach relies on various adsorption interactions between a carrier and a metal complex, cationic rhodium-diphosphine complexes were bound to anionic resins. The resulting hydrogenation catalysts could be recycled 20 times with almost constant activity and selectivity and with little leaching. An innovative modular method was developed by Augustine who used heteropoly acids as anchoring agents to attach a large variety of metal complexes to different supports. Compared with their homogeneous counterparts, immobilized Rh-catalysts exhibited approximately equal or in some cases better activities and enantioselectivities. In one case, a catalyst was recycled 15 times, giving a total turn over number of 600.

A special case of adsorption is the "supported aqueous phase" (SAP), whereby a water-soluble catalyst dissolved in a very polar solvent is adsorbed on a hydrophilic support. With such a catalyst, the hydrogenation of a C=C bond in the Na-proxen synthesis with e.e.'s of up to 95.7% was described.

2.6.3 Immobilization via entrapment

The method of entrapment of a catalyst within a polymer has recently been applied to several catalysts. Two types of entrapment have been used. Either a catalyst can be entrapped in a polymer by simple steric restrictions blocking the exit of a catalyst from the polymer, or, electronic interactions between the catalyst and the polymer matrix hold the catalyst in place.

The size of the metal complex rather than a specific adsorptive interaction is important. There are two different preparation strategies. Often called the 'ship in a bottle' approach, the first strategy is based on building up catalysts in well-defined cages of porous supports. Mn-epoxidation catalysts with different salen ligands were assembled inside zeolites. In zeolite EMT e.e.'s of up to 88% and in zeolite Y e.e.'s of up to 58% were obtained with *cis*-β-methylstyrene. However, both entrapped catalysts were much less active than their homogeneous counterparts. The other approach is to build up an inorganic sol gel or organic polymeric network around a preformed catalyst. A promising example was reported by the group of Jacobs who entrapped

Jacobsen's Mn-salen epoxidation catalyst[8] and Noyori's Ru-BINAP hydrogenation catalyst in polydimethylsiloxane. Leaching depended strongly on the size and the solubility of the metal complex and the swelling of the polymer. The best e.e.'s were 50% for epoxidation of 1,3-cyclooctadiene and 92% for the hydrogenation of methyl acetoacetate in presence of toluene-p-sulfonic acid.

2.6.4 Hydrogenation with immobilized catalysts[5]

Many catalysts were developed for transition metal-catalyzed asymmetric hydrogenations, the Ru-BINAP, complexes have become the most extensively. The approach to immobilization of the BINAP framework followed a more traditional technique of grafting a monomer onto functionalized crosslinked polystyrene (Scheme 2.1).
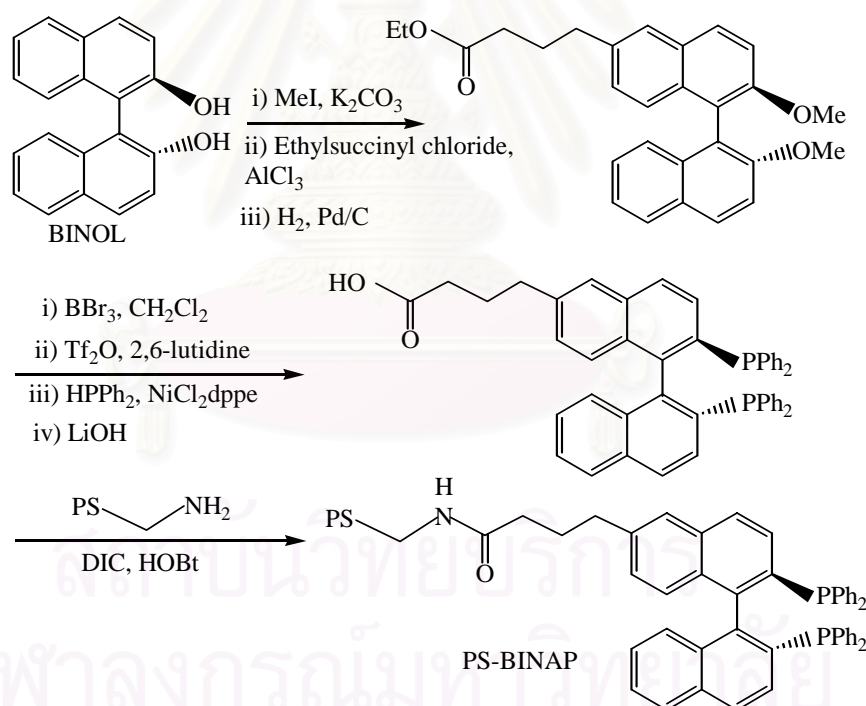
Scheme 2.1 Immobilization of the BINAP onto crosslinked polystyrene

In this case enantiomerically pure BINOL so as to impart maximum flexibility and mobility to the ligand and reduce unnecessary crosslinking. Functional group transformations provided diphosphine with a pendant acid linker. Standard peptide coupling to crosslinked aminomethylated polystyrene furnished the required

immobilized BINAP ligand. The active hydrogenation catalyst was formed according to the method of Genet by stirring with (COD)Ru(*bis*-methallyl) and hydrobromic acid to generate [Ru(PS-BINAP)Br$_2$] catalyst. This immobilized catalyst was assessed in the asymmetric hydrogenation of various carbon-carbon and carbon-oxygen double bonds. Best results were obtained in the hydrogenation of *B*-ketoesters such as shown below, (Scheme 2.2) giving the corresponding β-hydroxyester in an e.e. of 97% and 88% respectively the olefin of β-ketoester was also hydrogenated. However, the catalyst was shown to be active over several reuses with only a slight drop in activity and enantioselectivity.
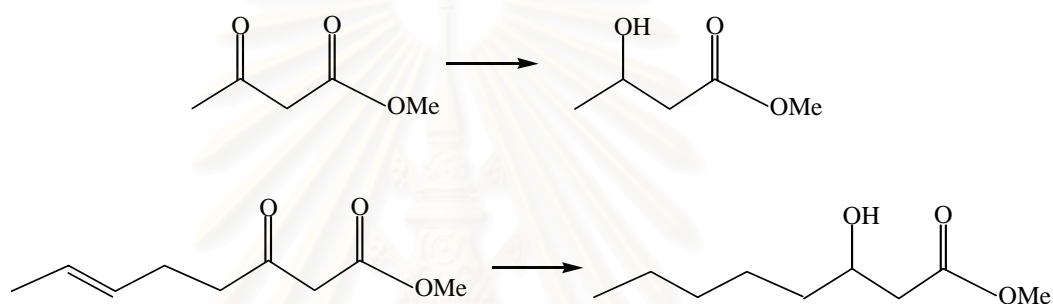
Scheme 2.2 Hydrogenation of β-ketoester, olefin β-ketoester with [Ru(PS-BINAP)Br$_2$].

2.7   Characterization of polymer supported catalyst[9]

Many heterogeneous catalysts are not well understood since characterization of these catalysts are difficult. Not all sites on the surface of catalyst have the same activity and physical or chemical characteristics. The characterization of a complex system such as a supported metal catalyst can be thoroughly accomplished only by using numerous different techniques.

Basically, the properties which need to be evaluated can be divided into two groups: (i) properties of the support, such as its grain size, morphology, porosity, chemical composition, kind and degree of functionalisation, degree of hydrophilicity / hydrophobicity, etc.; (ii) properties of the support metal particles, such as their size and size distribution, degree of crystallinity, presence of defects, distribution throughout the support grains, etc. All these properties may more or less contribute to the overall catalytic activity of the supported catalyst.

The most easily and widely applied technique continues to be infrared spectroscopy. Infrared spectroscopic investigations can be used to characterize by comparison of their spectra of molecular analogues.

NMR spectroscopy is used to characterize organometallic structure in polymer, ^{31}P-NMR spectroscopy has been used to characterize polymer supported, giving a sample with high signal strength and a nearly uniform environment of phosphorous in the polymer.

Polymer supported catalysts have also been characterized by quantitative electron microscope analysis to determine profiles of metals and other elements within individual beads of catalyst. A particle is sectioned, mounted and tranversed with an electron beam in a vacuum of a roughly 1 m^3 volume of the sample.

Mass spectrometry has been used to analyze volatilized polymers, determining the degree of crosslinking for poly-styrene-divinylbenzene as well as the degree of functionalisation of the chloromethylated polymer.

2.8   Catalytic hydrogenation[10]

The ease of hydrogenation of double bonds depends on the number and nature of substituents attached to the sp^2 carbon atoms. In general, increasing substitution results in decreasing rate of hydrogenation known, as the *Lebedev rule*. Terminal olefins exhibit the highest reactivity, and the rate of hydrogenation decrease in the order $RCH=CH_2 > R_2C=CH_2 > RCH=CHR > R_2C=CHR > R_2C=CR_2$. In this hydrogenation, *cis* isomers are hydrogenated in preference to the corresponding *trans* compounds.

2.8.1   The homogeneous hydrogenation[11]

The homogeneous hydrogenation of alkene is explained by two mechanisms. The first is the dihydride mechanism, in which the dihydride **1** is formed by oxidative addition of H_2, and the hydrogenation proceeds by the insertion of alkene to the metal hydride bond, followed by reductive elimination (Scheme 2.3). The other

hydrogenation is explained by the formation of the monohydride **2** (Scheme 2.4). Insertion of alkenes to the metal hydride is followed by attack of H_2 to give the hydrogenation product **3** with regeneration of the monohydride **2**. Hydrogenation proceeds by one of these mechanisms, depending on catalyst species.
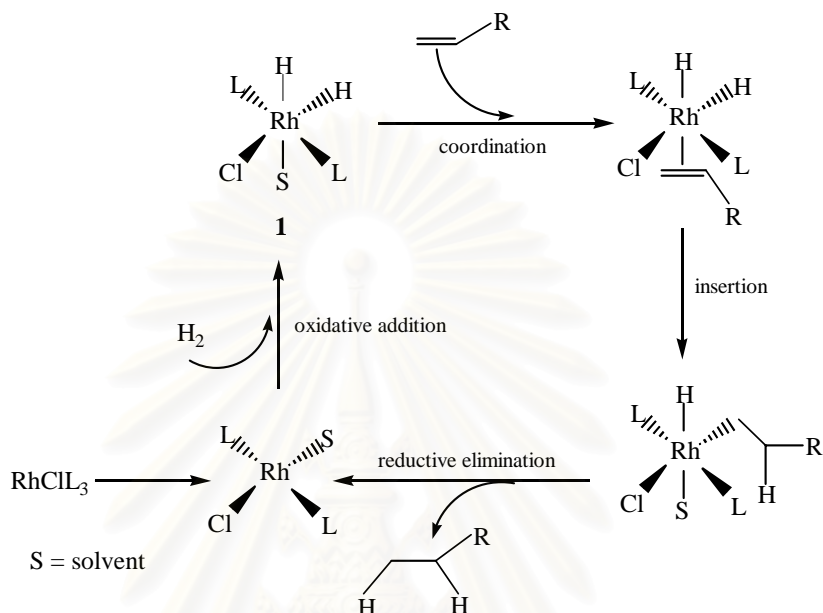
Scheme 2.3 Dihydride hydrogenation mechanism.[11]
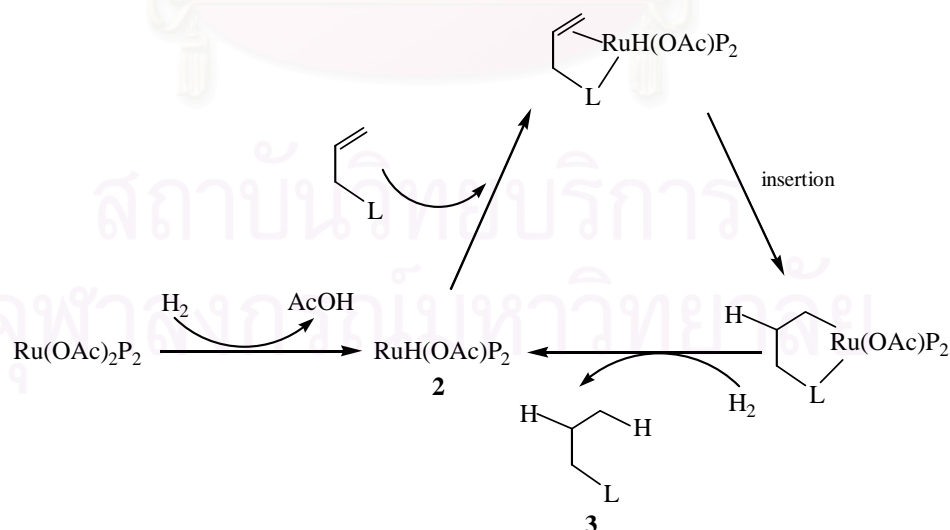
Scheme 2.4 Monohydride hydrogenation mechanism.[11]

2.8.2 The heterogeneous hydrogenation[10]

The generally accepted mechanism for the hydrogenation of double bonds over heterogeneous catalysts was first proposed by Horiuti and Polanyi. It assumes that both hydrogen and alkene are bound to the catalyst surface. The hydrogen molecule undergoes dissociative adsorption (Eq. 2.1), while the alkene adsorbs associatively (Eq. 2.2). Addition of hydrogen to the double bond occurs in a stepwise manner (Eqs. 2.3 and 2.4)

$$H_2 + 2M \rightleftharpoons H-M \qquad (2.1)$$

$$C=C + 2M \rightleftharpoons -\underset{M}{C}-\underset{M}{C}- \qquad (2.2)$$

$$-\underset{M}{C}-\underset{M}{C}- + H-M \overset{-2M}{\rightleftharpoons} -\underset{M}{C}-\underset{H}{C}- \qquad (2.3)$$

$$-\underset{M}{C}-\underset{H}{C}- + H-M \overset{-2M}{\rightleftharpoons} -\underset{H}{C}-\underset{H}{C}- \qquad (2.4)$$
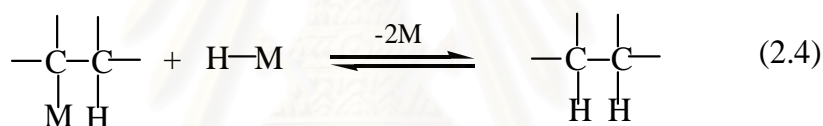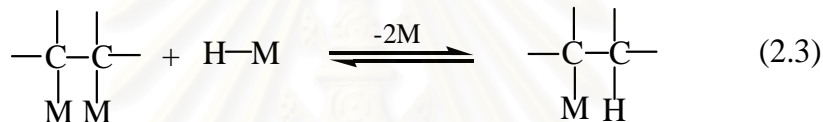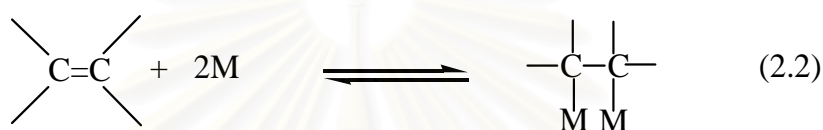
While the last step (Eq. 2.4) is virtually irreversible under hydrogenation conditions, both the adsorption of alkene (Eq. 2.2) and the formation of alkyl intermediate (half-hydrogenated state) (Eq. 2.3) are reversible. The reversibility of these steps accounts for the isomerization of alkenes accompanying hydrogenation.

2.9 Relationships between the preparation condition for metal containing polymers and their catalytic properties[12]

The metal complexes of the platinum group and those of first transition series with polymers are often used in hydrogenation of olefins, diene, alkyne and aromatics. Both linear and crosslinked polymers, grafted macromolecules and different bifunctional compounds, which are the products of condensation, are used as macroligands. Almost all types of macroligands, such as linear, soluble polymers with monodentate or chelate-type groups, three-dimensional polyligands and substances of

mixed type (mineral-polymer), etc., are widely used as supports for hydrogenation catalysts.

2.9.1 Influence of structure parameter and support nature[12]

The structure parameters of crosslinked polymer supports influence the hydrogenation process because of different factors. Specific surface area, pores sizes and distribution, surface selectivity in aromatic and aliphatic substance, the state of gel reaction, effect of solvation, diffusion limitation, etc., are the most important.

There are some examples of the influence of the structure parameters, chloromethylated or aminated styrene copolymer with divinylbenzene (CSDVB) with different amounts of cross-linking agent significantly affect the activity of fixed boron hydride in the hydrogenation of cinnamonic aldehyde into cinnamonic alcohol (Table 2.3).

Table 2.3 Characteristics of supports on the base of CSDVB

Support	%DVB	V_{pores}, (cm^3/g)	S (m^2/g)	r_{pores}, (nm)
I	10	0.040	14	10^2-10^4
II	2.0	0.192	182	10^2-10^4
III	30	0.330	222	10^2-10^4
IV	40	0.392	357	10^2-10^4

From the results, it can be indicated that, the catalyst derived from the support **I** is a gel-like polymer, so the rate of hydrogenation is controlled by the rate of substrate diffusion through the gel. The reaction rate increases in the sequence of supports as **IV ≥ III ≥ II** and correlates with characteristics of their microstructure. In the case of **IV**, the reagent is fixed on the surface of the microspheres, so that the availability of active centers is high.

There some examples of highly active catalysts derived from soluble oligomer ligands. Wilkinson catalyst, [RhCl(PPh$_3$)$_3$] attached to ethylene oligomers, Mn ~ 80-

1000, is effective in the hydrogenation of olefins at 363-383 K. The same catalyst attached to the highly developed surface of phosphynated polyethylene (PE) monocrystal (S_{sp}=200 m^2/g) under similar conditions shows a 6-fold activity increase in comparison with the catalyst conditions. Wilkinson catalyst immobilized by macroporous PE fibers[2] (pore diameter 400 nm, 60% porosity) and treated as mentioned above also find good use, the process is not controlled by substrate diffusion rate as it is in the case of crosslinked PS granules where the diffusion of substrate into the polymer is hindered.

The relative rates of hydrogenation by catalysts on some supports are as follows:

Wilkinson catalyst without support	1.00
Wilkinson catalyst on PS	0.12
Wilkinson catalyst on PE oligomers	0.89
Wilkinson catalyst on PE crystal	0.75
Wilkinson catalyst on PE-spaced fibers	0.69

The hydrogenation rate decreases also with an increase in the size of the unsaturated compound (in going from linear to cyclic olefins). This correlation is more significant in the case of PE fibers than that for PS. The transport of a polar substrate (allyl alcohol) into the non-polar PS spheres is hindered and thus decreases the hydrogenation rate (Table 2.4). In unswollen PE supports it increases with the rise in the polarity of the medium. Additionally the latter catalysts easily eliminate reagents after the reaction.

Table 2.4 A comparison of related hydrogenation rates on different substrates by a Wilkinson catalyst, immobilized by supports

Substrate	Wilkinson catalyst without support	PS-catalyst	PE (crystal) catalyst	PE (spaced fibers)- catalyst
Cyclohexene	1.00	1.00	1.00	1.00
1-Dodecene	1.23	0.60	0.95	0.91
Cyclododecene	1.29	0.23	0.78	0.74
Allyl alcohol	1.09	0.62	0.92	0.84
Cholesterole	1.20	-	0.68	0.58

The influence of the crosslinkage level on the catalyst activity and selectivity is confirmed by numerous experimental data. The activity of polymer immobilized catalysts is as a rule similar to that of the homogeneous molecular complexes and sometimes even above it for weakly crosslinked polymer as supports. The relatively high catalytic activity mentioned is a specific feature of polymer catalysis. However, a high mobility of polymer segments within weakly linked polymer matrices may lead to the formation of binuclear complexes that are less active than immobilized polyoxim-Pd^{2+} complexes containing the bond Pd-Pd were found to be highly effective in hydrogenation of a number of substrates. At the same time, their molecular analogue, bis(dimethylglycoximato)Pd^{2+} does not catalyze these processes. This distinction is probably because immobilized complexes are capable of providing coordinative vacancy by the rupture of Pd-Pd bonds, unlike the rigid structure of homogeneous, saturated Pd^{2+} complexes.

2.9.2 Influence of transition metal properties and the ratio M/L[12]

Comparisons of the activities of metal-polymer catalysts on the basis of different MX_n complexes attached to the same polymer matrix is not simple. There are many reasons for this. Firstly, it is rather difficult to provide the same metal complex content on the support. Moreover, activation of such catalysts yields different concentrations of active sites, which may alter catalyst properties, their distribution on the polymer support and accessibility to the substrate. Finally, metal centers are very specific for each substrate so that experiment data are not consistent generally and are attributed to the overall content of transition metal.

The catalyst activity depends in a complex way on both the metal nature (M = Pd, Pt) and the metal content. Thus, the extreme activity for octyne-1 hydrogenation by Pd complexes immobilized on nylon-66 is reached at a Pd content of 0.4 wt% whereas, at such content, Pt-containing catalysts are inactive. An increase of metal content leads to SCA (units mol of H_2/mol of Pd min) diminution for Pd catalyst in contrast with a rise for Pt-containing active species.

In the sequence of transition metal complexes (Rh^{3+}, Ru^{3+}, Ni^{2+}, Cu^{2+}, Co^{2+} Pd^{2+} and Mo^{6+}) immobilized on polymer supports with isonitrile groups, $PdCl_2$

complexes show the greatest activity in phenylacetylene to crosslinked isocyanines, results in substrate hydrogenation followed by isomerization; the more selective hydrogenation of cyclohexene proceeds with the use of polymer-supported ruthenium (III) complexes as catalysts.

2.9.3   Influence of the immobilized MX_n ligands[12]

The initial ligands which are retained in the inner coordination sphere of MX_n after immobilization, together with interchanged ions and/or counter ions etc., may affect complex stability, the process of active site formation and their activity and selectivity in hydrogenation reactions.

The interaction of halides metal complexes of the platinum group (especially K_2PdCl_4) with anion may lead to the formation of complexes with a halide deficiency, although their oxidation state is (+2) or (+1), as in palladium complexes. Such metal centers more easily transform into Pd^o than in $[PdCl_4]^{2-}$ under the action of reducing agents. However the nature of macrocomplex halide, may significantly affect the catalytic activity of the complexes formed. Consequently, nitrobenzene hydrogenation rates diminish as follows: $Cl > Br > I$.

In addition to the halides, carbonyls, nitrosyls, phosphines, AcAc, CH_3COO, as well as pyridine and dipyridyl(Dipy), can also be used as frame ligands or MXn. It is very difficult to estimate the influence of the ligands characteristics because these are often substituted by reagents during the catalytic process. However, the phosphine basicity and phosphorus substituents size have been shown to be important parameters affecting activity, selectivity and stability of metal containing polymer catalysts with phosphine ligands. The rate of cyclohexene hydrogenation by rhodium-containing immobilized catalysts decrease with an increase of phosphine basicity.

2.9.4   Influence of solvent properties[12]

In general the effects of solvent on the rate and mechanism of hydrogenation are manifested by numerous factors: bond energies both of the substrate and hydrogen with the catalyst surface; adsorption ability of solvent molecules; substrate and

product concentration distribution between catalyst surface and solution; activation and desorption rates; hydrogen solubility in the solvent and diffusion rate at the gas-liquid boundary; solvation of the reactive components; polar impurities capable of selective sorption; redox interactions between solvent, catalyst and especially the support. At the start a gradual swelling is accompanied by a rise in activity due to the increase of active sites accessibility.

Palladium macrocomplexes with ampholytes containing iminodiacetate functional groups are selective catalysts for cyclopentadiene hydrogenation to cyclopentene. The reaction rate increase with a rise in solvent polarity as shown in Figure 2.2.
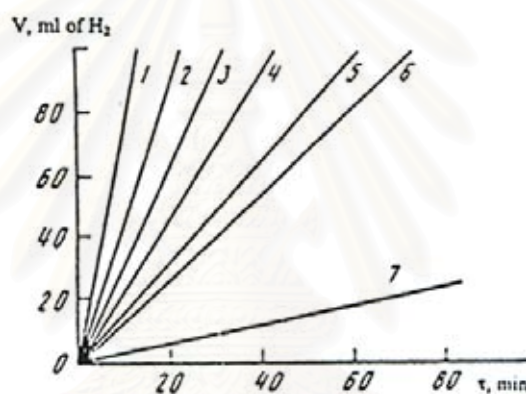
Figure 2.2 The influence of solvent nature on the rate of cyclopentadiene hydrogenation by macrochelate Pd complexes:

$1=CH_3OH$, $2=C_2H_5OH$, $3=HCON(CH_3)_2$, $4=CH_3(C_2H_5)CO$, $5=CH_3O(C_2H_5)CO$, $6=C_6H_6$ and $7=n\text{-}C_6H_{14}$

2.9.5   Influence of reaction temperature[12]

The rates of hydrogenation of both homogeneous and heterogeneous catalysts are as a rule well defined by the reaction temperature. This increases with temperature within an active range. Influence of temperature on the rate of hydrogenation by heterogenized metal complexes is more complex. This arises not only because the catalyzed reaction is controlled by the temperature but also by the state of macroligand-MX_n system.
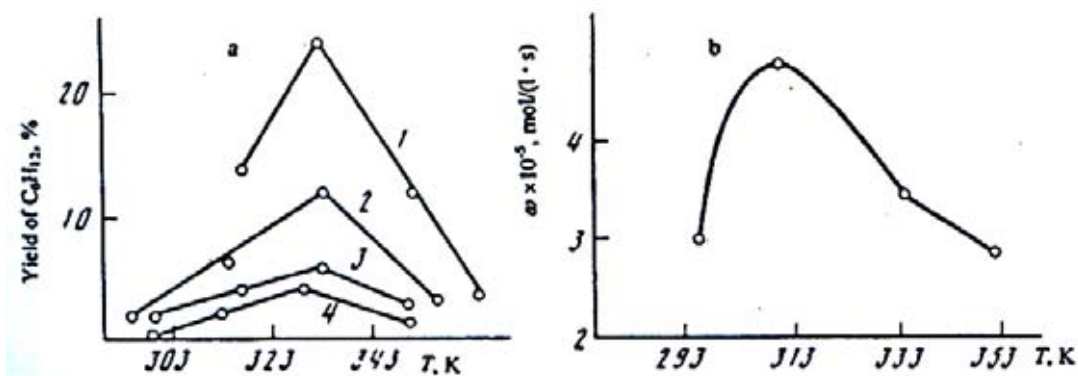
Figure 2.3 The influence of reaction temperature on the catalytic activity of metal polymer catalysts in hydrogenation of benzene (a) and allylbenzene (b).

(a); 1 = Pt-nylon-66, 2 = Rh-nylon-66, 3 = Ir-nylon-66 and 4 = Pd-nylon-66

(b); Ni^{2+} copolymer of butylacrylate, acrylonitrile, acrylic acid and methylolacrylmide 96:2:1:1 (mol %)

There are reasons for this typical temperature dependence. These include the possible decompositiion of polymer matrices, especially at elevated temperatures which can be initiated or accelerated by metal complexes. It may be that the curves drop downward because of metal center aggregation; these processes become especially significant at elevated temperature.

2.10 Literature reviews

2.10.1 Preparation and catalytic reactions of polymer supported catalysts

A number of reports of the synthesis and catalytic reactions of polymer supported catalysts include hydrogenation, hydroformylation, oxidation and epoxidation have been focused on a major advantage of such catalysts in the ease of separation and recyclability.

In 1997, Abraham *et al.*[13] reported the preparation of the polystyrene bound isoxazolinium chromate and chlorochromate, the structure of these catalysts as shown in Figure 2.4.
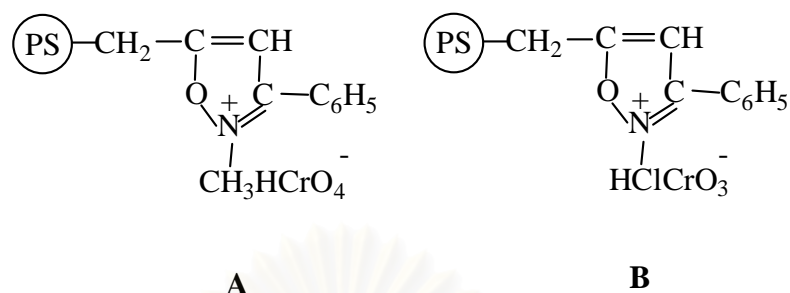
Figure 2.4 Structures of polystyrene-supported isoxazolinium chromate and chlorochromate resin[13]

These catalysts were used for catalyzed oxidation of alcohols to carbonyl compounds with high isolated yield (75-86%) and mild condition (30 °C). From the results it was found that as the temperature was increased, the time for maximun conversion was decreased gradually. These catalysts can be recycled and reused without appreciable loss of reactivity.

In 1998, Anderson *et al.*[14] has developed a polymer-supported analogue of dirhodium tetraacetate for use as an alkene hydrogenation and hydroformylation catalyst (Scheme 2.5). Their methodology involves the replacement of two of the carboxylate groups in $Rh_2(OAc)_4$ by a templated dicarboxylate ligand that positions each carboxyl group in a position to adajacent groups similar to that in the parent complex, this being attached to the polymer support via linker.
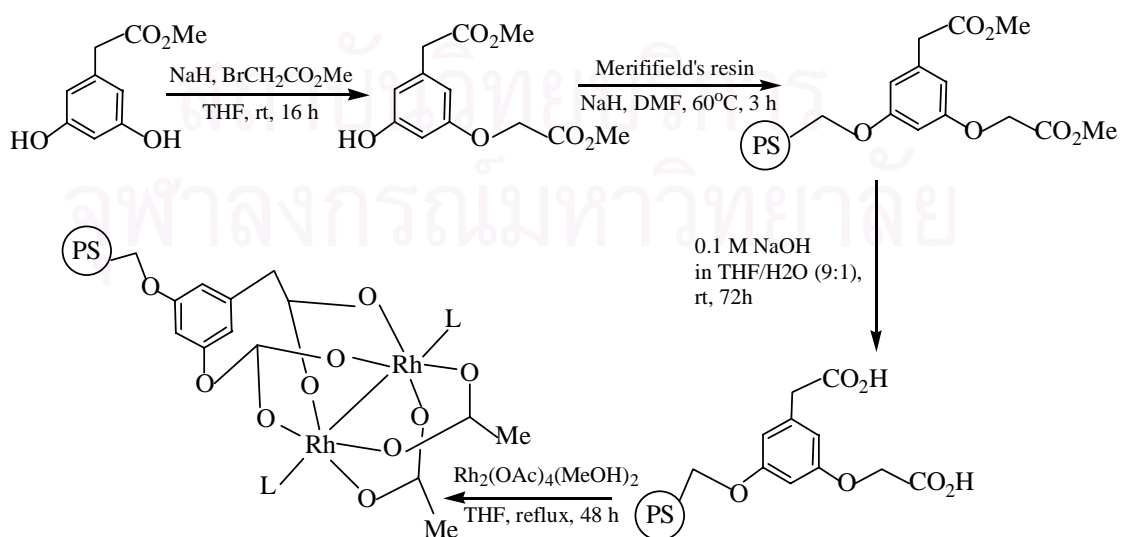
Scheme 2.5 Polystyrene bound dirhodium tetraacetate $Rh_2(OAc)_4$ complex.[14]

In 1999, Syamal *et al.*[15] reported the preparation of chelating resin containing ONNO donor quadridentate Schiff base complexes by the condensation of ethylenediamine, salicylaldehyde and 3-formylsalicylic acid, the structure of mixed Schiff base ligands (1-3) were shown in Figure 2.5. Then, the mixed Schiff base complexes were reacted with 2% crosslinked chloromethylated polystyrene and complexed with Cu(II), Ni(II), Co(II), Fe(III), Zn(II), Cd(II), Mo(VI) and U(VI). The reaction of chloromethylated polystyrene with the free ligand leads to almost 100% conversion. The polymer anchored Schiff base reacted with metal salt/metal complex in 1:2 (ligand:metal) molar ratio in DMF and 1:1 in methanol. The formation of the metal complexes (M), as shown in Scheme 2.6.
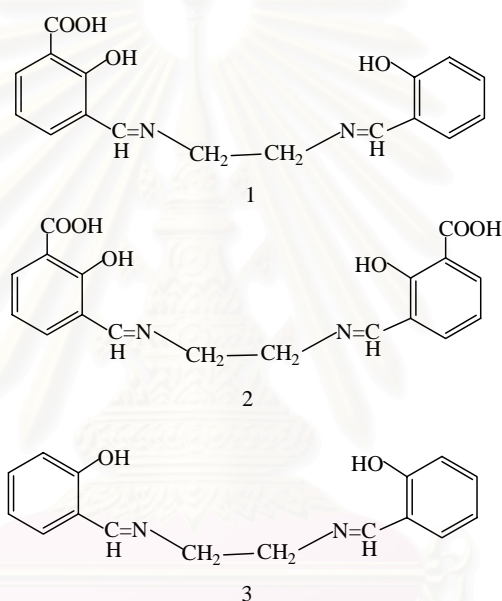
Figure 2.5 Structures of Schiff base ligands[15]
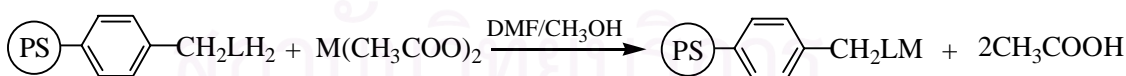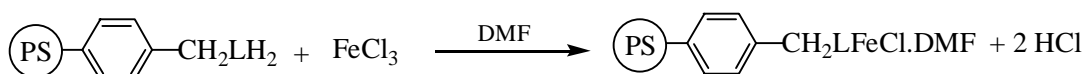
Scheme 2.6 The formation of the metal complexes.[15]

In 2000, Carre *et al.*[16] reported the preparation of chloromethylated polystyrene resins (Merrifield resin) by copolymerization of a mixture *m-/p-*chloromethylstyrene, styrene, and divinylbenzene, Figure 2.6. The chloromethylated polystyrene resins were characterized by FT-IR, ^{13}C NMR and microanalysis. In addition, it could be prepared to polymer-based titanium catalyst by treatment of the diphenylamine-modified polymer with TiCl$_4$, which was in transesterification reaction of methyl butylrate and 11-bromoundecanol producing the desired product, 11-bromoundecyl butylrate in 86% yield. It can be reused twice (79% yield). These chloromethylated polystyrene resins were used for polymer supported metal catalysts.
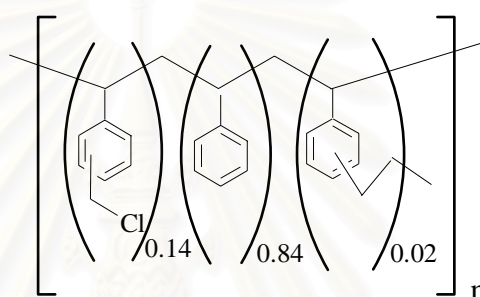
Figure 2.6 Crosslinked chloromethylated polystyrene (Merrifield resin)[16]

In 2001, Li *et al.*[17] studied the thermal stability of poly(styrene-*co-*divinylbenzene) with different crosslinking degree (6, 10, 15, 30 and 57%). The polymer beads were characterized by IR, DSC and TG. The results showed that thermal decomposition temperature of the beads was raised with increased crosslinking in the porous beads. From the results it can be indicated that 30% crosslinking degree was stable chemically and physically in the temperature range below 350 °C.

In 2001, Antony *et al.*[18] reported preparation of poly(styrene-*co-*divinylbenzene) bidentate Schiff base ligands anchoring iron (III) complex by functionalizing polymer with ethylenediamine(**A**) and 2-aminopyridine(**B**). The synthesis involves oxidizing polymer with dimethylsulfoxide (DMSO) and sodium hydrogencarbonate (NaHCO$_3$). Then immobilized iron (III) complex onto the polymer Schiff base were shown in Scheme 2.7. The polymer beads were characterized by IR, UV-Vis reflectance spectroscopy and DTA-TG. The iron (III) complex anchored on Schiff base bound poly(styrene-divinylbenzene) were found to be effective in the

epoxidation of *cis*-cyclooctene and styrene in the presence of *tert*-butylhydroperoxide under mild condition. The catalysts can be recycled several times without any loss in selectivity.
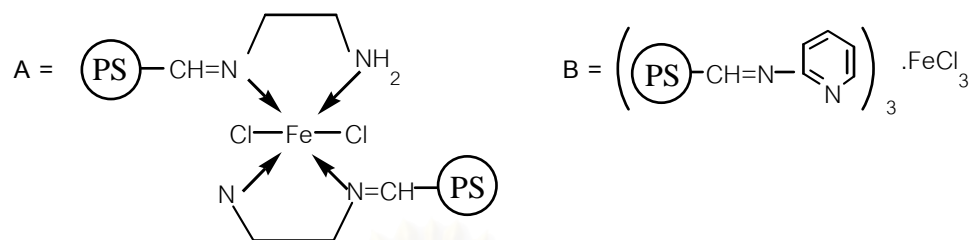
Scheme 2.7 Structure of polystyrene supported Schiff base iron (III) complex.

2.10.2 Polymer supported catalysts for hydrogenation

Reduction reactions and, more specifically, hydrogenation reactions often rely on the use of transition metal catalysts to affect their outcome. In addition, the ligands required to affect asymmetric versions of these reactions can be expensive to purchase or produce. Thus, many polymer supported reduction catalysts that can potentially be recycled have been developed. Generally, these catalysts have been prepared by attachment of a ligand to the polymer followed by incubation of the supported ligand with appropriate metal source.[19]

In 1971, Grubbs *et al.*[20] reported the preparation of diphenylphosphinomethyl polystyrene, incubated with tris(triphenylphosphine)rhodium (I) chloride for 2-4 weeks to give the supported Wilkinson's catalyst (Figure 2.7). This catalyst was then used for the hydrogenation of a series of alkenes, providing reaction rates close to those seen in solution.
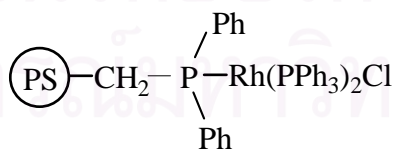
Figure 2.7 Polystyrene supported Wilkinson's catalyst[20]

In 1978, Pettit *et al.*[21] reported the preparation of chloromethylated polystyrene beads bound anthranilic acid and loaded with Pd (II) chloride (Scheme 2.8). This catalyst was used for hydrogenation of 4-octyne to *cis*-4-octene and formation of cyclooctene from 1,3- and 1,5-cyclooctadienes, the rate of hydrogenation

of a 1,3-diene was faster than that of a 1,5-diene. It was found that the rate of reaction depends on 1-octene and catalyst concentration and temperature.
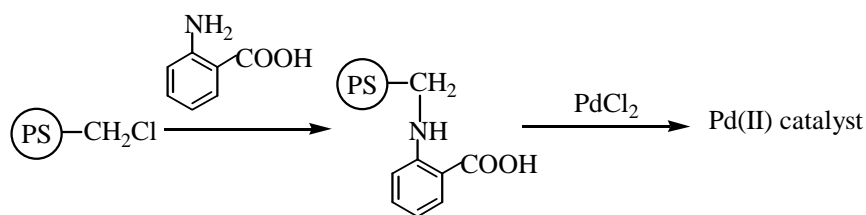
Scheme 2.8 Polystyrene bound anthranilic acid Pd (II) catalyst.[20]

In 1988, Gokak *et al.*[22] synthesized polymer supported cobalt catalysts, which used 2, 5 and 10 % divinylbenzene (DVB) styrene copolymer macroporous beads as polymeric support, used ethylenediamine or glycine as ligand and reacted with $CoCl_2.6H_2O$. The structures of the cobalt complexes were shown in Schemes 2.9-2.10. The catalysts were used for hydrogenation of 1-octene at 25-55 °C, hydrogen pressure of 1-5 atm, conversion was low (5%). Whereas 5% DVB catalyst in the presence of $NaBH_4$ at 55 °C and 3 atm, conversion was increased (15% of 1-octene).
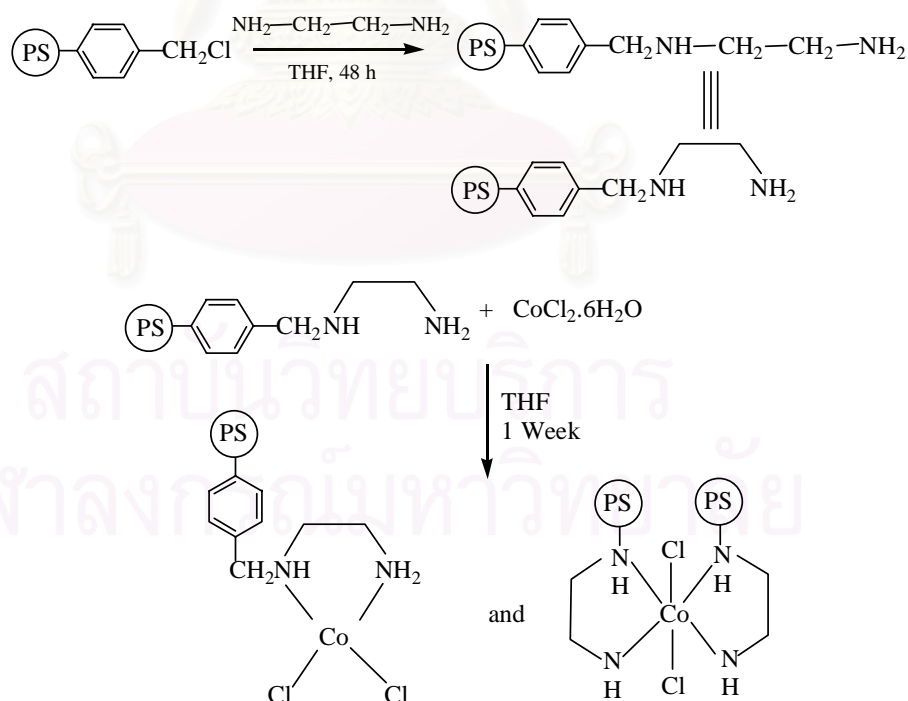
Scheme 2.9 Structures of polystyrene supported cobalt (ethylenediamine) complexes.[22]
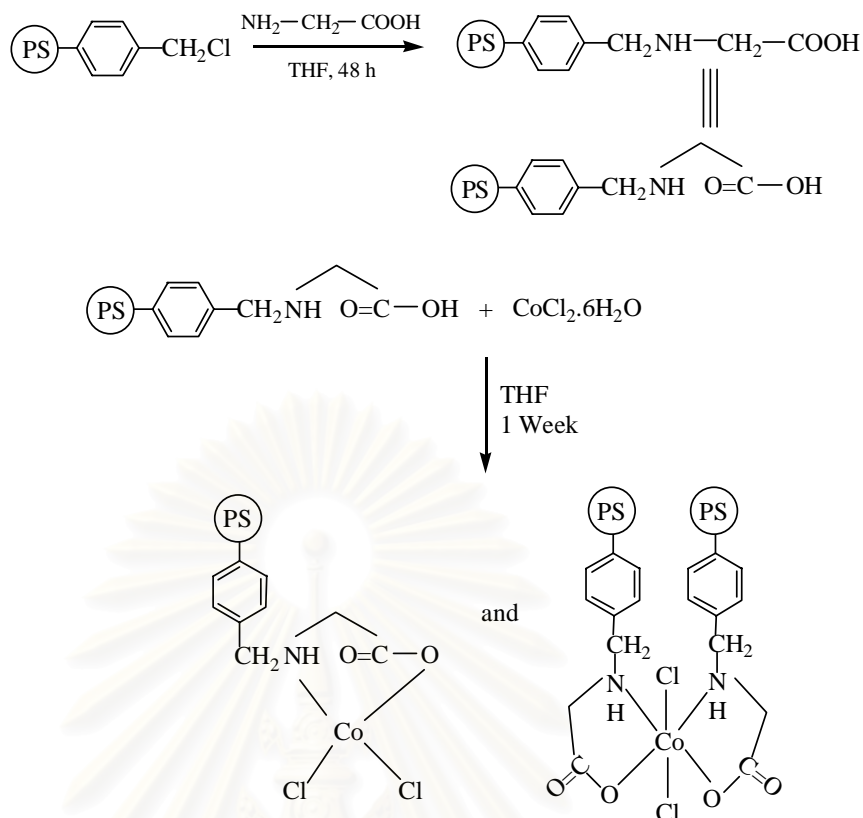
Scheme 2.10 Structures of polystyrene supported cobalt (glycine) complexes.[22]

In 1990, Shan *et al.*[23] reported the preparation of the polymer-supported ruthenium(trimethylenediamine) complex, by reacting 3 and 10% poly(styrene-*co*-divinylbenzene) porous beads with bifunctional ligand (trimethylenediamine) and $RuCl_3.xH_2O$, these catalysts were used for hydrogenation of cyclohexene at 30-50 ^{o}C, hydrogen pressure of 1 atm. Maximum reaction rate was maintained for about 10 h after which the rate decreased slowly. The influence of cyclohexene and catalyst concentration on the rate of reaction was investigated. The rate of reaction was increased when cyclohexene and catalyst concentration were increased. The polymer-supported catalysts were thermally stable at high temperature. Many possible structures of polymer-supported ruthenium complexes were proposed as shown in Scheme 2.11.
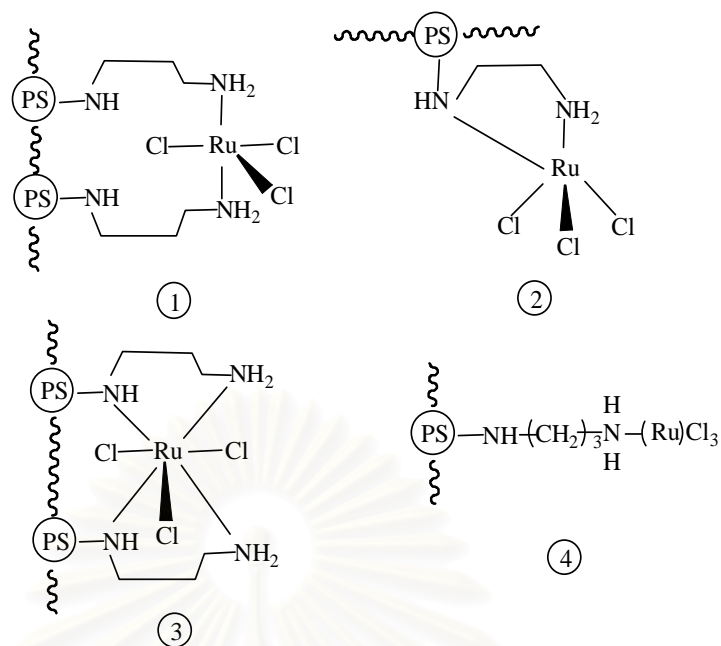
Scheme 2.11 Possible structures of polystyrene supported ruthenium(trimethylenediamine) complexes.[23]

In 1993, Shan *et al.*[24] studied kinetic of cyclohexene hydrogenation using polymer-supported ruthenium (III) trimethylenediamine complex in methanol. The polymer-supported metal catalyst was active and stable. The rate of hydrogenation was calculated and it depends on the amount of catalyst, cyclohexene concentration, hydrogen pressure and temperature.

In 1996, Patel *et al.*[25] reported the preparation 6% and 8% crosslink chloromethylated poly(styrene-divinylbenzene) treated with glycine (Scheme 2.12). The poly(styrene-divinylbenzene) bound glycine and complexed with ruthenium (II) were characterized by IR, UV-Vis reflectance spectroscopy and DTA-TG. Then the polymer bound glycine ruthenium (II) complexes were tested for the kinetics of the hydrogenation of nitrobenzene. The results indicate that 8% crosslinking polystyrene bound glycine has higher catalytic activity than 6% crosslinking.
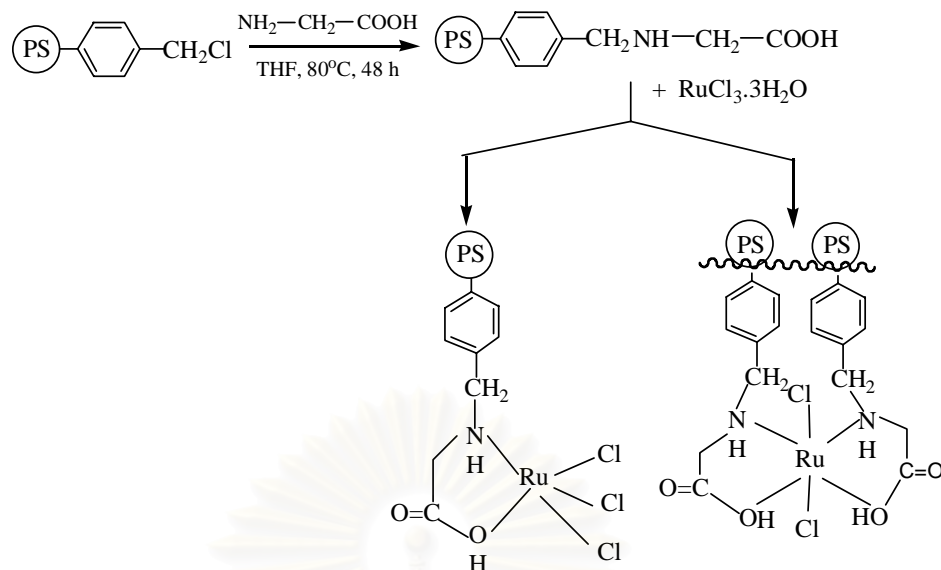
Scheme 2.12 Polystyrene bound glycine ruthenium (II) complex.[25]

In 1997, Dalal *et al.*[26] reported the preparation of chloromethylation of styrene-divinylbenzene copolymer with sequential attachment of ethylenediamine and salicyaldehyde, then complexed with palladium (II). The polymer bound palladium (II) complex was used for hydrogenation of 1-hexene. From the results it was found that the synthesized polymer bound palladium (II) complex has a higher catalytic activity than its homogeneous counterpart.
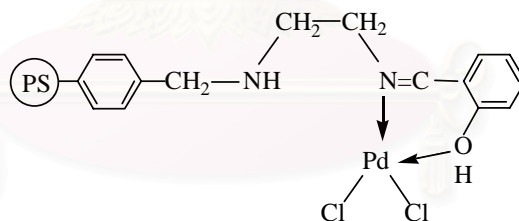
Figure 2.8 Structure of polystyrene supported Pd (II) complex[26]

In 2001, Dalal *et al.*[27] reported the preparation of crosslink poly(styrene-*co*-divinylbenzene-*co*-vinybenzylchloride) ruthenium (III) ethylenediaminetetraacetic acid (EDTA) ligand, the catalyst structure as shown in Scheme 2.13. The polymer beads were characterized by FT-IR, UV-vis, SEM, ESR and TGA. The polymer bound complex was used to study hydrogenation of 1-hexene to *n*-hexane under mild condition. Influence of substrate concentration, catalyst amount, reaction temperature and nature of the solvent were affected the rate of the hydrogenation. A decrease in swelling was observed as the nature of the solvent was changed from polar to non-polar. The metal loss 33% from the polymer supported was observed after five cycles.
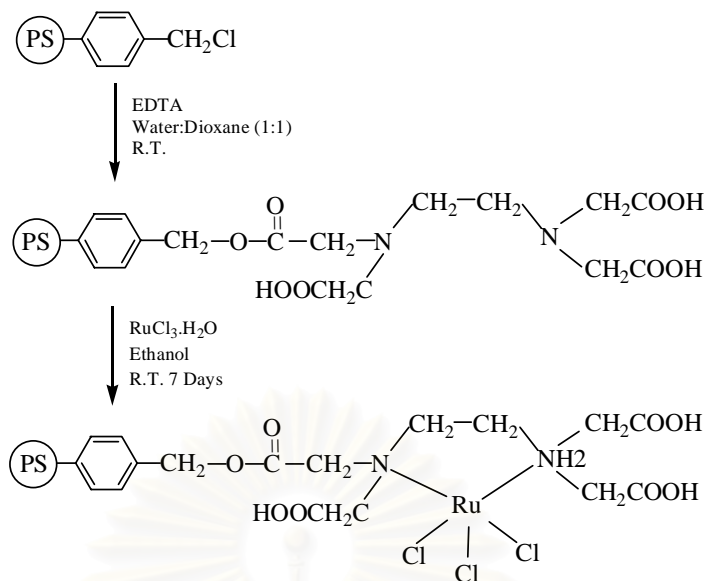
Scheme 2.13 Structure of polystyrene supported Ru (III) EDTA complex.[27]

In 2002, Bunchongsiln,[29] reported the preparation of the polystryrene-supported ruthenium catalysts with 2%, 5% and 10% DVB poly(styrene-*co*-divinylbenzene-*co*-vinylbenzylchloride) copolymer, reacting with bidentate ligands, 2-aminopyridyl and 1,3-diaminopropane and ruthenium trichloride. The posssible structure of these catalysts as shown in Figure 2.9.
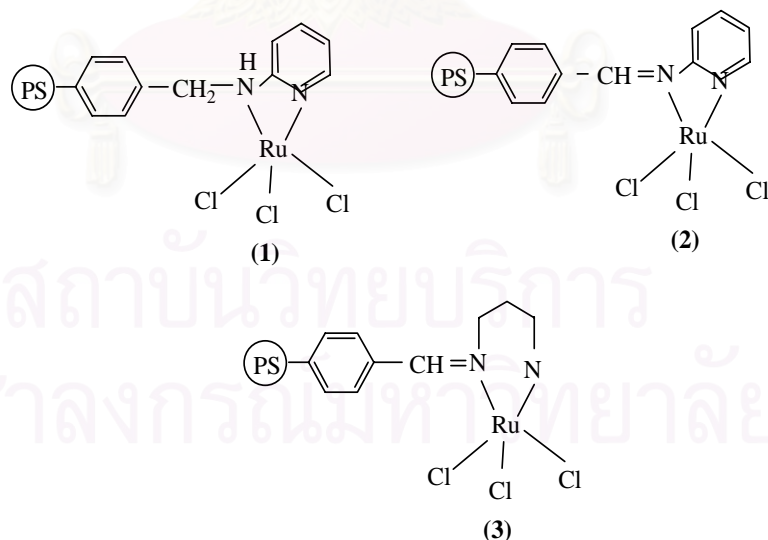
Figure 2.9 The possible structures of

    (1) polystyrene bound 2-aminopyridyl ruthenium catalyst

    (2) polystyrene Schiff base 2-aminopyridyl ruthenium catalyst

    (3) polystyrene Schiff base 1,3-diaminopropane ruthenium catalyst

It was found that, the 10% crosslinked polymer had less functionalization than the ones with 2% and 5% crosslinked. All of these catalysts can hydrogenate cyclooctene, giving high yield of cyclooctane > 95% at 60 $^\circ$C, hydrogen pressure 5 atm in 5 h and 5% crosslink catalyst gave higher conversion than the others. The %yield was increased when cyclooctene, amount of catalyst, hydrogen pressure and temperature were increased. The polystyrene supported catalysts were thermally stable at high temperature. The polystyrene supported ruthenium catalysts can be recycled with slightly loss in activity and did not leach out of ruthenium from the polymer support.

In 2003, Valhdkar *et al.*[29] reported the preparation of the polymer supported *L*-valine palladium (II) complex with 6%, 8% crosslinked poly(styrene-*co*-divinylbenzene-*co*-vinybenzylchloride), the possible structure of these catalysts were shown in Figure 2.10.
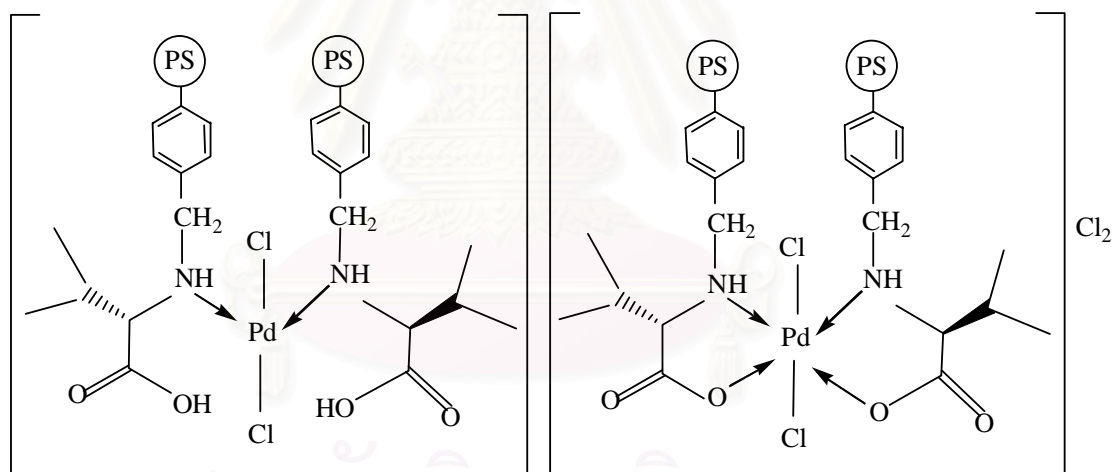
Figure 2.10 Polystyrene supported *L*-valine Pd (II) complex[29]

These catalysts can hydrogenate 1-octene, cyclohexene, acetophenone and nitrobenzene under mild conditions and high selectivity, the results were shown in Table 2.5. The catalyst was recycled five times with slightly loss of activity.

Table 2.5 Catalytic reduction of polymer supported *L*-valine Pd (II) complex[29]

Catalysts[a]	Substrate[b]	Yield (%)[c]	Products/ selectivity (wt.%)	TON[d]
Pd 8%	1-Octene	51.8	n-Octane (100)	189
Pd 6%		50.1	n-Octane (100)	175
Pd 8%	Cyclohexene	19.0	Cyclohexane (100)	69
Pd 6%		23.7	Cyclohexane (100)	83
Pd 8%	Nitrobenzene	22.1	Aniline (100)	81
Pd 6%		6.8	Aniline (100)	25
Pd 8%	Acetophenone[e]	24.0	1-Phenyl ethanol (100)	89
Pd 6%		13.9	1-Phenyl ethanol (100)	49

[a] 0.10g (Pd = 2.7×10^{-5} M Pd)

[b] 10.0 mmol

[c] Yield based on starting material

[d] Turnover number: mmol products/mmol Pd; time: 6 hours;

solvent: methanol (30 ml); temperature: 50 °C; pressure: 200 psi.

[e] Reaction conducted in presence of [t]BuOK

CHAPTER III

EXPERIMENTAL

In the present study of the hydrogenation of cyclooctene catalyzed by polystyrene supported cobalt complexes, the experiments were divided into:

1. Preparation and characterization of polystyrene supported cobalt catalysts.
2. Hydrogenation of cyclooctene with the prepared catalysts.
3. Recycling of polystyrene supported cobalt catalysts.
4. Test of cobalt leaching.

The details of the experiments were in the following.

3.1   Chemicals

All chemicals (analytical grade) used were obtained as follows:

Table 3.1 Chemicals, reagents and suppliers

Chemicals and reagents	Suppliers
Acetone	Merck KGaA., Germany
Acetonitrile	Merck KGaA., Germany
2-Aminopyridine	Merck KGaA., Germany
Benzene	Fluka Chemie A.G., Switzerland
Celite 545 (filter aid)	Fluka Chemie A.G., Switzerland
Cobalt (II) acetate	Fluka Chemie A.G., Switzerland
Cobalt (II) chloride	Fluka Chemie A.G., Switzerland
Conc. HCl	Fluka Chemie A.G., Switzerland
Conc. H_2SO_4	Fluka Chemie A.G., Switzerland
Conc. Nitric acid	Fluka Chemie A.G., Switzerland
18-Crown-6	Fluka Chemie A.G., Switzerland

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Table 3.1 Chemicals, reagents and suppliers (cont.)

Chemicals and reagents	Suppliers
Cyclooctane	Merck KGaA., Germany
Cyclooctene	Fluka Chemie A.G., Switzerland
Chloromethylated polystyrene bead (5%DVB, ~ 5.5 mmolCl/polymer)	Fluka Chemie A.G., Switzerland
1,3-Diaminopropane	Merck KGaA., Germany
Dichloromethane	Merck KGaA., Germany
Dimethylformamide (DMF)	Merck KGaA., Germany
Dimethyl sulfoxide (DMSO)	Fluka Chemie A.G., Switzerland
1,4-Dioxane	Aldrich Chemical Co., Switzerland
Ethanol	Merck KGaA., Germany
Ethyl benzene	Fluka Chemie A.G., Switzerland
4-Hydroxybenzaldehyde	Fluka Chemie A.G., Switzerland
Methanol	Merck KGaA., Germany
Petroleum ether 40-60 °C	Merck KGaA., Germany
Picolinic acid	Merck KGaA., Germany
Potassium carbonate (K_2CO_3)	Merck KGaA., Germany
8-Quinolinol	Fluka Chemie A.G., Switzerland
Salicyldehyde	Merck KGaA., Germany
Silica 60, 0.06-0.2 mm	Scharlau Chemie S. A., Spain
Sodium hydrogen carbonate ($NaHCO_3$)	Merck KGaA., Germany
Sodium sulfate anhydrous	Merck, Germany
Tetrahydrofuran (THF)	Fluka Chemie A.G., Switzerland
Triethylenetetramine	Fluka Chemie A.G., Switzerland
Ultra high purity hydrogen gas (99.99%)	Thai Industry Gas Co., Ltd., Thailand
Ultra high purity nitrogen gas (99.99%)	Thai Industry Gas Co., Ltd., Thailand

3.2 Equipment

All equipments, used in the catalyst preparation and hydrogenation, were listed as follows:

Schlenk line

Schlenk line consists of nitrogen and vaccum line. The vaccum line was equipped with solvent trap and a vacuum pump was shown in Figure 3.1.
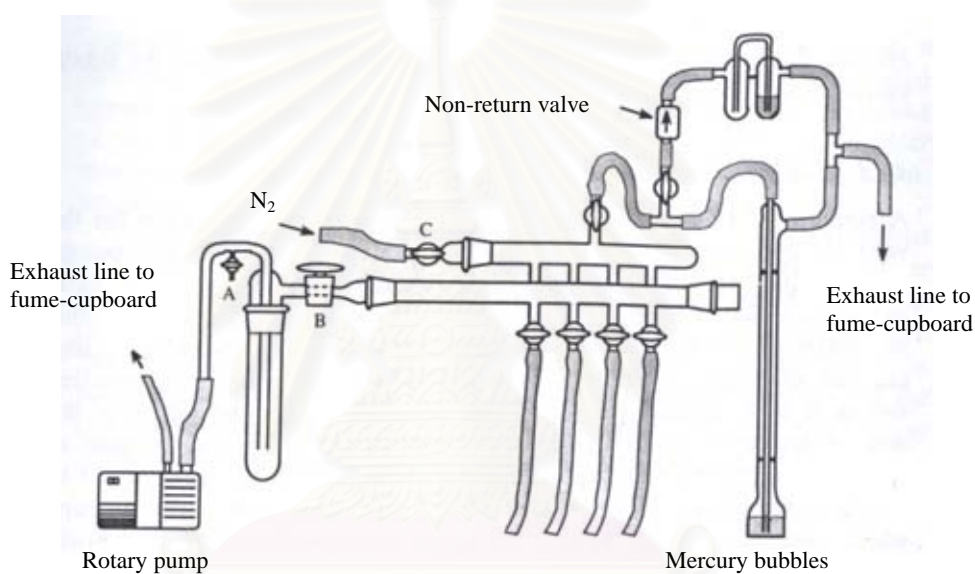
Figure 3.1 Schlenk line set up

Vacuum pump

A vacuum pump with a pressure of 10^{-1} to 10^{-3} mmHg was used for the vacuum line in the Schlenk line.

Schlenk flasks

A flask with a side-arm was used with inert gas (nitrogen). The standard requirements of a joint to connect to other items of glass wares provide access to the contents for connection to the manifold. Some typical examples are shown in figure 3.2.
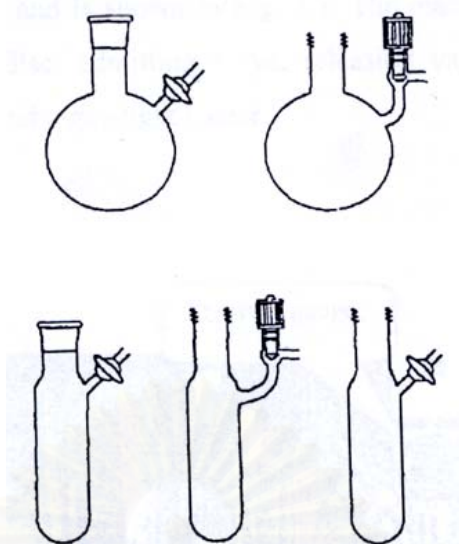
Figure 3.2 Schlenk flasks

Parr reactor

Parr reactor (size 600 ml), 4042 stainless-steel pressure reactor, was used for hydrogenation (Figure 3.3). The reactor consists of a pressure gauge, safety rupture disc, admitting valve, releasing valve and removing liquid valve, a thermometer and a gas-tight stirrer.
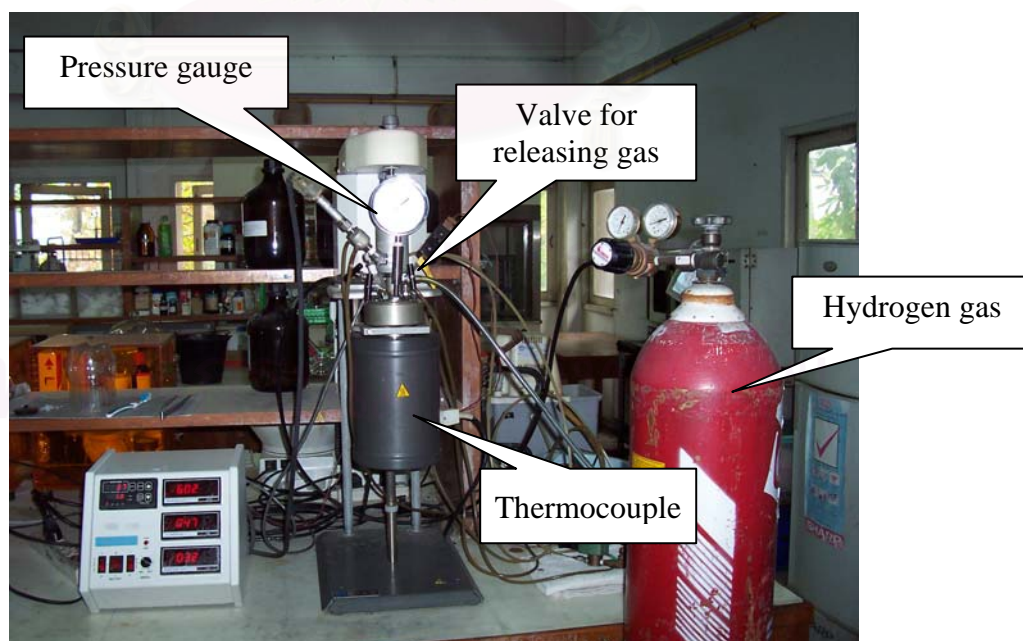
Figure 3.3 Parr reactor

3.3   Characterization methods

3.3.1   Fourier-transform infrared spectroscopy (FT-IR)

Fourier-transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer at Department of Chemistry, Chulalongkorn University. The samples were made into a KBr pellet. Infrared spectra were recorded between 400 to 4000 cm^{-1} in transmittance mode.

3.3.2   Gas-liquid chromatography (GC)

Capillary column gas chromatograph GC16A (Shimadzu) was used for the determination of % yield of cyclooctene and cyclooctane from the reaction mixture. A gas chromatogram of liquid products from reaction mixture of hydrogenation of cyclooctene, as shown in Appendix A. The conditions are as follows:

Column   : DB-1

Detector   : Flame ionization (FID)

Detector temperature   : 220 °C

Injector temperature   : 220 °C

Carrier gas   : Nitrogen

Flow rate   : 40 kPa.

Programmed temperature :

90 °C for 5 min

4 °C/min

50 °C for 1 min
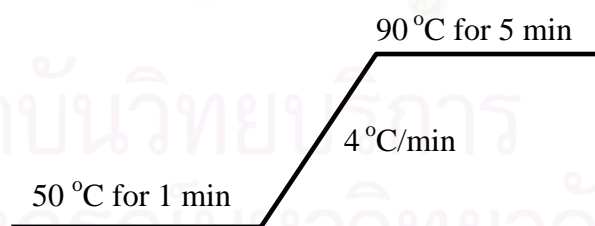
3.3.3   Thermogravimetric analysis (TGA)

Thermogravimetric measurements were performed on a TA instrument thermogravimetric analyzer (SDT 2960) at a heating rate of 10 °C/min under nitrogen atmosphere.

3.3.4 X-ray fluorescence spectrometer (XRF)

Cobalt content in the catalyst was determined using a SIS ONS X-ray fluorescence spectrometer ARL 8410 at the Department of Science Service, Ministry of Science and Technology.

3.3.5 Atomic absorption spectrometer (AAS)

Cobalt content in the polymer supported catalysts was measured using a Varian Spectra-AA300 atomic absorption spectrometer with air/acetylene flame, which is located at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

3.3.6 Sample preparation for AAS

In order to determine cobalt content in polystyrene supported cobalt catalysts, the catalysts were calcined in muffle furnace at 540 °C overnight. The residue was transferred to a beaker and concentrated nitric acid was added. The mixture was heated until dryness on the hot plate three times. After that the residue was dissolved and transferred to a 25 ml volumetric flask and made up volume with deionized water.

3.4 Purification of solvents

-Dry dioxane and dry THF were dried with sodium metal and benzophenone.

-Methanol was dried with magnesium methoxide, prepared by placing 5 g of clean dry magnesium turnings and 0.5 g of iodine in a 2 liter flask, followed by 50-70 ml of absolute methanol, and warmed the mixture. Heating was continued until all the magnesium was converted to magnesium methoxide. Up to 1 liter of methanol was added and after an hour reflux, it was distilled off.

3.5 Preparation of polystyrene supports

In order to be generally useful the chosen ligand must be readily available, be relatively inexpensive, be able to bind to a large variety of transition-metal species, be able to be bound to polymer support smoothly and efficiently and be chemically inert under a wide variety of potential reaction condition.

3.5.1 Polystyrene bound Schiff base 1,3-diaminopropane ligand, P-L$_1$[17]

Chloromethylated poly(styrene-*co*-divinylbenzene) beads (2.02 g) were oxidized to aldehyde by reacting with 20 ml dimethyl sulfoxide (DMSO) and sodium hydrogen carbonate (0.516 g) at 155 °C for 6 hours. The dried aldehyde bearing polymer was allowed to swell for 1 hour in dry methanol (20 ml). To this a solution of 1,3-diaminopropane (2 ml, 0.024 mol) in dry methanol was added dropwise with constant stirring. The contents were refluxed for 6 hours. After cooling to room temperature the polymer beads were filtered, washed thoroughly with methanol, petroleum ether (40-60 °C) and dried in vacuum at 70 °C for 12 hours.

3.5.2 Polystyrene bound Schiff base glycine ligand, P-L$_2$[22]

This was prepared by the same methodology as 3.5.1 but replaced 1,3-diaminopropane with glycine. The dried aldehyde bearing polymer was allowed to swell for 1 hour in THF- water-acetone (4:2:1) 20 ml. To this a solution of glycine (1.81 g, 0.024 mol) in the same solvent was added and refluxed for 24 hours. After cooling the pale yellow polymer beads were filtered, washed with THF, distilled water and acetone then dried in vacuum at 70 °C for 12 hours.

3.5.3 Polystyrene bound Schiff base triethylenetetramine ligand, P-L$_3$

This was prepared by the same methodology as 3.5.1 but replaced 1,3-diaminopropane with triethylenetetramine (3.58 ml, 0.024 mol).

3.5.4 Polystyrene bound Schiff base 2-aminopyridyl ligand, P-L$_4$[18]

This was prepared by the same methodology as 3.5.1 but replaced 1,3-diaminopropane with 2-aminopyridine (2.25 g, 0.024 mol).

3.5.5 Polystyrene bound 2-aminopyridyl ligand, P-L$_5$[30]

This was prepared by swelling 5% chloromethylated poly(styrene-*co*-divinylbenzene) beads (1.00 g) in dry methanol (20 ml) for 45 min. To this a solution of 2-aminopyridine (2.25 g, 0.024 mol) in dry methanol was added dropwise over a period of 15 min using the addition funnel with constant stirring. The reaction was refluxed for 2 days. After cooling to room temperature the polymer beads were filtered, washed thoroughly with methanol and dried in vacuum at 70 °C for 12 hours.

3.5.6 Polystyrene bound 1,3-diaminopropane Schiff base salicaldehyde ligand, P-L$_6$[31]

Chloromethylated poly(styrene-*co*-divinylbenzene) beads (2.02 g) were swollen in dry THF (20 ml) for 45 min. To this a solution of 1,3-diaminopropane (2 ml, 0.024 mol) in dry methanol was added dropwise using the addition funnel with constant stirring. The reaction was refluxed for 2 days. After cooling to room temperature the polymer beads were filtered, washed thoroughly with deionized water, methanol, dry dioxane and dried in vacuum at 70 °C for 12 hours. Then a solution of salicylaldehyde (1.16 ml, 0.024 mol) in benzene was slowly added and refluxed for 1 day. After cooling to room temperature the polymer beads were filtered, then purified with methanol using soxhlet extraction method and dried in vacuum at 70 °C for 12 hours.

3.5.7 Polystyrene bound 4-hydroxybenzaldehyde bound 2-aminopyridyl ligand, P-L$_7$[32,33]

Chloromethylated poly(styrene-*co*-divinylbenzene) beads (1.00 g) were swollen in dry dioxane (20 ml) for 45 min. It was added 4-hydroxybenzaldehyde (0.67 g, 5.5 mmol), K$_2$CO$_3$(0.73 g, 2.75 mmol) and 18-crown-6 (0.072 g, 0.28 mmol). The mixture was refluxed under N$_2$ for 1 day. After cooling to room temperature the polymer beads were filtered, washed with dioxane and warm distilled water and then dried in vacuum at 70 °C for 12 hours. Then the polymer beads was kept contact in dry methanol (20 ml) for 45 min, to this a solution of 2-aminopyridine (2.25 g, 0.024 mol) in methanol was added dropwise with constant stirring and one drop of conc. HCl was added. The contents were refluxed for 2 days. After cooling to room temperature the polymer beads were filtered, washed with methanol and deionized water, then dried in vacuum at 70 °C for 12 hours.

3.5.8 Polystyrene bound picolinate ligand, P-L$_8$

This was prepared by the same methodology in 3.5.5 but replaced 2-aminopyridine with picolinic acid (2.95 g, 0.024 mol).

3.5.9 Polystyrene bound 8-quinolinate ligand, P-L$_9$

This was prepared by the same methodology in 3.5.5 but replaced 2-aminopyridine with 8-quinolinol (3.48 g, 0.024 mol).

3.6   Preparation of polystyrene supported cobalt catalysts

Two types of cobalt compounds used to load onto the polystyrene supported were cobalt (II) chloride and cobalt (II) acetate.

The loading of the metal was carried out as follows: 0.50 g of polystyrene anchoring ligand beads were kept in contact with dry methanol (20 ml) for 45 min. To this was added hydrated cobalt (II) chloride (0.2974 g, 1.25 mmol) or hydrated cobalt (II) acetate (0.3114 g, 1.25 mmol), stirred for 10 days at room temperature. The polymer beads were filtered, washed with methanol and dried in vacuum at 70 °C for 12 hours.

3.7   Preparation of homogeneous catalysts[34-36]

3.7.1   Cobalt (II) picolinate complex, L_8-$CoCl_2$

This complex was synthesized by reacting 2 equiv. of picolinic acid in small volume of ethanol and an ethanolic solution of 2.5 equiv. sodium hydroxide was added, refluxed and stirred vigorously until a solid started to separate. On cooling, the white powder was separated by filtration and washed with ethanol. Then, slowly added ethanolic solution of 1 equiv. $CoCl_2.6H_2O$ into the ethanolic solution of white powder, refluxed and stirred for 6 hours. On cooling, light purple solid was separated, washed with ethanol, diethyl ether and dried in vacuum.

3.8   Swelling test[22]

Measurement of swelling is done by equilibration of 0.1000 g of the polystyrene-supported cobalt catalyst with 5 ml of the selected solvent for 30 min. After that, the catalyst was filtered. The adhering liquid was further removed by centrifugation (30 min, 1500 rpm).

$$\text{Percent swelling} = ((W_2 - W_1)/W_1) \times 100$$
$$\text{Where; } W_1 = \text{unswollen weight}$$
$$W_2 = \text{swollen weight}$$

3.9   Hydrogenation of cyclooctene with catalysts

The hydrogenation of cyclooctene (1.3 ml, 10 mmol) was performed in a Parr reactor. The stirring of the reaction mixture was maintained at an optimized rate of 600 rpm to minimize diffusion and gas-to-liquid or liquid-to-solid mass-transfer.[37-38] The parameters affecting the hydrogenation process were investigated. Catalytic activity of the catalyst was reported by %yield based on cyclooctene and turnover number (mmol cyclooctane/mmol cobalt).

A: Effect of types of solvent

Different types of solvent were investigated: methanol, acetonitrile, and dimethylformamide.

B: Effect of work-up methods

The reaction mixture was filterd and worked-up by 3 different methods;
(i) The reaction mixture was acidified with 25% H_2SO_4, extracted with hexane then neutralized with saturated solution of $NaHCO_3$ and dried over anhydrous Na_2SO_4,
(ii) Filtered the reaction mixture through a pad of celite, eluted with hexane and
(iii) Filtered the reaction mixture through a pad of celite, eluted with methanol.

Finally, the products were analyzed by GC and ethyl benzene was used as internal standard.

C: Effect of amount of catalyst

Effect of amount of catalyst was observed by varying 0.0100, 0.0250 and 0.0500 g.

D: Effect of amount of substrate

Effect of amount of substrate was observed by varying 2, 5, and 10 mmol.

E: Effect of temperature

Effect of temperature was observed by varying 50, 60 and 70 °C.

F :Effect of hydrogen pressure

Effect of hydrogen pressure was investigated by varying 3, 6 and 9 atm.

G: Effect of reaction time

Effect of reaction time was observed by varying time: 1-4 hours.

3.10   Recycling of catalyst[28]

After being used in cyclooctene hydrogenation, the polystyrene supported cobalt catalyst was separated from the reaction mixture by filtration, washed with methanol and dried in vacuum at 70 °C for 12 hours. Then it was reused for hydrogenation of cyclooctene at the same condition of fresh catalyst.

3.11   Test of catalyst leaching of metal from polystyrene support.[28]

In order to study metal leaching in polystyrene supported cobalt catalysts, the catalyst (0.03 g) was stirred and refluxed in 10 ml methanol for 24 hours. Then, it was filtered, washed with methanol and dried in vacuum at 70 °C for 12 hours. Finally, it was used for hydrogenation of cyclooctene at the same condition of fresh catalyst.

CHAPTER IV

RESULTS AND DISCUSSION

4.1   Anchoring ligand to polystyrene supports

4.1.1   Polystyrene containing Schiff base ligands

In the preparation of polystyrene anchoring Schiff base ligands, 5% crosslink poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) was oxidized by using DMSO and NaHCO$_3$ at 155 °C to an aldehydic functionality[18] as shown in equation (4.1).

$$\text{PS} - \bigcirc - CH_2Cl \xrightarrow[\text{NaHCO}_3]{\text{DMSO}} \text{PS} - \bigcirc - CHO \qquad (4.1)$$
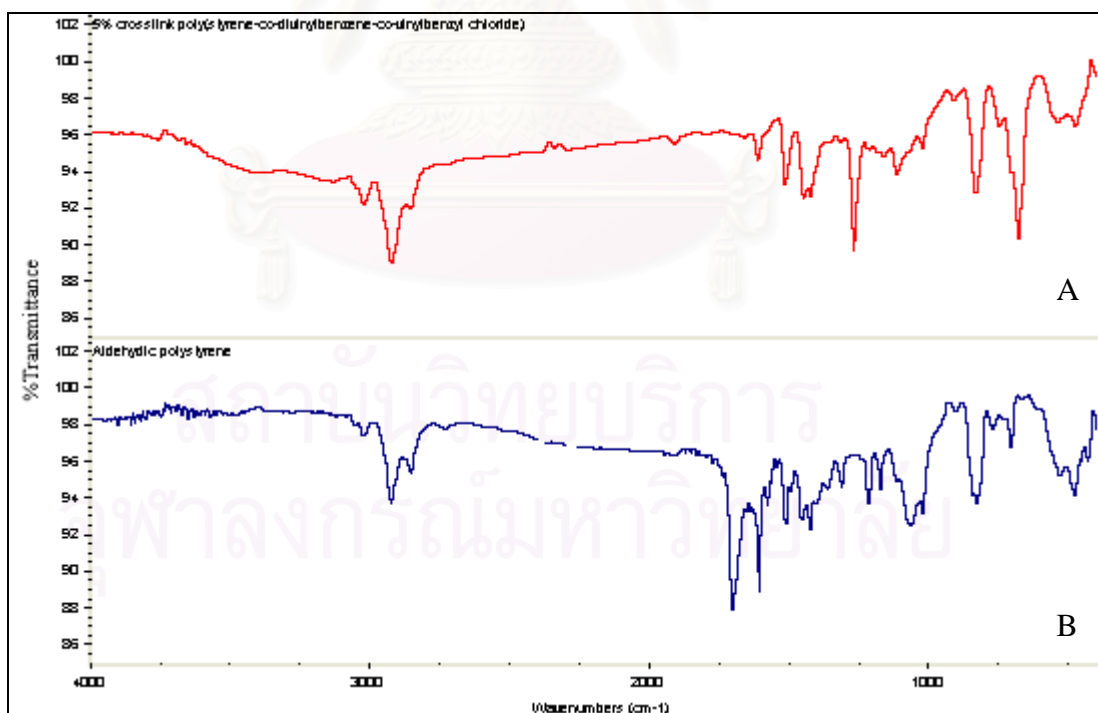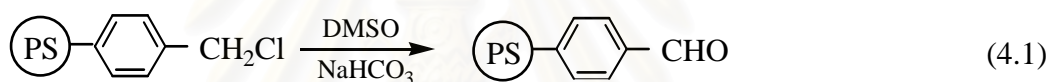
Figure 4.1 The FT-IR spectra of 5% crosslink poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) (A) and aldehydic polystyrene (B)

FT-IR Spectra of 5% crosslink poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) and aldehydic polymers are shown in figure 4.1.

The polystyrene support in figure 4.1 (A), the C-H aliphatic stretching peak appeared around 2950-2900 cm^{-1} and aromatic stretching peaks between 1600-1500 cm^{-1} from the styrene/divinylbenzene support provided a standard and were used for comparing the spectra of the supported ligands.

In figure 4.1 (B), the aldehydic polymer shows the absorption peaks different from the starting polystyrene beads, appeared medium absorption peaks at 2850 cm^{-1} assigned to C-H aliphatic stretching vibration of aldehyde and the new peak at 1694 cm^{-1} assinged to C=O stretching vibration of aromaic aldehyde.

After that the aldehydic polystyrene beads were refluxed with 1,3-diaminopropane (L$_1$), glycine (L$_2$), triethylenetetramine (L$_3$) and 2-aminopyridyl (L$_4$) ligands in dry methanol, the possible structures of the resulting polystyrene bound Schiff base ligand are shown in equations (4.2) - (4.5).

$$\text{(PS)} \diagup\!\!\!\diagdown \text{— CHO} \xrightarrow[\text{MeOH}]{\text{1,3 diaminopropane}} \text{(PS)} \diagup\!\!\!\diagdown \text{—CH=N} \quad NH_2 \tag{4.2}$$

P-L$_1$
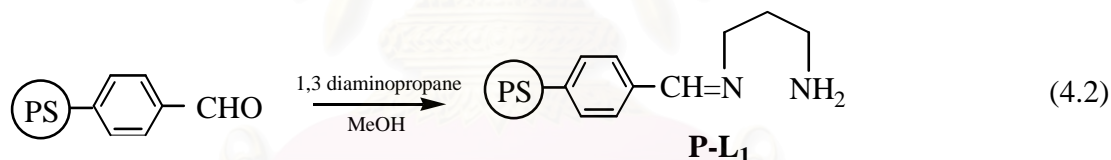
Polystyrene bound Schiff base 1,3-diaminopropane [pale yellow]

$$\text{(PS)} \diagup\!\!\!\diagdown \text{— CHO} \xrightarrow[\text{MeOH}]{\text{glycine}} \text{(PS)} \diagup\!\!\!\diagdown \text{—CH=N-CH}_2\text{-COOH} \tag{4.3}$$

P-L$_2$
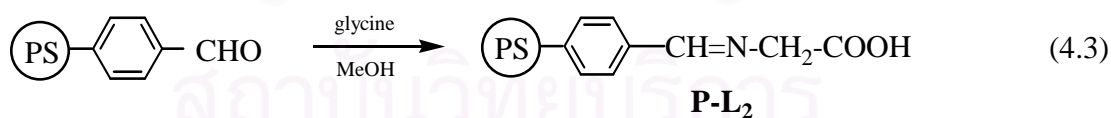
Polystyrene bound Schiff base glycine [pale yellow]

$$\text{(PS)} \diagup\!\!\!\diagdown \text{—CHO} \xrightarrow[\text{MeOH}]{\text{trimethylenetetramine}}$$

$$\text{(PS)} \diagup\!\!\!\diagdown \text{— CH=N-(CH}_2)_2\text{NH-(CH}_2)_2\text{NH(CH}_2)_2\text{NH}_2 \tag{4.4}$$
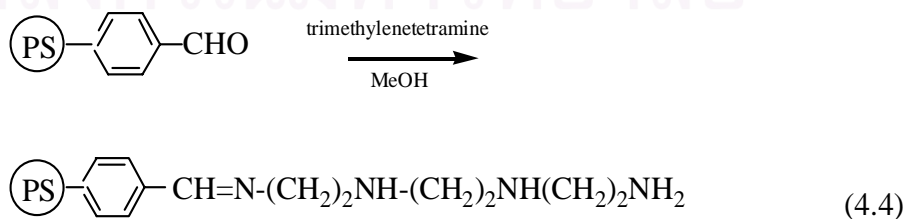
P-L$_3$

Polystyrene bound Schiff base triethylenetetramine [pale yellow]

(4.5)
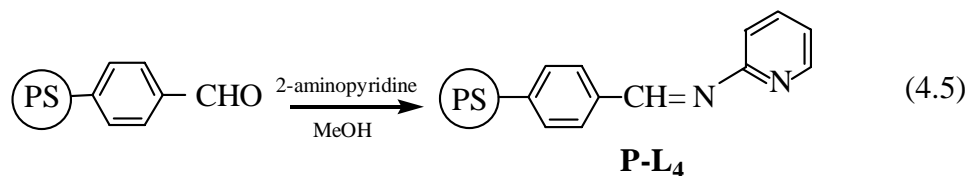
Polystyrene bound Schiff base 2-aminopyridyl [pale yellow]

The FT-IR spectra of polystyrene bound Schiff base ligands P-L$_1$ to P-L$_4$ exhibited the characteristic absorption peaks, as presented in figures 4.2(A)-4.5(A) and summarized in table 4.1.

Table 4.1 The assignment for the FT-IR spectra of P-L$_1$ to P-L$_4$

Wave number (cm^{-1})				Assignment
P-L$_1$	P-L$_2$	P-L$_3$	P-L$_4$	
3400-3300	3600-3300	3400-3300	3400-3300	O-H st., N-H st.
3019	3014	3013	3015	C-H aromatic st.
-	1766	-	-	C=O st.
1641	1694	1647	1648	C=N st.
-	-	-	1514, 769	Pyridine ring
697	697	672	672	C-Cl st.

For P-L$_1$ spectra, the broad band appeared around 3400-3300 cm^{-1} was assigned to the N-H stretching vibration of amine group. The formation of the Schiff base on the polystyrene support was indicated by a strong band appearing at 1641 cm^{-1} assigned to the C=N stretching vibration.

For P-L$_2$ the absorption peak appeared at 1694 cm^{-1} was assinged to the C=N stretching vibration, and the strong peak at 1766 cm^{-1} was assigned to the C=O stretching vibration from glycine ligand. These evidences indicating that the chloride group on polystyrene support was replaced by the amine group from the ligands.

For P-L$_3$, the broad absoprtion peak appeared around 3400-3300 cm^{-1} was assigned to the N-H stretching vibration of an amine group from triethylenetetramine ligand. The formation of the imine group on the polystyrene support was indicated by a new strong band appeared at 1647 cm^{-1} assigned to C=N stretching vibration.

Finally, for P-L$_4$ the strong absorption peaks appeared at 1514 and 769 cm^{-1} was assigned to the pyridyl ring stretching vibration indicating that the chloride group was replaced by the amine group from the ligands. The C-Cl stretching vibration of all polystyrene supported ligands appeared around 697-672 cm^{-1}, indicated that some chlorides were still remained.[39-40]

4.1.2 Polystyrene anchoring sequencial Schiff base ligands and other ligands

The polystyrene anchoring with 2-aminopyridyl (P-L$_5$) 1,3-diaminopropane Schiff base salicyldehyde (P-L$_6$), 4-hydroxybenzaldehyde Schiff base 2-aminopyridyl (P-L$_7$), picolinate (P-L$_8$) and 8-quinolinate (P-L$_9$) ligands, were prepared and the possible structures are shown in equations (4.6) – (4.12).

The FT-IR spectra of polystyrene bound P-L$_5$ to P-L$_9$ exhibited the characteristic absorption peaks, as presented in figures 4.11(A)-4.15(A) and summarized in table 4.2.

(4.6)
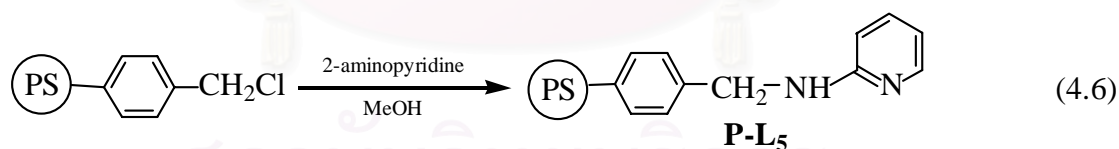
Polystyrene bound 2-aminopyridyl ligand [white]

(4.7)

(4.8)
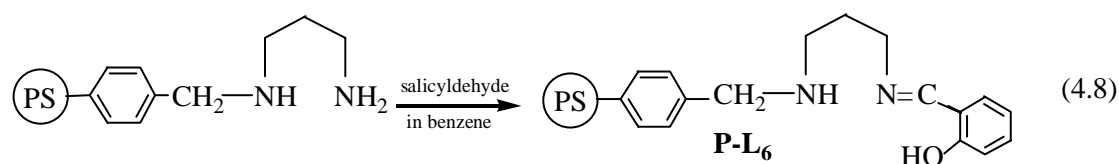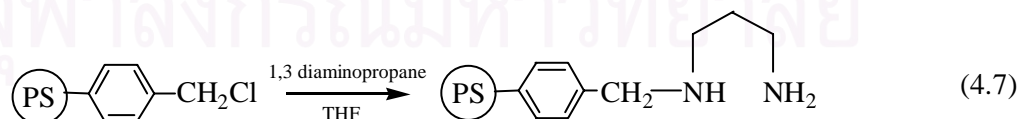
Polystyrene bound 1,3 diaminopropane Schiff base salicyldehyde [orange]

(4.9)

(4.10)
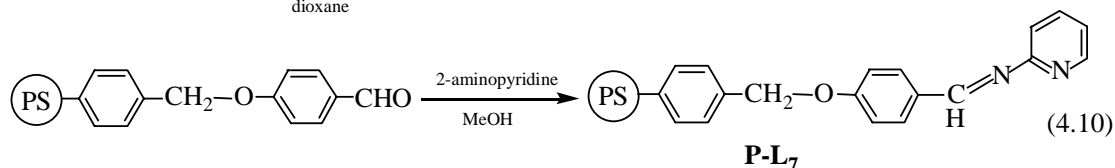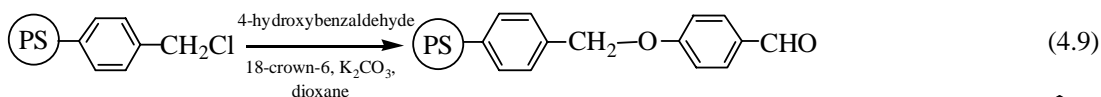
Polystyrene bound 4-hydroxybenzaldehyde Schiff base 2-aminopyridyl [cream]

(4.11)
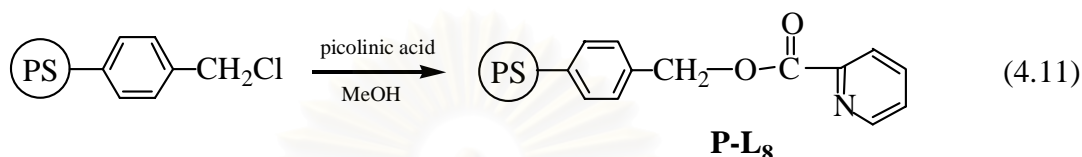
Polystyrene bound picolinate [white]

(4.12)
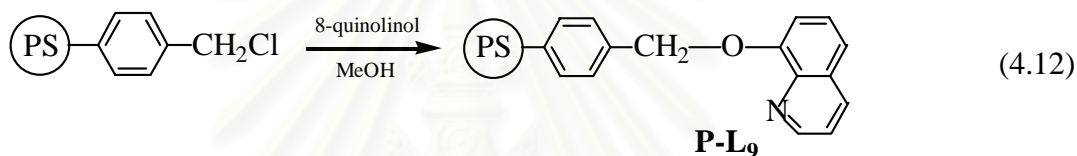
Polystyrene bound 8-quinolinate [white]

Table 4.2 The assignment for the FT-IR spectra of P-L$_5$ to P-L$_9$

Wave number (cm^{-1})					Assignment
P-L$_5$	P-L$_6$	P-L$_7$	P-L$_8$	P-L$_9$	
3400-3200	3600-3200	-	3600-3300	3600-3300	O-H, N-H st.
3108	3019	3019	3014	3013	C-H aromatic st.
-	-	-	1724	-	C=O st.
-	1641	1641	1650	1658	C=N st.
1157	1217	-	-	-	C-N st.
-	1118	1108	1093	1098	C-O st.
1514, 769	-	1509, 769	1504, 749	1509, 754	Pyridine ring
672	697	646	682	672	C-Cl st.

For P-L$_5$, appeared a medium peak at 1157 cm^{-1} assigned the C-N stretching vibration, indicated that chloride group on polystyrene was replaced by aminopyridyl ligand. The broad band appeared around 3400-3200 cm^{-1} assigned to the N-H stretching vibration of amine group and the strong peaks appeared at 1514 and 769

cm^{-1} assigned to pyridyl ring from the ligand. These evidences indicated that ligand was chemically linked to the support.

For P-L$_6$, FT-IR spectrum broad band around 3600-3200 cm^{-1} due to the presence of N-H and O-H groups from 1,3-diaminopropane and salicyldehyde ligands. A medium band appeared around 1118 cm^{-1} indicated the C-O stretching vibration. The subsequent reaction of aldehyde with and amine group produces a peak at 1641 cm^{-1} corresponding to the stretching vibration of the iminic C=N.

For P-L$_7$, the absorption peak at 1641 cm^{-1} indicated the existence of the imine group in the polystyrene bound ligands which was also observed for P-L$_6$. A medium peak at 1108 cm^{-1} was assigned to C-O stretcing vibration. The strong peaks at 1509 and 769 cm^{-1} were assigned to pyridyl ring from the ligand. These evidences indicated that the ligand was chemically linked to the support.

For P-L$_8$ and P-L$_9$, the absorption around 1098-1093 cm^{-1} was assigned to the C-O stretching vibration. For P-L$_8$ the peak at 1724 cm^{-1} was assinged to C=O stretching vibration. The strong peaks at 1509-1504 and 754-749 cm^{-1} were assigned to pyridyl ring from the ligands. These results indicated that the chloride group on polystyrene was replaced by amine and hydroxyl groups from the ligands.

Finally, the C-Cl stretching vibration of all polystyrene bound ligands were presented around 697-646 cm^{-1}, indicating the remaining unreacted chloride. It should be mentioned that from XRF technique, about 0.08 mmol of chloride were present in P-L$_7$, starting from 5.5 mmol of chloride in the original polystyrene. This indicated that the remaining 0.3% of unreacted chloride agreed with the FT-IR data shown table 4.2. This similar observation has also been made previously.[39]

4.2 Preparation of polystyrene supported cobalt catalysts

The FT-IR spectra of poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) anchoring Schiff base 1,3-diaminopropane cobalt (II) complexes, P-L$_1$-CoCl$_2$ and P-L$_1$-Co(OAc)$_2$ exhibited the characteristic absorption peaks, are presented in figure 4.2 and table 4.3.
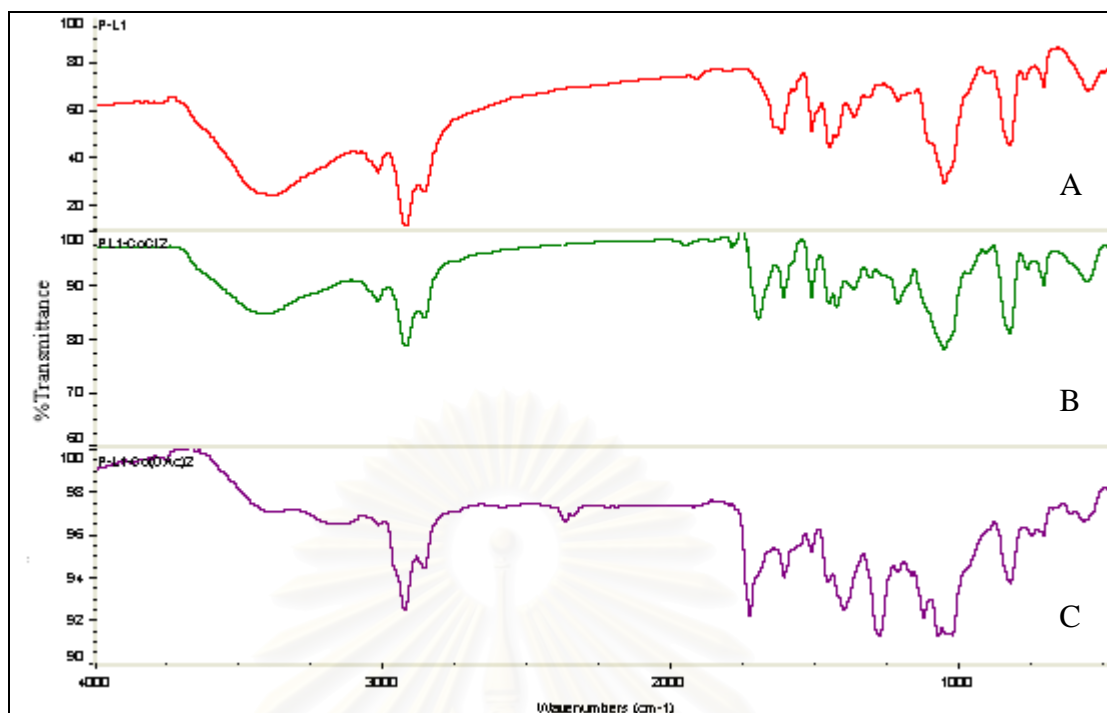
Figure 4.2 The FT-IR spectra of P-L$_1$ (A), P-L$_1$-CoCl$_2$ (B) and P-L$_1$-Co(OAc)$_2$ (C)

Table 4.3 The assignment for the FT-IR spectra of P-L$_1$-CoCl$_2$ and P-L$_1$-Co(OAc)$_2$

Wave number (cm^{-1})		Assignment
P-L$_1$-CoCl$_2$	P-L$_1$-Co(OAc)$_2$	
3300-3200	3300-3200	N-H st.
3019	3019	C-H aromatic st.
-	1730	C=O st.
1614	1639	C=N st.
697	697	C-Cl st.

These catalysts showed N-H stretching vibration around 3300-3200 cm^{-1} and C=N stretching vibration of imine group around 1639-1614 cm^{-1}. For P-L$_1$-Co(OAc)$_2$, appeared the new absorption peak at 1730 cm^{-1} that corresponds to the C=O stretching vibration, this peak belongs to acetate group from cobalt complex. The wave number of N-H and C=N streching vibration are shifted to lower frequency compared with the free ligand (N-H st. 3400-3300 and C=N st. 1641 cm^{-1}), from these evidences can be concluded that coordination of the polystyrene bound ligand to the cobalt complex occurred.[40-41]

The possible structures of these two catalysts are proposed as shown in figures 4.3 and 4.4.
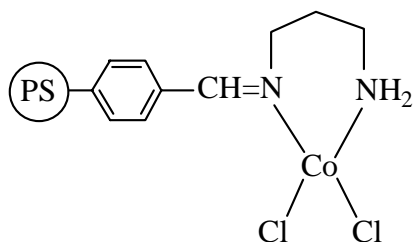
Figure 4.3 Polystyrene bound Schiff base 1,3-diaminopropane cobalt (II) chloride, P-L$_1$-CoCl$_2$ [light blue]
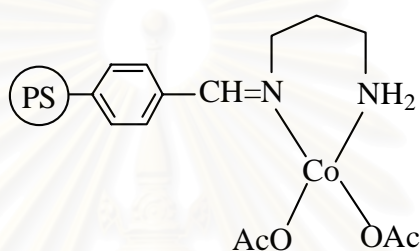
Figure 4.4 Polystyrene bound Schiff base 1,3-diaminopropane cobalt (II) acetate, P-L$_1$-Co(OAc)$_2$ [light gray]

In addition, the other ligands were used to make poly(styrene-co-divinylbenzene-co-vinylbenzyl chloride) anchoring Schiff base, they are: glycine, triethylenetetramine and 2-aminopyridine. Each ligand was reacted with cobalt (II) chloride to form polystyrene supported cobalt catalysts.

The FT-IR spectra of polystyrene supported cobalt (II) chloride complexes, P-L$_2$-CoCl$_2$ to P-L$_4$-CoCl$_2$ are shown in figures 4.5(B)-4.7(B) and the characteristic absorption peaks are summarized in table 4.4.
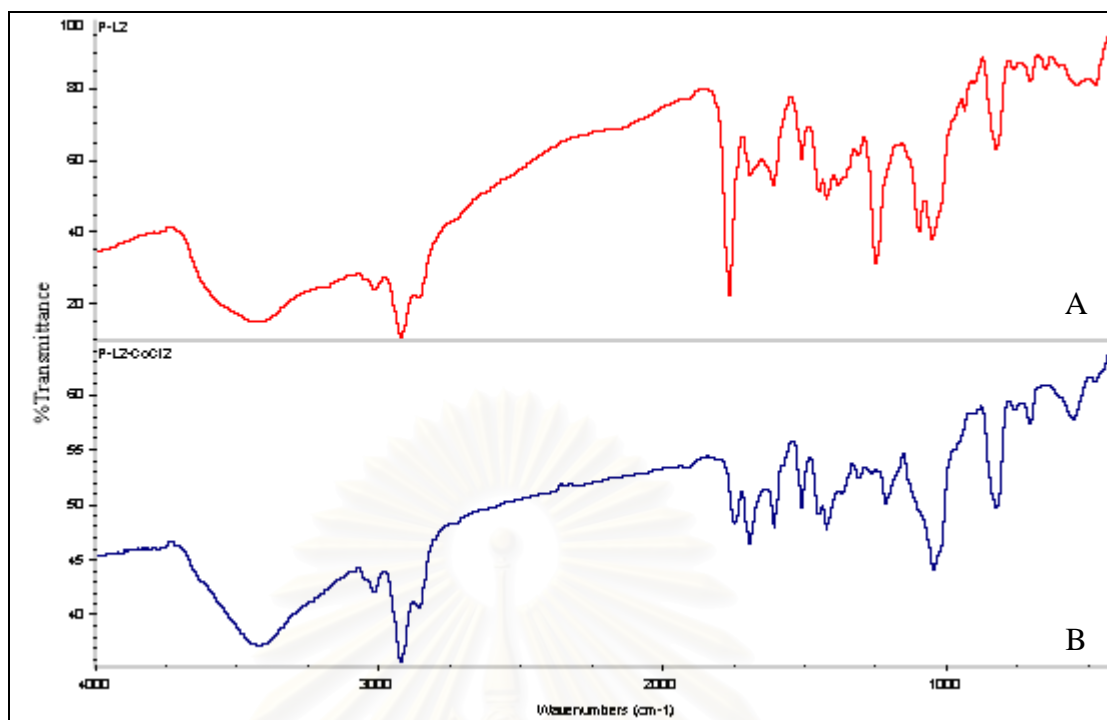
Figure 4.5 FT-IR spectra of P-L$_2$ (A) and P-L$_2$-CoCl$_2$ (B)
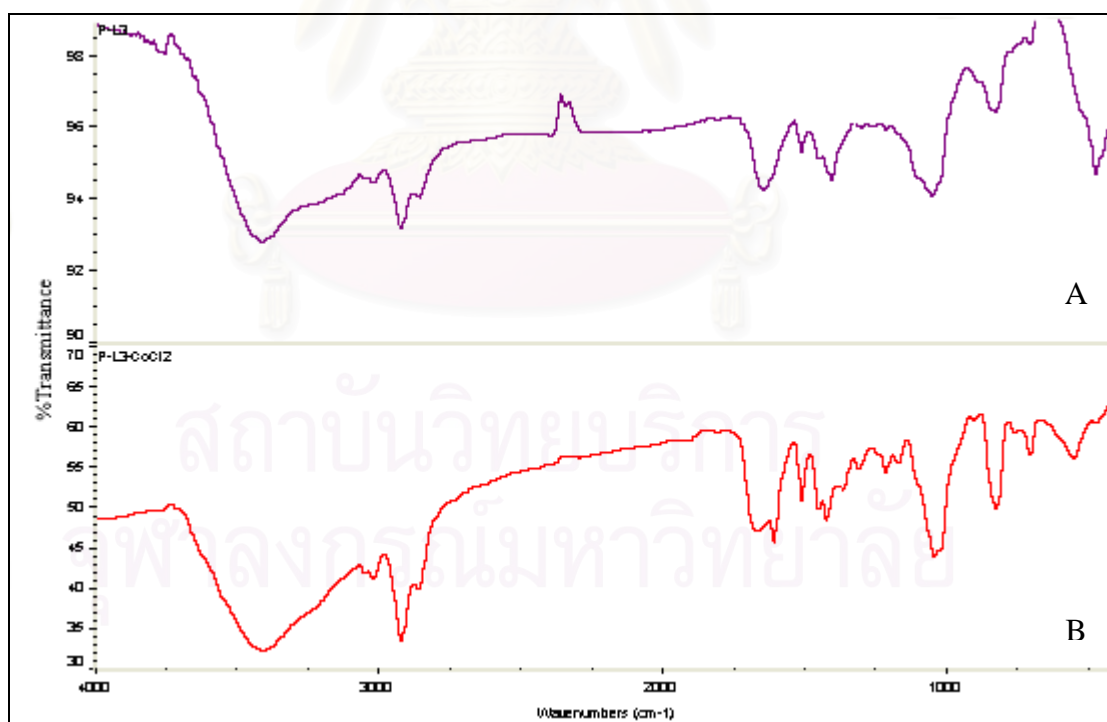
Figure 4.6 FT-IR spectra of P-L$_3$ (A)and P-L$_3$-CoCl$_2$ (B)
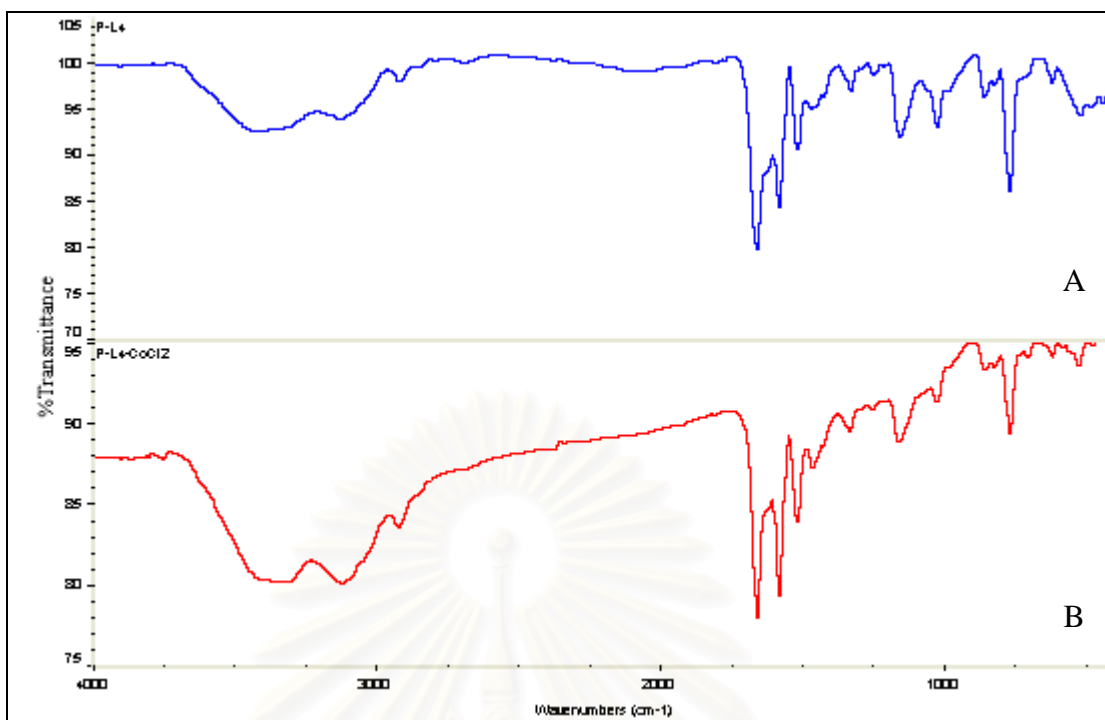
Figure 4.7 FT-IR spectra of P-L$_4$ (A) and P-L$_4$-CoCl$_2$ (B)

Table 4.4 The assignment for the FT-IR spectra of polystyrene supported cobalt (II) chloride complexes, P-L$_2$-CoCl$_2$ to P-L$_4$- CoCl$_2$.

Wave number (cm^{-1})			Assignment
P-L$_2$-CoCl$_2$	P-L$_3$- CoCl$_2$	P-L$_4$- CoCl$_2$	
3600-3200	3400-3300	3400-3300	O-H ,N-H st.
3013	3013	3015	C-H aromatic st.
1755	-	-	C=O st.
1689	1639	1641	C=N st.
-	-	1509,764	Pyridine ring
708	672	672	C-Cl st.

For P-L$_2$-CoCl$_2$, the C=O stretching vibration (from glycine) and C=N stretching vibration (Schiff base ligand) were presented at 1755 and 1689 cm^{-1} (1766 and 1694 cm^{-1} for free ligands), these results indicated that the metal ion was coordinated.

The same results were obtained from P-L$_3$-CoCl$_2$, the N-H stretching vibration (triethylenetetramine ligand) and C=N stretching vibration were appeared around 3400-3300 and 1639 cm^{-1}, respectively (3400-3300 and 1647 cm^{-1} for free ligands).

For P-L$_4$-CoCl$_2$ catalyst the C=N stretching vibration appeared at 1641 cm^{-1} and the pyridyl ring stretching vibration appeared at 1509, 764 cm^{-1}. The shift to lower frequency (1648 and 769 cm^{-1} for free ligands) confirms the coordination of the ligand to the cobalt ion.

The possible structures of P-L$_2$-CoCl$_2$ to P-L$_4$-CoCl$_2$ are proposed as shown in figures 4.8-4.10.
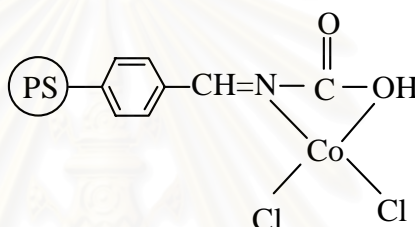
Figure 4.8 Polystyrene bound Schiff base glycine cobalt (II) chloride, P-L$_2$-CoCl$_2$
         [light green]
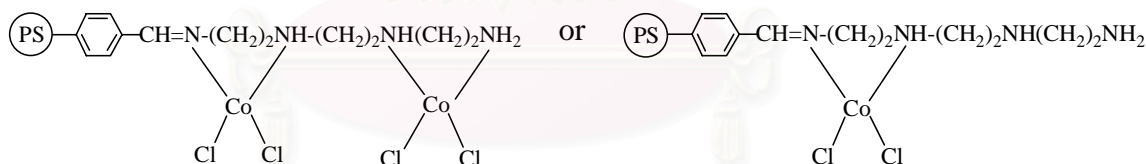
Figure 4.9 Polystyrene bound Schiff base triethylenetetramine cobalt (II) chloride,
         P-L$_3$-CoCl$_2$ [dark green]
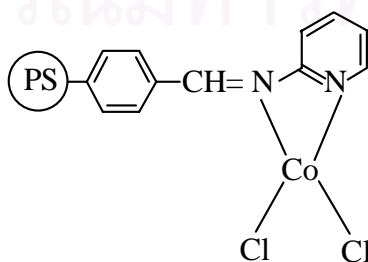
Figure 4.10 Polystyrene bound Schiff base 2-aminopyridyl cobalt (II) chloride,
         P-L$_4$-CoCl$_2$ [light green]

The FT-IR spectra of polystyrene supported cobalt (II) chloride complexes, P-L$_5$-CoCl$_2$ to P-L$_9$-CoCl$_2$ exhibited the characteristic absorption peaks are shown in figure 4.11-4.15 and table 4.5.
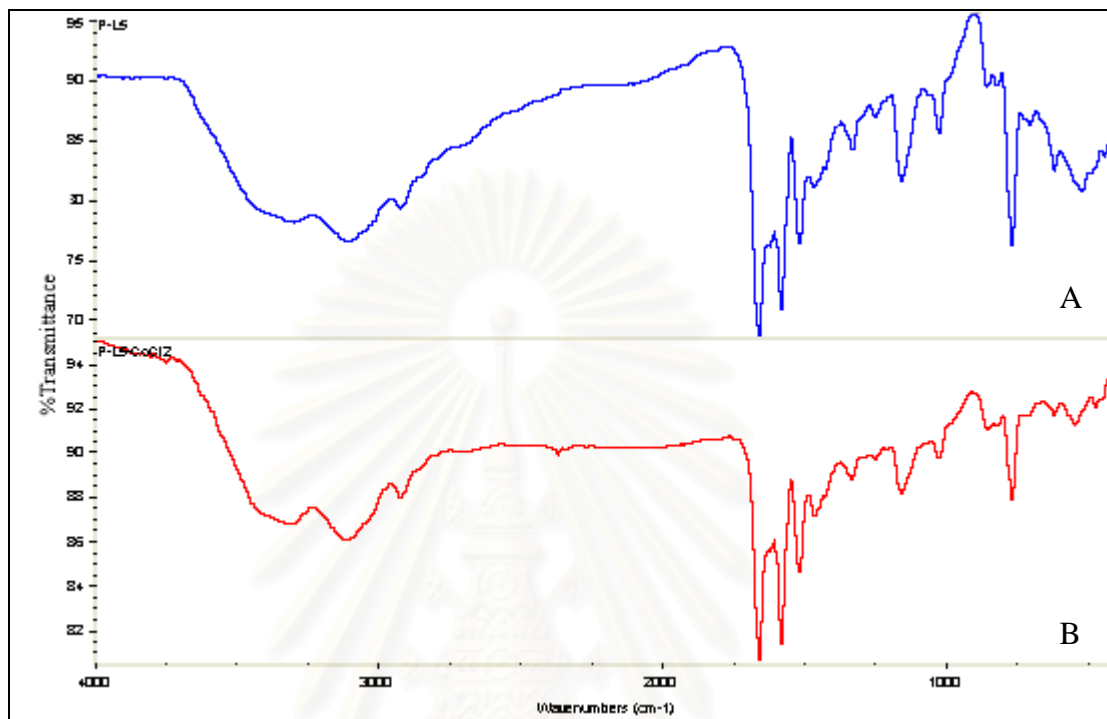
Figure 4.11 FT-IR spectra of P-L$_5$ (A) and P-L$_5$-CoCl$_2$ (B)
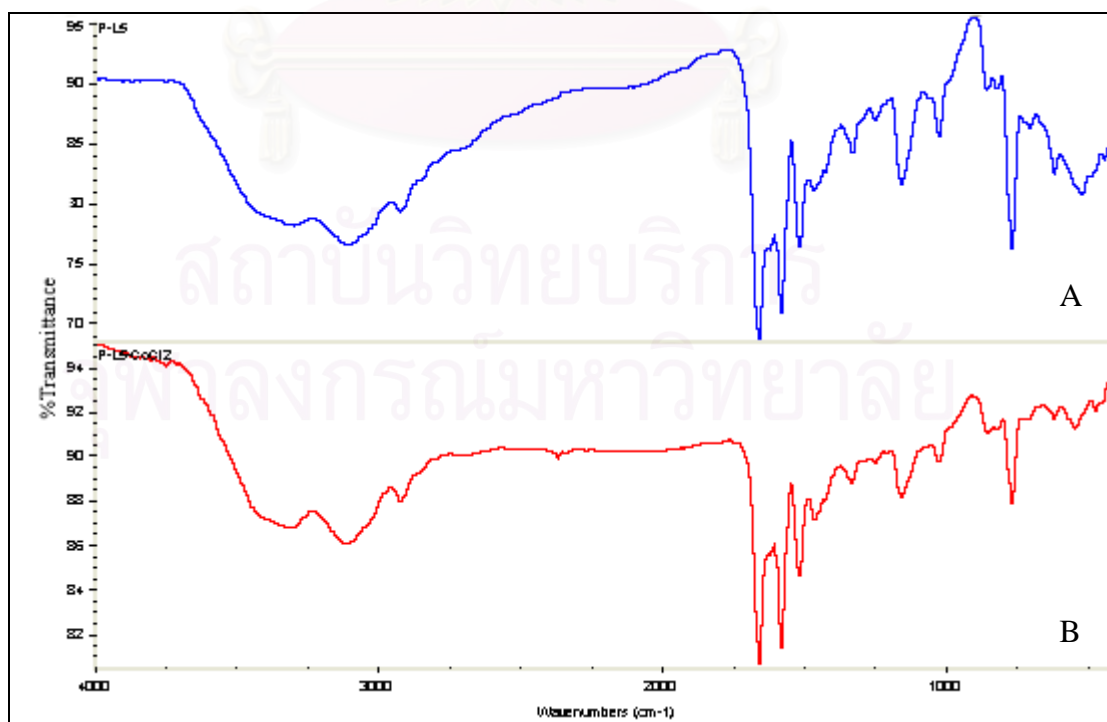
Figure 4.12 FT-IR spectra of P-L$_6$ (A) and P-L$_6$-CoCl$_2$ (B)
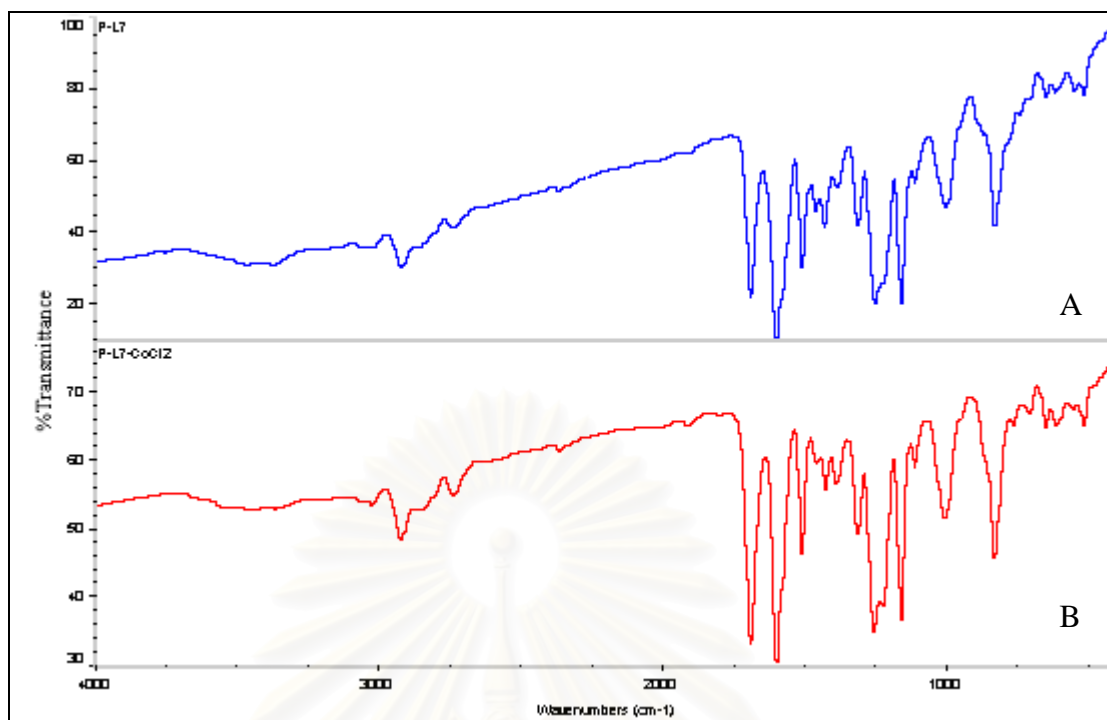
Figure 4.13 FT-IR spectra of P-L$_7$ (A) and P-L$_7$-CoCl$_2$ (B)
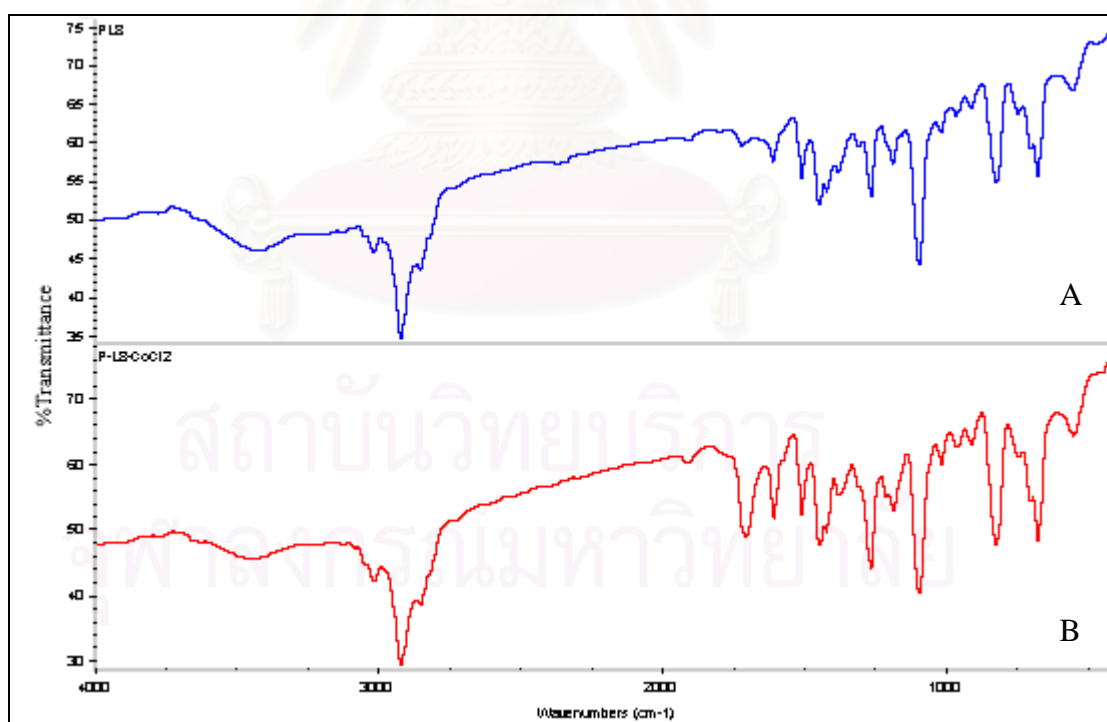
Figure 4.14 FT-IR spectra of P-L$_8$ (A) and P-L$_8$-CoCl$_2$ (B)
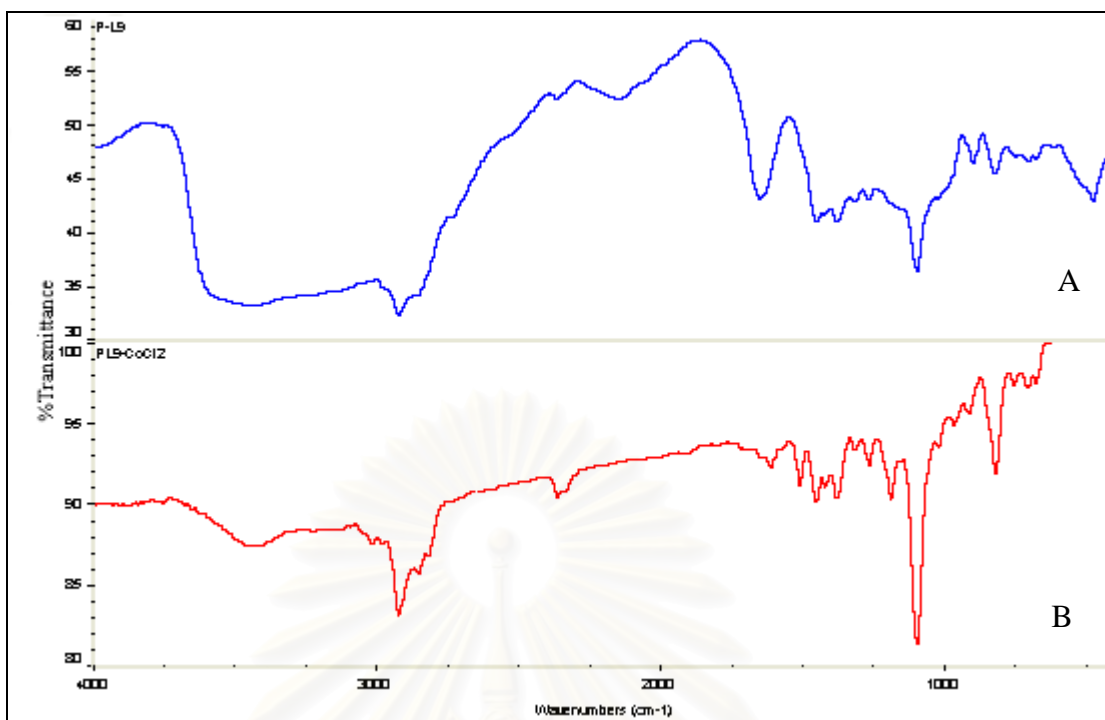
Figure 4.15 FT-IR spectra of P-L$_9$ (A) and P-L$_9$-CoCl$_2$ (B)

Table 4.5 The assignment for the FT-IR spectra of polystyrene supported cobalt (II) chloride complexes, P-L$_5$-CoCl$_2$ to P-L$_9$- CoCl$_2$

Wave number (cm^{-1})					Assignment
P-L$_5$- CoCl$_2$	P-L$_6$- CoCl$_2$	P-L$_7$- CoCl$_2$	P-L$_8$- CoCl$_2$	P-L$_9$- CoCl$_2$	
3400-3200	3600-3200	-	3600-3300	3600-3300	O-H, N-H st.
3108	3019	3019	3014	3013	C-H aromatic st.
-	-	-	1704	-	C=O st.
-	1635	1634	1630	1650	C=N st.
1157	-	-	-	-	C-N st.
-	1010	1001	1094	1081	C-O st.
1514, 764	-	1509, 759	1509, 744	1509, 749	Pyridine ring
672	697	646	672	672	C-Cl st.

For P-L$_5$-CoCl$_2$, the N-H stretching vibration and pyridyl ring stretching vibration appeared at 3350 and 1514, 749 cm^{-1} which were lower than those in the free ligands (at 3395 and 1514, 769 cm^{-1}), indicated that the metal ion was coordinated.

In the case of Schiff base bearing polystyrene, P-L$_6$-CoCl$_2$ and P-L$_7$-CoCl$_2$, a strong band of C=N stretching vibration shifted to lower frequency at around 1635-1634 cm^{-1} (1641 cm^{-1} for free ligands), indicated that the metal ion was coordinated.

For P-L$_8$-CoCl$_2$, the C=O stretching vibration and pyridyl ring stretching vibration shifted to lower frequency 1704 and 1509, 744 cm^{-1} (1724 cm^{-1} and 1504, 749 for free ligand), indicated that the metal ion was coordinated.

For P-L$_9$-CoCl$_2$, the C-O stretching vibration and pyridyl ring stretching vibration appeared at 1081 and 1509, 749 cm^{-1}, undergoes a lower shift from free ligands (1098 and 1509, 754 cm^{-1}, respectively). These results revealed the coordination of the ligand to the cobalt ion.

The possible structures of P-L$_5$-CoCl$_2$ to P-L$_9$-CoCl$_2$ are proposed as shown in figures 4.16 - 4.20, respectively.
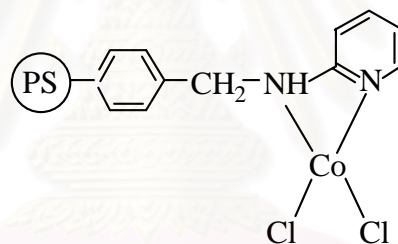
Figure 4.16 Polystyrene bound 2-aminopyridyl cobalt (II) chloride, P-L$_5$-CoCl$_2$
[light blue]
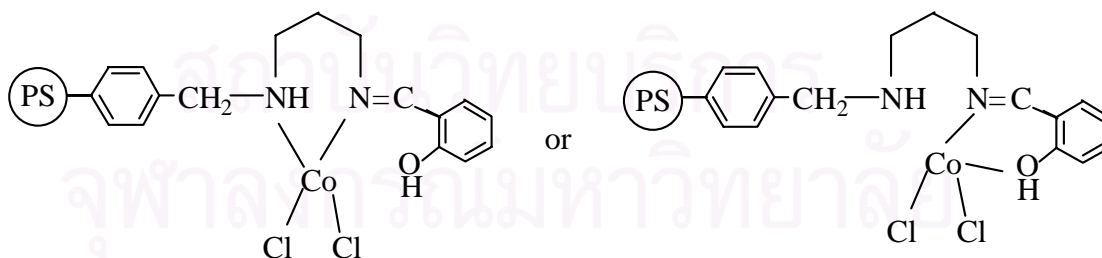
Figure 4.17 Polystyrene bound 1,3-diaminopropane Schiff base salicyldehyde cobalt
(II) chloride, P-L$_6$-CoCl$_2$ [dark green]
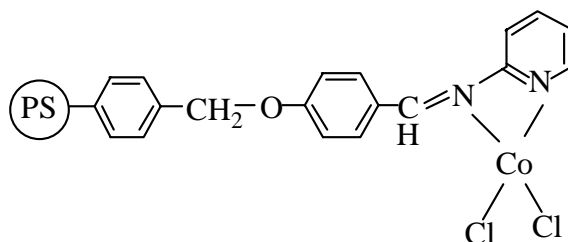
Figure 4.18 Polystyrene bound 4-hydroxybenzaldehyde Schiff base 2-aminopyridyl

cobalt (II) chloride, P-L$_7$-CoCl$_2$ [light blue]
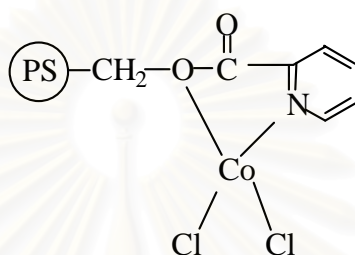
Figure 4.19 Polystyrene bound picolinate cobalt (II) chloride, P-L$_8$-CoCl$_2$ [light blue]
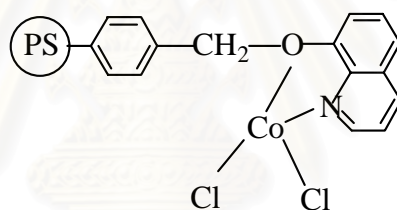
Figure 4.20 Polystyrene bound 8-quinolinate cobalt (II) chloride, P-L$_9$-CoCl$_2$

[light green]

In summary, it can be proposed according to spectroscopic data and related
literature that cobalt complexes are mononuclear (in some complexs, however,
dinuclear cannot be ruled out) with tetrahedral coordination about Co (II) with
chelating ligand through nitrogen and/or oxygen atoms.

Table 4.6 Cobalt content in the polystyrene supported cobalt catalysts

Entry	Catalyst	%Cobalt by XRF technique	%Cobalt by AAS technique
1	P-L$_1$-CoCl$_2$	0.29	0.21
2	P-L$_9$-CoCl$_2$	0.39	0.37

Both AAS and XRF techniques gave similar cobalt content, with a slightly lower content in AAS. Therefore, only AAS technique was chosen for determination of all catalysts.

Table 4.7 Cobalt content in the polystyrene supported cobalt catalysts by AAS technique

Entry	Catalyst	%Cobalt
1	P-L_1-CoCl$_2$	0.21
2	P-L_1-Co(OAc)$_2$	1.12
3	P-L_2-CoCl$_2$	0.20
4	P-L_3-CoCl$_2$	2.19
5	P-L_4-CoCl$_2$	0.64
6	P-L_5-CoCl$_2$	0.15
7	P-L_6-CoCl$_2$	1.76
8	P-L_7-CoCl$_2$	0.77
9	P-L_8-CoCl$_2$	0.36
10	P-L_9-CoCl$_2$	0.37

In this experiment, all of polystyrene supported ligands were loaded with the same condition. The metal analysis by using AAS technique was shown that for the non-Schiff base ligand catalyst, P-L_5-CoCl$_2$ had the lower cobalt content than P-L_4-CoCl$_2$, it seems that Schiff base ligand coordinates with metal better than non-Schiff base ligand.

The relationships between high cobalt content and more donor atoms was observed in P-L_3-CoCl$_2$ and P-L_6-CoCl$_2$ which may be possibly due to these two catalysts had more donor atoms.

4.3 Homogeneous catalyst

In order to estimate and compare the relative catalytic efficiency between the heterogeneous catalyst and homogeneous catalyst, we choose one homogeneous cobalt catalyst for the study.

Cobalt complex with picolinate ligand was prepared as shown in equation (4.13).

$$2 \underset{N}{\bigcirc}\text{COOH} + 2.5\ \text{NaOH} \xrightarrow{\text{EtOH}} \underset{N}{\bigcirc}\text{COO}^-\ ^+\text{Na} \xrightarrow[\substack{1\text{equiv.}\\ \text{CoCl}_2.6\text{H}_2\text{O}}]{\text{EtOH}} \text{Co(II)(pic)}_2\text{Cl}_2 \quad (4.13)$$
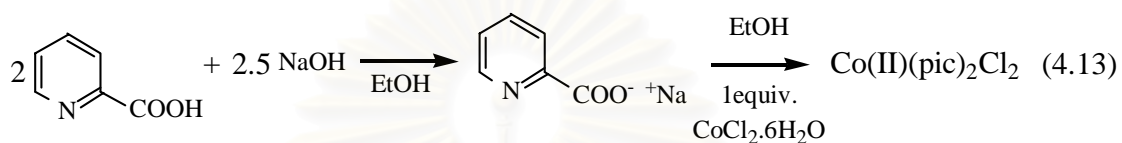
It was characterized by FT-IR. The spectrum and assignment of peaks were shown in figure 4.21 in table 4.8.
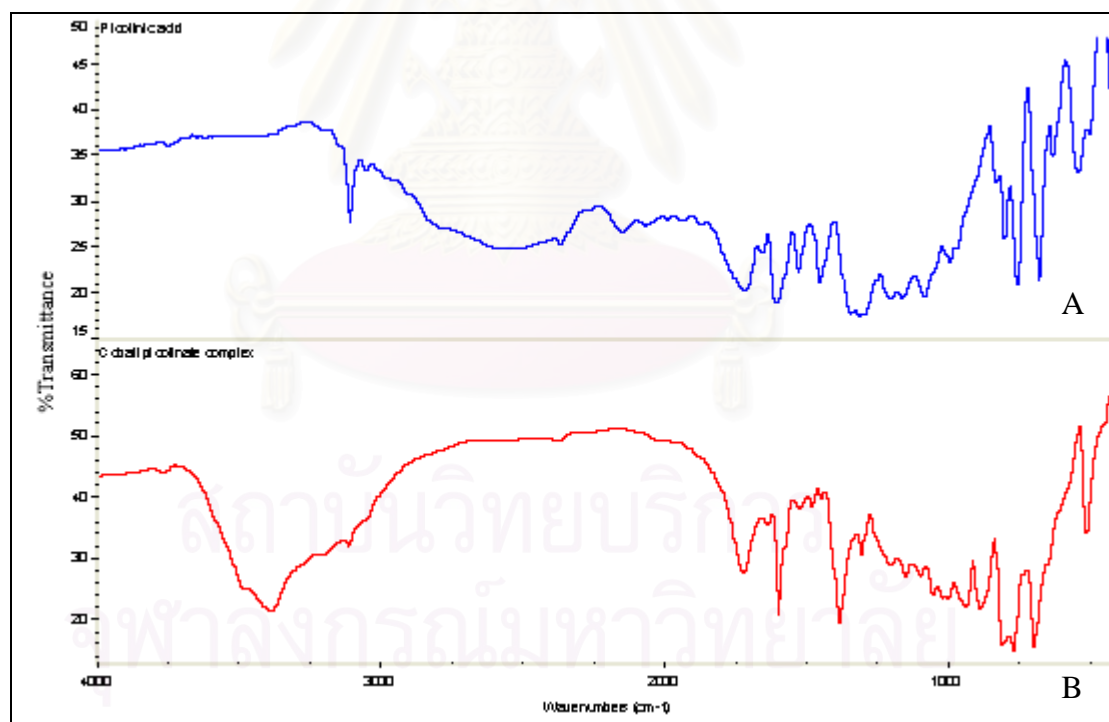
Figure 4.21 The FT-IR spectra of picolinic acid (A)and cobalt picolinate complex (B)

Table 4.8 The assignment for the FT-IR spectra of picolinic acid and cobalt picolinate

Wave number (cm^{-1})		Assignment
Free ligand	Complexe	
3040	3040	C-H aromatic st.
1714	1720	C=O st.
1522, 748	1524, 750	Pyridine ring

For the free ligand, the sharp peak at 3100 cm^{-1} was due to the single hydroxyl group on the carboxylic acid group and broad absorption peaks around 2600-2400 cm^{-1} were due to carbonyl C-C=O group of the pure ligand. For the cobalt picolinate complex no such peaks were observed. The C-H aromatic stretching of free ligand and complex appeared around 3040 cm^{-1}. The strong absorption peaks 1500 and 700 cm^{-1} were due to the pyridine rings which were slightly shifted to higher frequency upon complexation. The C=O stretching vibration peak was shifted from 1714 to 1720 cm^{-1}, due to the coordination to the metal ions,. These evidences revealed the coordination of the ligand to the cobalt ion.[35-36]

4.4 Thermal stability of polystyrene supported cobalt catalysts

For comparison, the thermal stabilities of crosslinked polystyrenes with different crosslinking degrees were displayed in figure 4.22. The results indicated a single step degradation of crosslinked polystyrenes in the 422-454 °C temperature range.[17,41]
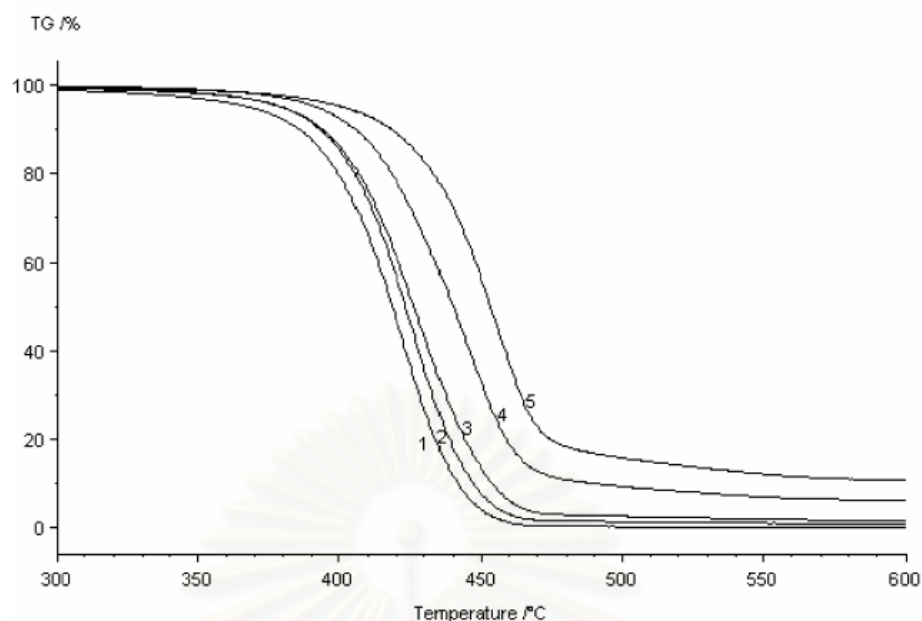
Figure 4.22 The thermogravimetric curves of five crosslinked polystyrene with difference crosslinking degree (1, 6%; 2, 10%; 3, 15%; 4, 30% and 5, 56%)[17]

To show the thermal stability of the prepared catalysts, some representative polystyrene supported catalysts were measured with TGA shown in figures 4.23 and figure 4.24.
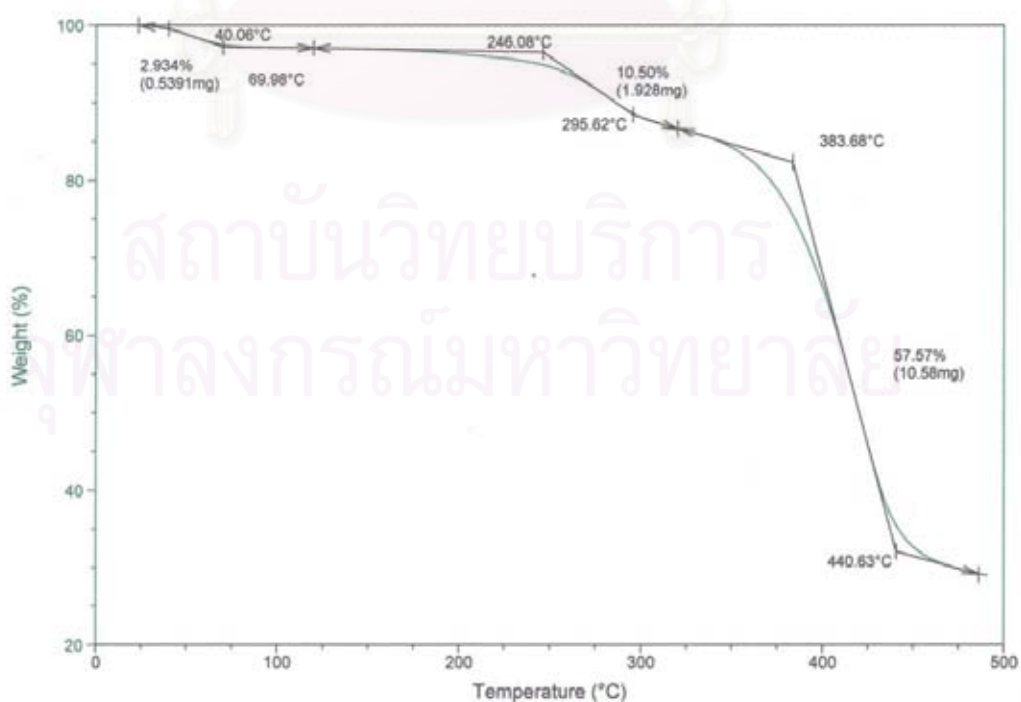
Figure 4.23 The thermogravimetric curves of P-L$_4$-CoCl$_2$
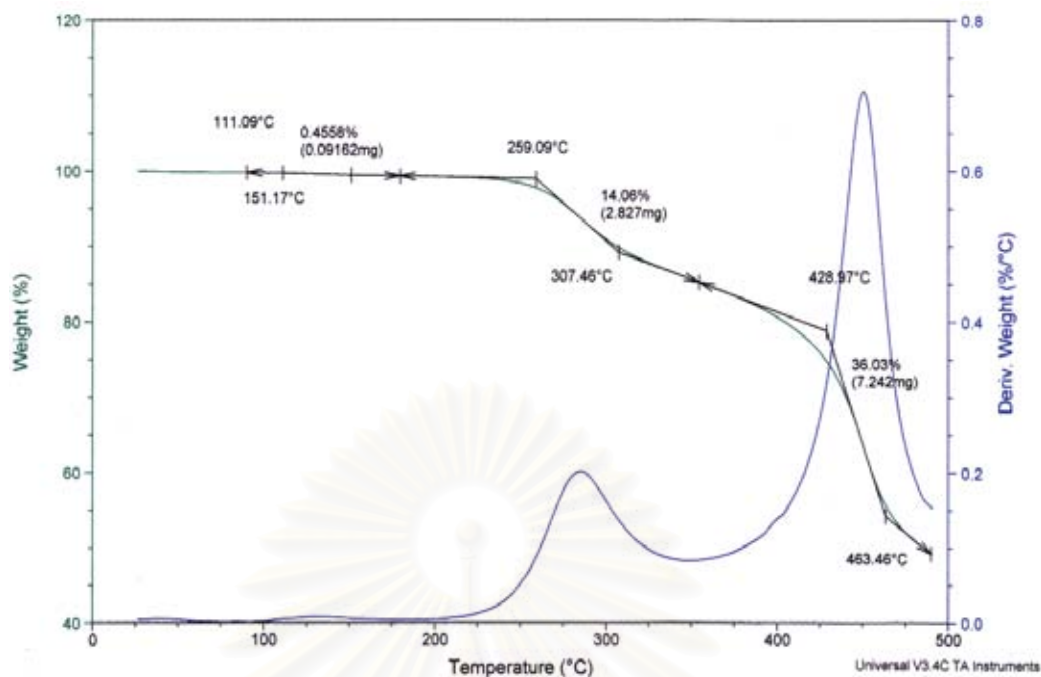
Figure 4.24 The thermogravimetric curves of P-L$_7$-CoCl$_2$

Table 4.9 The thermogravimetric data of P-L$_4$-CoCl$_2$ and P-L$_7$-CoCl$_2$

Sample	Degradation temp. (^{o}C)	Weight loss (%)
P-L$_4$-CoCl$_2$	440	57
	246	10
P-L$_7$-CoCl$_2$	428	36
	259	14

From figures 4.23 and 4.24, it was found that the polystyrene supported catalysts undergo degradation in many steps:

(1) at ~ 100 ^{o}C due to loosely bound surface moisture or volatiles on the surface of catalysts.

(2) at around 240-260 ^{o}C, weight loss of about 10-14 %, the ligands and the chlorides might dissociate from the catalyst surface, such a degradation profile was not seen in the starting polymer (figure 4.22).

(3) at above 430 ^{o}C, weight loss of about 36-57%, decomposition of polymer support.

4.5   Swelling test

The role of the solvent is one of the foremost factors affecting the reaction. In immobilized systems, the solvent causes support swelling and chain flexibility. Swelling in different solvent was performed using representative chosen catalyst, P-L_4-$CoCl_2$, the results were shown in figure 4.25.
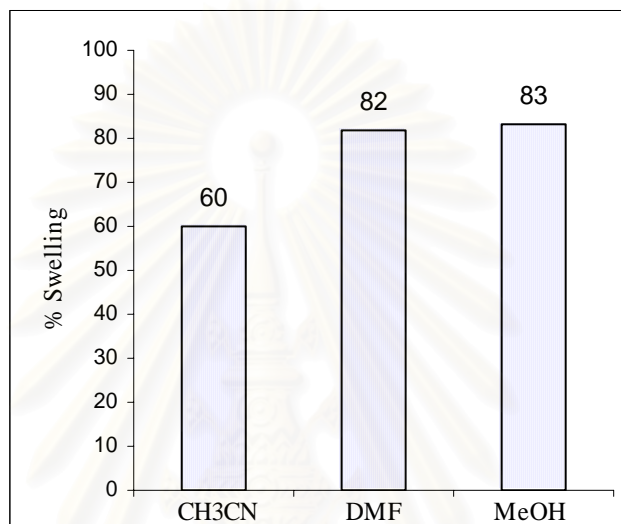
Figure 4.25 Percent swelling of catalyst in some solvents

It was indicated that the polystyrene supported catalyst swells more in both methanol and dimethylformamide, these may be due to the hydrophobic nature of polystyrene support.[13] This result is good agreement with previous report,[25,26] for polystyrene as a support shown the highest swelling in methanol among the other organic solvents, a decrease in swelling was observed as the nature of the solvent was changed from polar to non-polar.

4.6   Cyclooctene hydrogenation with heterogeneous catalysts

4.6.1   Hydrogenation of cyclooctene using different types of solvent

The choice of a suitable solvent is an important factor for studying the catalytic behavior of polystyrene supported cobalt catalysts. The solvents chosen to use in this study are easily available. The result is shown in table 4.10.

Table 4.10 Effect of solvents

Solvent	% Yield
Methanol	50
Dimethylformamide	8
Acetonitrile	4

Condition:catalyst P-L$_4$-CoCl$_2$ 0.0250g (Co 2.09 µmol), 3 hours, 50 ℃, P$_{H2}$ 3 atm, cyclooctene 10 mmol and solvent 50 ml

From the results, the activity is high when using methanol as solvent. This may be due to the swelling ability of methanol which increases access the reactants to reactive sites within the polymer matrix.[33]   Dimethylformamide is also a good solvent for the swelling of polymer, but in contrast, it gave low yield, this revealed that swelling is not the only factor affecting the activity. Another probable reason for the higher activity in methanol might be due to the higher solubility of hydrogen gas in methanol.[43]

4.6.2   Comparison of work-up methods

The work-up methods of the reaction mixture for analysis of the substrate and product were studied as mentioned in section 3.9 :

(i)   Acidified with 25 % H$_2$SO$_4$ and extracted with hexane.

(ii) Filtered through a pad of celite and eluted with hexane.

(iii) Filtered through a pad of celite and eluted with methanol.

The results were illustrated in table 4.11.

Table 4.11 Hydrogenation of cyclooctene using different work-up methods

Entry	Work-up method	%Yield	-ene (mmol)	-ane (mmol)	%Mass balance
1	Acidified – extracted/ hexane	51	2.6	5.1	77
2	Filtered/Celite – eluted/ hexane	50	2.6	5.0	76
3	Filtered/Celite – eluted/methanol	68	3.2	6.8	100

Condition: catalyst P-L$_1$-Co(OAc)$_2$ 0.0250 g (Co 3.87µmol), 3 hours, 60 °C and P$_{H2}$ 9 atm, cyclooctene 10 mmol and methanol 50 ml

The results on the work-up methods show that filtering through Celite and eluted with methanol gives good mass balance when using hexane as eluting solvent, biphase occurs. Therefore, this method was used for all next experiments.

4.6.3 Comparison of metal loading methods

As in the method of metal loading, long time is needed, therefore to reduce time, refluxing the reaction mixture was attempted. The results are shown in table 4.12.

Table 4.12 Hydrogenation of cyclooctene using different metal loading methods

Entry	Method	%Yield
1	Stirred for 10 days	54
2	Refluxed for 2 days	52
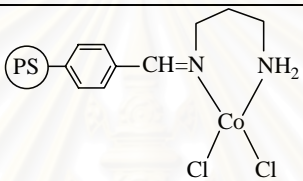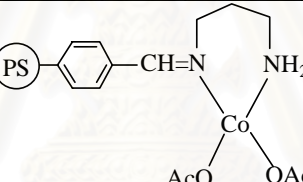
Condition: catalyst 0.0250 g, 3 hours, 60 °C, P$_{H2}$ 9 atm, cyclooctene 10 mmol and methanol 50 ml

From the result, it can be seen that to reduce reaction time for metal loading, the reaction mixture can be refluxed for 2 days with the same result as stirring for 10 days.

4.6.4 Effect of types of cobalt compounds

Two types of cobalt complexes were tested: cobalt chloride and cobalt acetate.

Table 4.13 Hydrogenation of cyclooctene using different types of cobalt compound

Catalyst	Possible structure	%Yield	TON
P-L$_1$-CoCl$_2$		59	1525
P-L$_1$-Co(OAc)$_2$		68	1757

Condition: Co 3.87µmol, 3 hours, 60 °C, P$_{H2}$ 9 atm, cyclooctene 10 mmol, and methanol 50 ml

TON, turnover number: mmol cyclooctane/mmol cobalt

From the results P-L$_1$-Co(OAc)$_2$ was more active than P-L$_1$-CoCl$_2$, this may be due to the fact that acetate ion is a better leaving group than chloride ion. Which are in accordance with the previously reported, in 2002, Costa *et al*.,[44] reported the preparation Pd(L)Cl and Pd(L)OAc complexes by reacting *N*-pyridin-2-yl-*N'*-pyridin-2-ylmethylene-hydrazine (L) with palladium (II) chloride and palladium (II) acetate. These complexes were used as catalysts in the homogeneous hydrogenation of styrene at 1 atm, 40 ºC and THF as a solvent, after 6 hours Pd(L)OAc gave 100% ethyl benzene whereas Pd(L)Cl gave only to a 65%. Therefore the reactivity of the complexes is strongly influenced by the nature of the counter ion.

To investigate the optimum condition for hydrogenation of cyclooctene, P-L$_4$-CoCl$_2$ catalyst was chosen to be studied for further experiments below. The parameters studied are: amount of catalyst, amount of substrate, temperature, hydrogen pressure and reaction time.

4.6.5 Effect of amount of catalyst

Table 4.14 Hydrogenation of cyclooctene with cobalt catalyst in different amount

Entry	Amount of catalyst (g)	Cobalt (µmol)	%Yield
1	0.0100	0.84	45
2	0.0250	2.09	71
3	0.0500	4.35	58

Condition: catalyst P-L$_4$-CoCl$_2$,3 hours, 60 °C, P$_{H2}$ 9 atm, cyclooctene 10 mmol, and methanol 50 ml

When the amount of catalyst was increased or cobalt content increased, the % yield was enhanced (entries 1 and 2). This result could be explained by the increase of active sites. But when amount of catalyst was further increased, % yield decreased (entry 3), this might be due to the occurrence of agglomerization.

4.6.6 Effect of amount of substrate

Amount of substrate was varied in the range of 2, 5, and 10 mmol.

Table 4.15 Hydrogenation of cyclooctene using different amount of substrate

Entry	Cyclooctene (mmol)	%Yield
1	2	58
2	5	64
3	10	71

Condition: catalyst P-L$_4$-CoCl$_2$ 0.0250 g (Co 2.09 µmol), 3 hours, 60 °C, P$_{H2}$ 9 atm and methanol 50 ml

From the results it can be concluded that % yield was dependent on amount of substrate in the range studied.

4.6.7 Effect of temperature

To study the effect of reaction temperature for catalytic hydrogenation, the experiment was carried out at different temperature. The results as shown in table 4.16.

Table 4.16 Hydrogenation of cyclooctene using different temperature

Entry	Temperature (^{o}C)	%Yield
1	50	57
2	60	71
3	70	47

Condition: catalyst P-L$_4$-CoCl$_2$ 0.0250 g (Co 2.09 μmol), cyclooctene 10 mmol, 3 hours, P$_{H2}$ 9 atm and methanol 50 ml

When the temperature was increased, %yield was enhanced. But at 70 ^{o}C, % yield decreased. From the results could be explained that high temperature causes phase change in the polymer matrices. It was previously reported that polymeric reactions are known to be coupled with mobility of chain segments controlling catalytic properties of immobilized metal complexes. A rise in chain mobility of chain segments may lead to change in coordination unsaturation of the transition metal ion of the active center and active sites deactivation.[12] In addition, hydrogenation is exothermic, raising the temperature generally decrease the equilibrium of the reaction.

4.6.8 Effect of hydrogen pressure

Hydrogen pressure is another important parameter for hydrogenation condition. The hydrogen pressure examined reaction was 3, 6 and 9 atm by fixing the other parameters. The results are shown in table.4.17.

Table 4.17 Effect of pressure for hydrogenation of cyclooctene

Entry	Reaction Temp. (^{o}C)	P_{H2} (atm)	%Yield
1	60	3	55
2	60	6	61
3	60	9	71

Condition: catalyst P-L$_4$-CoCl$_2$ 0.0250 g (Co 2.09 µmol), 3 hours, cyclooctene 10 mmol and methanol 50 ml

From the results, the %yield increased with increasing hydrogen pressure. It was explained that the increasing hydrogen pressure enhances reaction of the reactants and the surface of catalyst.

4.6.9 Effect of reaction time

The effect of reaction time was observed, the result shows that %yield increased with time.
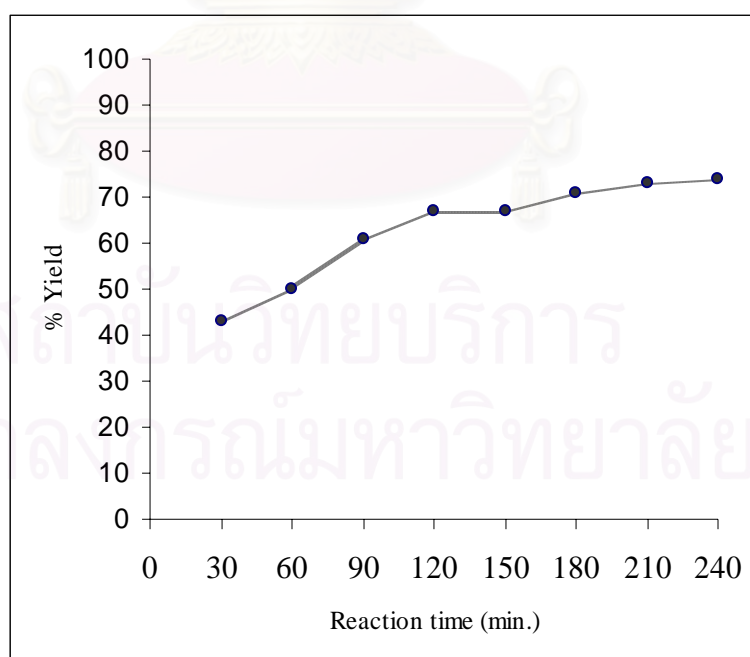
Figure 4.26 Effect of reaction time on hydrogenation of cyclooctene using
P-L$_4$-CoCl$_2$

4.6.10 Effect of types of ligand

The effect of ligands type of polystyrene supported cobalt catalysts for catalytic hydrogenation of cyclooctene were observed in the same condition (cobalt 2.09 µmol), the results are shown in table 4.18.

Table 4.18 Hydrogenation of cyclooctene with cobalt catalysts containing different ligand

Entry	Catalyst	Polymer supported structure	% Yield	TON
1	P-L$_1$-CoCl$_2$	(PS)—〈benzene〉—CH=N⌒NH$_2$	72	3445
2	P-L$_2$-CoCl$_2$	(PS)—〈benzene〉—CH=N—C(=O)—OH	69	3301
3	P-L$_3$-CoCl$_2$	(PS)—〈benzene〉—CH=N-(CH$_2$)$_2$NH-(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$	75	3588
4	P-L$_4$-CoCl$_2$	(PS)—〈benzene〉—CH=N—〈pyridine, N〉	71	3397
5	P-L$_5$-CoCl$_2$	(PS)—〈benzene〉—CH$_2$—NH—〈pyridine, N〉	72	3445
6	P-L$_6$-CoCl$_2$	(PS)—〈benzene〉—CH$_2$—NH⌒N=C—〈benzene〉 with HO	79	3780
7	P-L$_7$-CoCl$_2$	(PS)—〈benzene〉—CH$_2$—O—〈benzene〉—CH=N—〈pyridine, N〉	76	3636
8	P-L$_8$-CoCl$_2$	(PS)—〈benzene〉—CH$_2$—O—C(=O)—〈pyridine, N〉	75	3588
9	P-L$_9$-CoCl$_2$	(PS)—〈benzene〉—CH$_2$—O—〈quinoline, N〉	74	3541

Condition: Co 2.09 µmol, 3 hours, 60 °C, P$_{H2}$ 9 atm, cyclooctene 10 mmol and methanol 50 ml

TON, turnover number: mmol cyclooctane/mmol cobalt

All of polystyrene supported cobalt catalysts can hydrogenate cyclooctene with high yield (69-79%). The slightly more activity were observed for the catalyst (P-L$_3$-CoCl$_2$), (P-L$_6$-CoCl$_2$) and (P-L$_7$-CoCl$_2$). The possible reason might be due to the longer linkage, the more mobility and flexibility of the chain inside the matrix

were increased the efficiency to allow the double bonds to make contact with the active sites.[45]

The lowest catalytic activity was observed for polystyrene bound Schiff base glycine (P-L_2-CoCl$_2$), gave 69%. To compare this experimental condition with the previous report. In 1988, Gokak *et al*.[22], reported preparation of 2% crosslinked polystyrene bound non-Schiff base glycine cobalt complex used for catalytic hydrogenation of 1-octene at 45 ºC, 3 atm, in presence of NaBH$_4$ and THF as a solvent, this catalyst showed, 10% conversion, a very low activity compared to P-L_2-CoCl$_2$.

4.7 A comparison between homogeneous and supported catalysts

A compaison catalytic activity of homogeneous and supported catalysts for hydrogenation of cyclooctene were studied by using the same experimental condition. The results are shown in table 4.19.

Table 4.19 Hydrogenation of cyclooctene with homogeneous and supported catalysts

Entry	Catalyst	%Yield[a]	TON[b]
1	Homogeneous catalyst	67	5982
2	Supported catalyst	60	5025

Condition: catalyst L_8-CoCl$_2$ and P-L_8-CoCl$_2$, cobalt 1.12 µmol,

3 hours, 60 °C, P_{H2} 9 atm and methanol 50 ml

[a] Yield based on starting material

[b] Turnover number: mmol cyclooctane/mmol Cobalt

From the results, the % yield and TON of homogeneous catalyst were higher than those of the supported catalyst, this could be related to difference in the reactant concentration at active sites for the polymer bound and dissolved catalysts. The diffusion of reactant molecules to the active sites may be inhibited by the matrix of support.[45] Higher activity of homogeneous catalyst compared to heterogeneous counterpart is commonly reported.[29,45]

4.8   Recycling and leaching test of catalysts

In this study, the heterogenized catalyst was recovered after hydrogenation in order to be reused. After the reaction, the catalyst was filtered, then washed with solvent and dried to constant weitht before reusing in the next cycle. It was reused for hydrogenation of cyclooctene at the same condition as for the fresh catalyst. The results are presented in table 4.20.

Table 4.20 % Yield of recycled catalyst in hydrogenation of cyclooctene

Catalyst	Times of use	%Yield
P-L$_4$-CoCl$_2$	Fresh	71
	1	68
	2	68

Condition: catalyst P-L$_4$-CoCl$_2$ 0.0250g (Co 2.09 µmol), 3 hours, cyclooctene 10 mmol and methanol 50 ml

After being used once and twice, %yield was slightly dropped from 71% to 68%. In addition, the catalyst was tested for leaching of cobalt from the support, the result shows that similar %yield was obtained (68%) for the catalyst after leaching. This means that cobalt attached well on the polystyrene support. Therefore the catalysts can be reused successfully with only slight loss of activity and little leaching of metal from the support.

4.9 Proposed mechanism

The mechanism of alkene hydrogenation using polystyrene supported cobalt catalyst was reported earlier and shown in scheme 4.1.
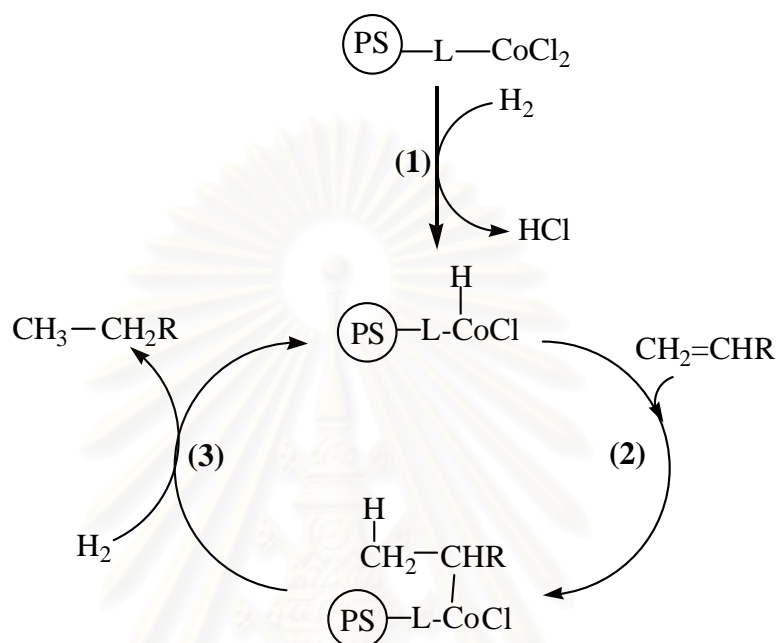
Scheme 4.1 Proposed mechanism of hydrogenation by using polystyrene supported cobalt catalyst.

(1) Hydride species was formed from the heterolytic scission of hydrogen molecule.

(2) Substrate (cyclooctene) was adsorbed on the catalyst surface, while the hydrogen migration or insertion to add to the double bond of substrate.

(3) Alkene was hydrogenated to alkane. Finally, another molecule of hydrogen was adsorbed on the surface of the catalyst. A similar mechanism for heterogeneous catalyst was reported else where.[29]

CHAPTER V

CONCLUSION AND SUGGESTIONS

In this research, 5% crosslink poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride)cobalt catalysts were prepared by following steps: (i) anchoring ligand on polystyrene support, (ii) cobalt loading on the polystyrene support. These catalysts were characterized by FT-IR, XRF, AAS and TGA techniques. The evidence for anchoring of ligands onto the polystyrene support is the appearance and loss of IR peaks that correspond to the introduction of functional groups. The peaks in the region around 3600-3200 cm^{-1} corresponded to N-H and O-H stretching vibration of ligand on the polystyrene support. For polystyrene containning aminopyryl ligand appeared the strong absorption peaks around 1500 and 700 cm^{-1} assigned to the pyridyl ring stretching vibration. For ether linkage appeared the absorption peak of the C-O stretching vibration around 1100 cm^{-1}. For polystyrene bound Schiff base ligands, appeared the absorption peak of imine around 1600 cm^{-1} assigned to the C=N stretching vibration. These evidences indicated the formation of ligands on the support. After cobalt loading, the lower shift in wave number was observed, indicated the coordination of metal with the donor atoms. The complexation of polystyrene supported cobalt catalyst occurred through 'N' atom of amino group, pyridine ring and 'O' atom of ether group to the cobalt metal. It was found from TGA that polystyrene supported cobalt catalysts have high thermal stability. The content of metal on polystyrene support was determined by XRF and AAS techniques. It was found that polystyrene Schiff base triethylenetetramine cobalt (II) chloride has more cobalt content than the other catalysts. These might due to the fact that it had more donor atoms. All catalysts can catalyze hydrogenation of cyclooctene efficiently, it giving high yield of cyclooctane (>69%) at 60 ^{o}C, hydrogen pressure of 9 atm in 3 h. The %yield was increased when catalyst concentration, hydrogen pressure and reaction time were increased. Finally, the catalysts can be reused at least 3 times with slightly loss of activity and little leaching of metal from the support.

Suggestions

From all results and discussion, the future work should be focused on the following:

1. The catalytic activity for hydrogenation should be increased by using additive and reducing agent.

2. The prepared polystyrene supported cobalt catalysts should be used in other reaction such as hydroformylation.

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APPENDICES

APPENDIX A

Gas chromatography determined product of cyclooctene hydrogenation. Cyclooctane product was identified using standard addition method.


```
C-R8A CHROMATOPAC     CH=1      DATA=1:@CHRM1.C00        ATTEN= 4    SPEED=  5.0

  -  0.0

  -  2.0
                                                          Methanol
  -  4.0
                                                                            4.478

  -  6.0

  -  8.0

  - 10.0    Ethylbenzene
              11.326
  - 12.0             Cyclooctene
                13.178
  - 14.0      14.225        Cyclooctane


C-R8A CHROMATOPAC CH=1   Report No.=15      DATA=1:@CHRM1.C00   04/07/25  17:52:32

** CALCULATION REPORT **
CH PKNO    TIME       AREA      HEIGHT   MK  IDNO    CONC              NAME
1    1     4.478    1544751    127471                96.8139
     2    11.326       8771      1656                 0.5497
     3    13.178      21333      3883                 1.337
     4    14.225      20734      3591                 1.2994
                    ---------  --------             ----------
         TOTAL      1595587    136601                 100
```

Figure A-1 A gas chromatogram of liquid mixture for correction factor calculation.

Calculation of the correction factor

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section). Ethylbenzene was used as internal standard.

A: exact amount of cyclooctane prepared = 7.70×10^{-4} mol

B: exact amount of cyclooctene prepared = 7.44×10^{-4} mol

C: exact amount of internal standard was added = 6.53×10^{-5} mol

D: peak area of cyclooctane prepared = 20734

E: peak area of cyclooctene prepared = 21333

F: peak area of the internal standard = 8771

G: total volume of the reaction = 5 ml.

The calculation of the correction factor can be described as follows:

Correction factor of cyclooctane:

The amount of cyclooctane from the reaction mixture

$$= (C \times D / F) = H$$
$$= 6.53 \times 10^{-5} \times 20734 / 8771$$
$$= 1.54 \times 10^{-4}$$

The amount of cyclooctane in G ml (total volume of the reaction)

$$= H \times G = I$$
$$= 1.54 \times 10^{-4} \times 5$$
$$= 7.72 \times 10^{-4}$$

Thus, the correction factor of cyclooctane can be calculated as:

$$= A / I$$
$$= 7.70 \times 10^{-4} / 7.72 \times 10^{-4}$$
$$= 1.00$$

Correction factor of cyclooctene:

The amount of cyclooctene from the reaction mixture

$$= (C \times E / F) = K$$
$$= 6.53 \times 10^{-5} \times 21333 / 8771$$

$$= 1.59 \times 10^{-4}$$

The amount of cyclooctene in G ml (total volume of the reaction)

$$= K \times G = L$$

$$= 1.59 \times 10^{-4} \times 5$$

$$= 7.94 \times 10^{-4}$$

Thus, the correction factor of cyclooctene can be calculated as:
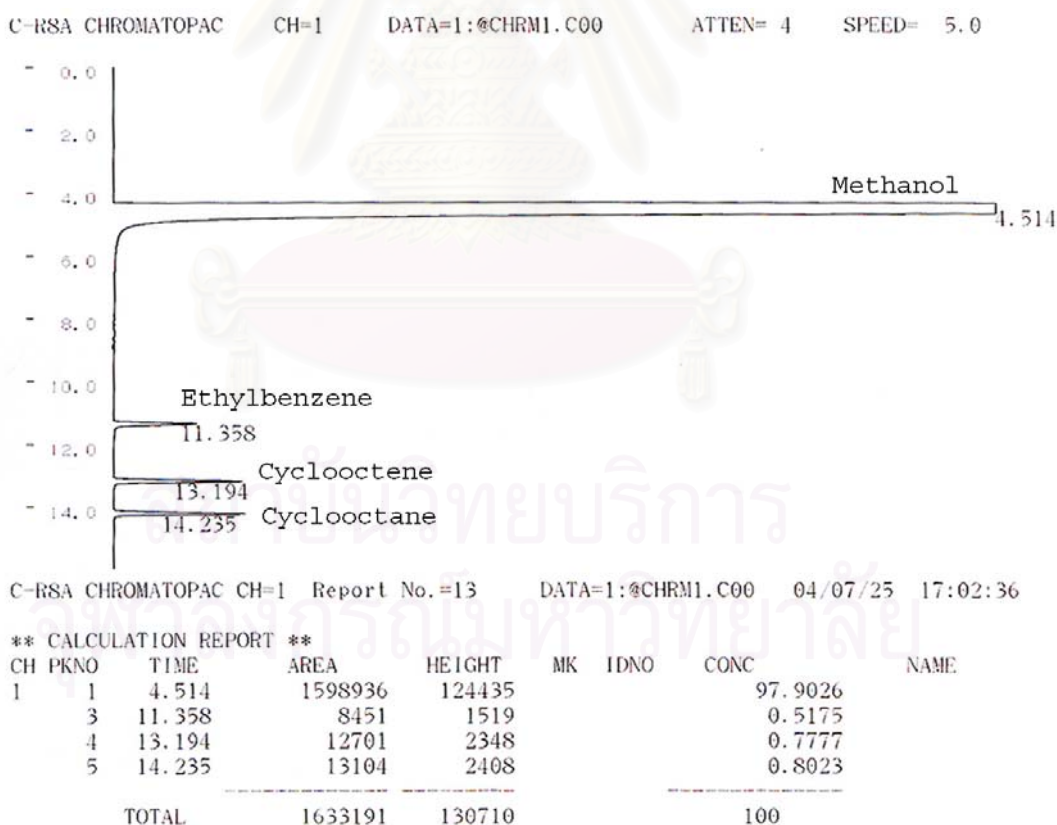
$$= B / L$$

$$= 7.44 \times 10^{-4} / 7.94 \times 10^{-4}$$

$$= 0.94$$

The correction factors of chemicals are listed as follows:

Cyclooctane = 1.00

Cyclooctene = 0.94

```
C-RSA CHROMATOPAC     CH=1      DATA=1:@CHRM1.C00        ATTEN= 4     SPEED= 5.0
```



```
C-RSA CHROMATOPAC CH=1   Report No.=13      DATA=1:@CHRM1.C00   04/07/25  17:02:36

** CALCULATION REPORT **
CH PKNO    TIME      AREA      HEIGHT   MK   IDNO    CONC              NAME
1    1     4.514    1598936    124435                97.9026
     3     11.358      8451      1519                 0.5175
     4     13.194     12701      2348                 0.7777
     5     14.235     13104      2408                 0.8023
                    ---------  --------              --------
         TOTAL      1633191    130710                  100
```

Figure A-2 A gas chromatogram of liquid products from reaction mixture of hydrogenation of cyclooctene.

Calculation of the amount of the chemicals in the reaction mixture

A_{rxn}: exact amount of cyclooctene (substrate) = 0.01 mol

B_{rxn}: exact amount of internal standard was added = 6.53×10^{-5} mol

C_{rxn}: peak area of cyclooctane = 13104

D_{rxn}: peak area of cyclooctene = 12701

E_{rxn}: peak area of the internal standard = 8451

F_{rxn}: total volume of the reaction = 51.3 ml.

Calculation of %yield of cyclooctane:

Mole of cyclooctane

$$= (B_{rxn} \times C_{rxn} \times F_{rxn} / E_{rxn}) \times \text{correction factor}$$
$$= 6.53 \times 10^{-5} \times 13104 \times 51.3 / 8451 \times 1.00$$
$$= 5.19 \times 10^{-3} \text{ mol}$$

Thus, %yield of cyclooctane

$$= 5.19 \times 10^{-3} / A_{rxn} \times 100$$
$$= 5.19 \times 10^{-3} / 0.01 \times 100$$
$$= 51.9\%$$

Calculation of %conversion of cyclooctene:

Mole of cyclooctene $= (B_{rxn} \times D_{rxn} \times F_{rxn} / E_{rxn}) \times \text{correction factor}$
$$= 6.53 \times 10^{-5} \times 12701 \times 51.3 / 8451 \times 0.94$$
$$= 4.73 \times 10^{-3} \text{ mol}$$

Thus, %conversion $= (A_{rxn} - 4.73 \times 10^{-3}) / A_{rxn} \times 100$
$$= 0.01 - 4.73 \times 10^{-3} / 0.01 \times 100$$
$$= 52.7\%$$

VITAE

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