การเตรียมตัวเร่งปฏิกิริยารูทีเนียมบนตัวรองรับพอลิเมอร์ สำหรับไฮโดรจิเนชันของไซโคลออกทีน

นางสาว สิรินธร บรรจงศิลป์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2545

ISBN 974-17-1431-9

PREPARATION OF POLYMER-SUPPORTED RUTHENIUM CATALYSTS FOR HYDROGENATION OF CYCLOOCTENE

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Program of Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2002

ISBN 974-17-1431-9

Thesis Title	Preparation of Polymer-Supported Ruthenium Catalysts for Hydrogenation of Cyclooctene
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สิรินธร บรรจงศิลป์ : การเตรียมตัวเร่งปฏิกิริยารูทีเนียมบนตัวรองรับพอลิเมอร์สำหรับไฮโดรจิเนชันของไซโคลออกทีน (PREPARATION OF POLYMER-SUPPORTED RUTHENIUM CATALYSTS FOR HYDROGENATION OF CYCLOOCTENE)
อ. ที่ปรึกษา : รศ.ดร. วิมลรัตน์ ตระการพฤกษ์ อ.ที่ปรึกษาร่วม : รศ.ดร.ศุภวรรณ ตันตยานนท์, จำนวนหน้า 107 หน้า. ISBN 974-17-1431-9

ในงานวิจัยนี้ได้ทำการเตรียมตัวเร่งปฏิกิริยารูทีเนียมบนตัวรองรับพอลิเมอร์ โดยใช้ 2%, 5% และ 10% ไดไวนิลเบนซิน พอลิ(สไตรีน-โค-ไดไวนิลเบนซิน-โค-ไวนิลเบนซิล คลอไรด์) โคพอลิเมอร์ทำปฏิกิริยากับไบเดนเตทลิแกนด์ (2-แอมิโนพิริดิล และ 1,3-ไดแอมิโนโพรเพน) ที่มีไนโตรเจนเป็นอะตอมที่ให้อิเล็กตรอน กับรูทีเนียมไทรคลอไรด์ ตัวเร่งปฏิกิริยาเหล่านี้ได้ตรวจพิสูจน์เอกลักษณ์ด้วยเทคนิค FT-IR, XRF, EA และ TGA และใช้เป็นตัวเร่งปฏิกิริยาสำหรับไฮโดรจิเนชันของไซโคลออกทีน ได้ศึกษาผลของพารามิเตอร์ต่างๆ ได้แก่ อุณหภูมิ เวลา ความดันของแก๊สไฮโดรเจนและ ปริมาณของตัวเร่งปฏิกิริยาและสารตั้งต้นต่อปฏิกิริยาไฮโดรจิเนชัน พบว่าตัวเร่งปฏิกิริยาที่เตรียมขึ้นทั้งหมดสามารถเร่งปฏิกิริยาไฮโดรจิเนชันของไซโคลออกทีนให้ไซโคลออกเทนในปริมาณสูง (> 95%) ที่อุณหภูมิ 60 องศาเซลเซียส ความดันของแก๊สไฮโดรเจน 5 บรรยากาศ ในเวลา 5 ชั่วโมง ตัวเร่งปฏิกิริยาบนตัวรองรับพอลิเมอร์มีเสถียรภาพทางความร้อนที่สูง สารประกอบเชิงซ้อนรูทีเนียมบนตัวรองรับพอลิเมอร์ไม่หลุดออกเมื่อแช่ในเมทานอลเป็นเวลา 24 ชั่วโมง นอกจากนี้ยังพิสูจน์ได้ว่าสามารถนำกลับมาใช้ใหม่ได้

ตัวเร่งปฏิกิริยารูทีเนียมระบบเอกพันธุ์ คือ รูทีเนียม-2-แอมิโนพิริดิล, รูทีเนียม-1,3-ไดแอมิโนโพรเพน และ รูทีเนียม-1,3-ได(2,6-ไดไอโซโพรพิลเฟนิล)ไดแอมิโนโพรเพน ได้ใช้เร่งปฏิกิริยาไฮโดรจิเนชันของไซโคลออกทีน ที่ภาวะเดียวกันกับข้างต้นด้วย

หลักสูตร...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต……………….…..…………
สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่ออาจารย์ที่ปรึกษา………..………
ปีการศึกษา…..2545……………….. ลายมือชื่ออาจารย์ที่ปรึกษาร่วม…………...

4372448823: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: HYDROGENATION OF CYCLOOCTENE/ POLYMER SUPPORTED RUTHENIUM CATALYSTS

SIRINDHORN BUNCHONGSILN: PREPARATION OF POLYMER-SUPPORTED RUTHENIUM CATALYSTS FOR HYDROGENATION OF CYCLOOCTENE. THESIS ADVISOR : ASSOC.PROF. WIMONRAT TRAKARNPRUK, Ph.D. THESIS CO-ADVISOR: ASSOC.PROF. SUPAWAN TANTAYANON, Ph.D.; 107 pp. ISBN 974-17-1431-9

In this thesis, polymer-supported ruthenium catalysts were prepared by using 2%, 5% and 10% DVB poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) copolymer, reacting with bidentate ligands (2-aminopyridyl and 1,3-diaminopropane), in which N is an donor atom, with ruthenium trichloride. These catalysts were characterized by FT-IR, XRF, EA and TGA techniques and used as catalyst for cyclooctene hydrogenation. The influence of various parameters such as temperature, time, hydrogen pressure, and the amounts of catalyst and substrate on the hydrogenation has been studied. It was found that all prepared catalysts could catalyze hydrogenation of cyclooctene, giving high yield of cyclooctane (>95%) at 60 ^{o}C, hydrogen pressure of 5 atm in 5 h. The polymer- supported catalysts have high thermal stability. The ruthenium complex on the polymer support did not leach out after 24 h of immersion in methanol. In addition, it was proved to be able to be reused.

Homogeneous ruthenium catalysts: ruthenium-2-aminopyridyl, ruthenium-1,3-diaminopropane and ruthenium-1,3-di(2,6-diisopropylphenyl) aminopropane were also used to catalyze hydrogenation of cyclooctene in the same above condition.

Program...Petrochemistry and Polymer Science... Student's…………………………
Field of study…Petrochemistry and Polymer Science Advisor's………………………..
Academic year ….2002…. Co-advisor's……………………..

ACKNOWLEDGEMENTS

The author would like to express her gratitude to her advisor, Associate Professor Dr. Wimonrat Trakarnpruk and Associate Professor Dr. Supawan Tantayanon for providing valuable advice, encouragement and giving the assistance throughout the course of this research. In addition, the author also wishes to express deep appreciation to Professor Dr. Pattarapan Prasassarakich, Assistant Professor Dr. Warinthorn Chavasiri, and Dr. Oravan Sanguanruang serving as the chairman and members of her thesis committee, respectively, for their valuable suggestions and comments.

Appreciation is also extended to Program of Petrochemistry and Polymer Science and the Department of Chemistry, Faculty of Science, Chulalongkorn University for granting financial support to fulfill this study and provision of experimental facilities.

Further acknowledgement is extended to her friends for their help and encouragement during her graduate study. Finally, the author is very appreciated to her family and her good friends whose names are not mentioned here for their love, assistance and encouragement throughout her entire education. Without them, the author would have never been able to achieve this goal.

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DVB	divinyl benzene
Fig	figure
NMR	nuclear magnetic resonance
Ø	phenyl
Ⓟ	crosslinked poly(styrene-*co*-divinylbenzene)
^{o}C	degree Celsius
cm^{-1}	unit of wave number
nm	unit of wavelength
ml	milliliter
rpm	round per minute
atm	atmosphere
Eq	equation
st.	stretching
wt/v	weight per volume
h	hour
VBC	vinylbenzyl chloride
P-2AP	polymer bound 2-aminopyridyl ligand
5P-SB-2AP	5% polymer bound Schiff base-2-aminopyridyl ligand
5P-SB-DP	5% polymer bound Schiff base-1,3-diaminopropane ligand
2P-Ru-2AP	2% polymer-supported Ru(III)-2-aminopyridyl
5P-Ru-2AP	5% polymer-supported Ru(III)-2-aminopyridyl
10P-Ru-2AP	10% polymer-supported Ru(III)-2-aminopyridyl
5P-Ru-SB-2AP	5% polymer-supported Ru(III)- Schiff base 2-aminopyridyl
5P-Ru-SB-DP	5% polymer-supported Ru(III)-Schiff base 1,3-diaminopropane
2P-Rh-2AP	2% polymer-supported Rh(III)-2-aminopyridyl
Ru-2AP	ruthenium-2-aminopyridyl complex
Ru-DP	ruthenium-1,3-diaminopropane complex
Ru-DA	ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane complex

CHAPTER I

INTRODUCTION

A catalyst provides a new reaction pathway that has a lower activation energy and the catalyzed reaction proceeds through a new and energetically more favorable pathway.[1] To be useful, a catalyst must have three predominant characteristics: activity, stability, and selectivity. Low activity is undesirable and impracticable, as it necessitates either excessively long contact time or high temperatures to achieve the required conversion. Catalyst stability, i.e., a long life or an easy *in situ* regenerability, is the next important property. Since a catalyst only operates by forming chemical bonds with at least one of the reactants or its fragments, stronger bonds might be formed with one of the by-products of the reaction. One important reason to strive for high selectivity is, therefore, to avoid the formation of such by-products, which poison the catalyst surface.[2]

More generally, the selectivity of a catalyst is of interest when it is required only one out of several thermodynamically permitted reactions. Homogeneous catalysts, comprised of discrete, soluble metal complexes, are in most cases more active and operate at lower temperatures and pressures than their heterogeneous counterparts. The metal center activity is controlled by supporting ligands. Homogeneous systems are characterized by well studied and interpreted catalytic activity, high activity under mild reaction conditions. Additional advantages include the introduction of preferred orientations, an altered stereochemistry about the metal atom, a changed equilibrium between the metal atoms and their ligands, and advantageous stabilization of catalytically active but normally unstable structures.[3]

In heterogeneous systems the metal centers are either a part of the support surface, or part of a surface metal crystallite, and have no soluble analogs. Heterogeneous catalysts have several advantages, including acceptable thermal and mechanical stability, high activity for a wide range of reactions, and capacity for used in packed and fluidized beds as well as ready separation from reaction products. Disadvantages may include design and improvement limits due to frequently ill-defined actives sites, limited accessibility and effectiveness of the catalytic components, and severe and costly reaction conditions, i.e., high temperatures and pressures. The hope is that the immobilization of transition metal complexes on solid supports eventually will give superior hybrid catalysts possessing the advantages of both traditional catalyst systems with few disadvantages.[4]

One method consists of the 'heterogenization' of a homogeneous catalyst by anchoring the catalyst on a solid support, i.e. an inorganic material or an organic polymer, in order to perform the separation of the catalyst from the reaction mixture, by filtration. However, lower activities and selectivity are mostly observed. In all cases, the choice of the polymer is crucial: a large swelling with the reaction solvent is necessary. Moreover, the active sites must be at the proper location. Most of the existing systems involve crosslinked polystyrene, polyacrylate or polypeptide supported reagents. In order to combine the advantages of homogeneous (mobility, accessibility of the active sites) and heterogeneous catalysis (easy separation), soluble polymer-supported catalysts could be employed. Then, by precipitation upon addition of an appropriate solvent followed by filtration, the catalyst is recovered. [5]

The poly(styrene-divinylbenzene) copolymer beads are of interest in recent years due to their great number of applications in variety of industrial purposes, for example, in the manufacture of resins for gel permeation chromatography, polymeric supports for size exclusion chromatography, ion exchange resins, polymer-supported catalyst, absorbent in chemical, medical, and agricultural applications.[6,7]

The reaction with the homogeneous catalyst has been studied in great detail and a comparison between the homogeneous catalyst and the polymer-supported analogue can provide information on the advantages and disadvantages of polymer supports in catalysis. The use of polystyrene as ligand to prepare macromolecular catalysts containing transition metals is made attractive by the easy accessibility of the polymer and the possibility of introducing required modifications.[8]

Selective hydrogenation of polyunsaturated organic compounds is a subject drawing great interest and attention of the synthetic chemists in recent years.[9, 10] This is due to the fact that in many cases this reaction is the key step in the synthesis and manufacture of many useful fine chemicals such as drugs, perfumes, pesticides, food additives, petrochemicals and so on.

In recent years, the tailoring of functional polystyrene-supported metal (Ru, Rh, Pd) catalysts for selective hydrogenation of polyunsatured cycloolefins and unsaturated carbonyl compounds was studied.[11] A number of ruthenium complexes have been used, mainly due to their higher catalytic activity under mild operating condition.

1.1 The objectives of the thesis

1.1.1 To prepare the crosslinked chloromethylated poly(styrene-*co*-divinylbenzene) beads.
1.1.2 To prepare the polymer-supported ruthenium catalysts.
1.1.3 To test the catalytic activity in hydrogenation of cyclooctene.

1.2 The scopes of the thesis

The experiments were divided into following:

1.2.1 Preparation of the crosslinked polymer supports (2%, 5%, 10% DVB).
1.2.2 Preparation of functionalised polymer support by anchoring ligands.
1.2.3 Preparation of polymer-supported ruthenium catalysts and homogeneous ruthenium catalysts.
1.2.4 Hydrogenation of cyclooctene with the prepared catalysts.
1.2.5 Recycling catalyst for hydrogenation of cycooctene.
1.2.6 Test of catalyst leaching from polymer supports.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Hydrogenation of alkenes

With increasing crude oil prices, there is a growing trend towards renewable raw materials. Fats (triglycerides) are being used in increasing quantities as raw materials in the chemical industry. The glycerides are oxidized, hydrogenated, and aminated to remove undesired functional groups, to shorten the chain length, or to introduce other functional groups. Many of these steps are carried out catalytically, and for economic reasons should take place at low temperatures and pressures in order to attain high selectivities.[12]

Olefin hydrogenation with Wilkinson’s catalyst, one of the well-known catalyst for hydrogenation of an olefin is rhodium complex in the presence of phosphine. The reaction takes place under mild conditions: 1 atm of hydrogen and 25^{o}C. Phosphine complexes of ruthenium and iridium are similar to the complexes of rhodium as hydrogenation catalysts. Wilkinson and co-workers discovered the remarkable catalytic properties of the rhodium phosphine complex $RhCl(PPh_3)_3$ and of other rhodium phosphine complexes [*e.g.*, $Rh(CO)Cl(PPh_3)_2$] for the olefin hydroformylation reaction.

Halpern and co-workers investigated the Wilkinson’s catalyst hydrogenation and led to identification of individual rhodium complexes, of the reaction intermediates and determination of the kinetics of individual step in the cycle. The quantitative kinetics is given with the cycle in Fig. 2.1.[13]

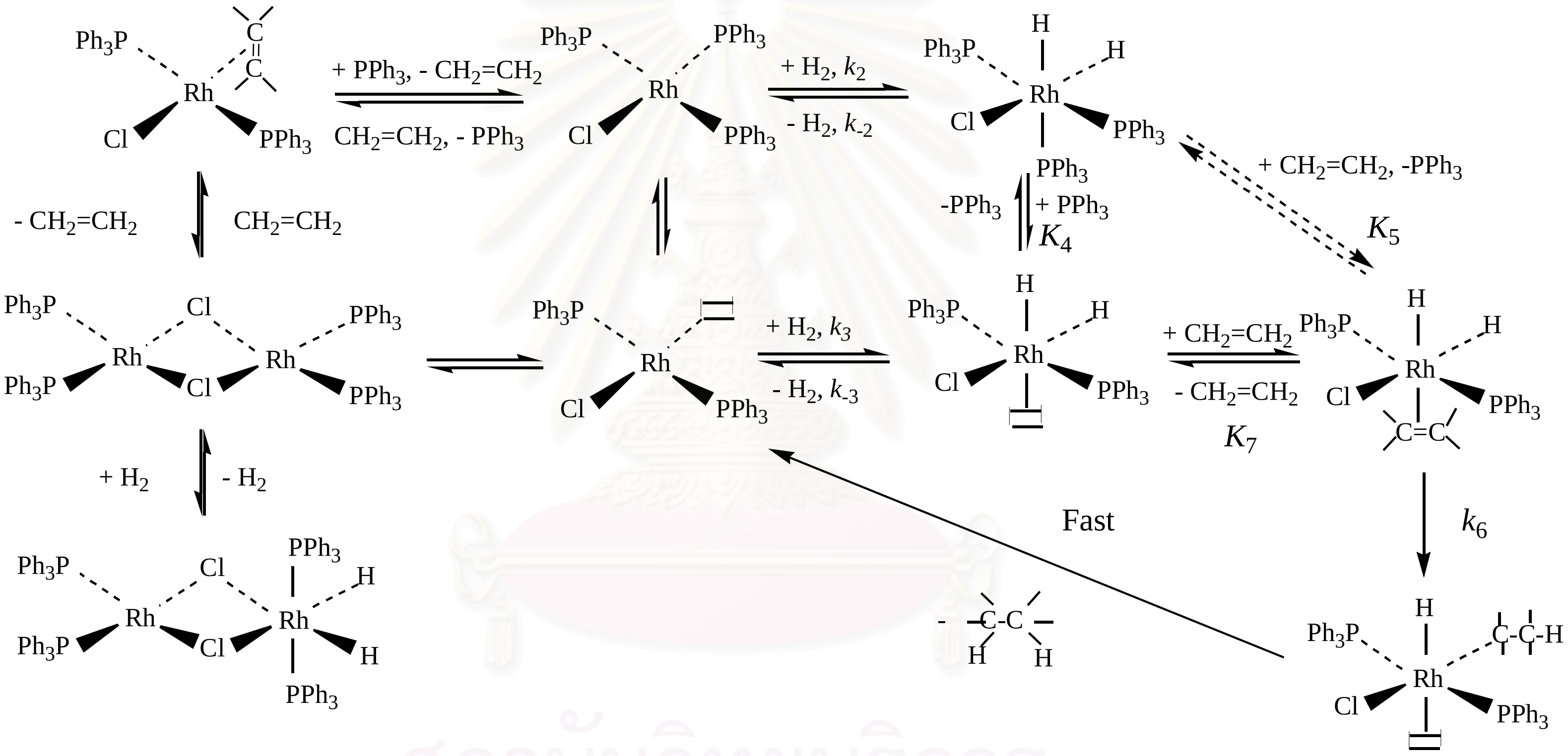


Figure 2.1 Catalytic cycle for the Wilkinson’s catalyst hydrogenation, as determined by Halpern *et al.*[13]

In the investigation of the catalytic hydrogenation, several rhodium complexes were directly observed and characterized, either being crystallized from the solution or identified in solution by ^{31}P NMR spectroscopy. These complexes are $RhCl(PPh_3)_3$, $RhCl(PPh_3)_2$(olefin), $Rh_2Cl_2(PPh_3)_4$, $RhH_2Cl(PPh_3)$, and $Rh_2H_2Cl_2(PPh_3)_4$. Examination of the catalytic cycle of Fig. 2.1 (including the quantitative kinetics) shows that these complexes are not involved in the kinetically significant steps of the cycle. In a sense, they represent dead ends; their presence indicates a draining away of Rh from the catalytic cycle. There is a generally important lesson about catalysis here. The species that can be observed during catalysis often are not directly involved in the cycle, and the identification of the species present in high concentrations can easily lead to a misinterpretation of the cycle. The exceptions are usually the cycle of least interest-those that involve slow catalytic reactions.[13]

The Wilkinson hydrogenation cycle was resolved in a series of kinetics experiments, usually not involving the complete cycle. In one set of experiments, the kinetics of hydrogenation of $RhCl(PPh_3)_3$ was determined spectrophotometrically; when less than an excess of triphenylphosphine was present, the reaction was so fast that stopped-flow techniques had to be used.[13]

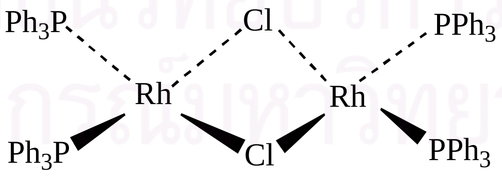
Analysis of the kinetics data led to the conclusion that the kinetically significant path for hydrogenation involved dissociation of a PPh_3 ligand from $RhCl(PPh_3)_3$, giving the coordinatively unsaturated (14-electron) complex $RhCl(PPh_3)_2$. (A solvent molecule may be weakly coordinated to the Rh in this complex.) The subsequent hydrogenation of $RhCl(PPh_3)_2$ (an oxidative addition) is extremely rapid. The resulting unsaturated complex undergoes a ligand association with PPh_3; this is a rapid (equilibrium) step, the product being $RhClH_2(PPh_3)_3$. This indirect route to this complex is much more efficient than the direct hydrogenation of $RhCl(PPh_3)_3$, the rate of which was measured separately; the reactivity of $RhCl(PPh_3)_2$ with H_2 is at least 10^4 times that of $RhCl(PPh_3)_3$. The three-coordinate complex $RhCl(PPh_3)_2$ has a strong tendency to dimerize, giving the species with bridging Cl ligands shown in Fig.2.1; the equilibrium constant for the dimerization is extremely large, but H_2 intercepts the highly reactive intermediate during catalysis virtually as fast as it is formed and thereby prevents its diversion into the “dead end” dimer. In other experiments, the kinetics of the reaction between $RhClH_2(PPh_3)_3$ and cyclohexene (present in large excess) was established, and kinetics of the overall cycle established the rate constant for the virtually irreversible insertion step, which is often so small that the step may be approximated as rate determining.

It should be emphasized that all the species shown inside the dashed line in Fig. 2.1 (i.e., those in the catalytic cycle) were not observable; they were “invisible” during the catalysis because their concentrations were too low to be measured. The cycle was pieced together from results of separate experiment determining kinetics and equilibria under conditions chosen so that the catalytic cycle proceeded only very slowly or not at all.

The Wilkinson hydrogenation cycle illustrates the occurrence of the familiar oxidative addition, reductive elimination, and insertion reaction. Keys to the success of the rhodium phosphine complexes in olefin hydrogenation catalysis are the following:

1.Rh exists in two oxidation states separated by two units, allowing the oxidative addition and reductive elimination to occur readily.

2.There is no intermediate that is so stable as to form bottlenecks in the cycle. The intermediates are in delicate balance. They are all present in low concentrations, and they react predominantly within the cycle rather than to give dead-end complexes. When the phosphine concentration is too high or the hydrogen concentration too low, most of the rhodium is present as $RhCl(PPh_3)_3$ and the dimeric complex.



When olefins that are too tightly bound to the rhodium are used (e.g., ethylene or 1,3-butadiene), the catalysis is also slowed down. These compounds are competitive inhibitors. Competing ligands such as pyridine are bonded to the rhodium so tightly that they shut down the cycle; these ligands are called poisons.

The reactivities of the intermediate species are strongly influenced by those ligands bonded to the metal that are not reactants in the catalytic cycle, in this case the phosphines. The data of Table 2.1 illustrate this point, showing more than a fiftyfold variation in catalytic activity with changes in the substituent groups.

Table 2.1 Relative activity of rhodium complexes as catalyst precursors in the Wilkinson hydrogenation of cyclooctene[14]

Rh Complex	Relative Activity
$RhCl[P(p\text{-}C_6H_4Cl)_3]_3$	2
$RhCl[P(p\text{-}C_6H_5)_3]_3$	41
$RhCl[P(p\text{-}C_6H_4\text{–}CH_3)_3]_3$	86
$RhCl[P(p\text{-}C_6H_4\text{–}OCH_3)_3]_3$	100

2.2 Homogeneous catalysts

The driving force for the introduction of new processes is economic considerations, which are largely influenced by the production costs. Selectivity is becoming the decisive factor in industrial processes. Mainly as a result of increasing purity demands, for example, in polymer chemistry and in the pharmaceutical sector. Higher selectivity means that better use is made of raw materials and therefore lower formation of side products, which must be removed in expensive separation processes or pollute the environment.

In the case of basic chemicals the chances for new catalytic processes are small, but they are better for higher value chemicals such as fine and specialty chemicals. Pharmaceuticals and agrochemicals are two areas where homogeneous catalysts have advantages.

In homogeneous catalysis, the reactants are both in same phase, either gas or liquid. Depending upon the nature of the ligands, the metal atom may be in a low positive, zero, or low-negative state. Several different structures may exist in equilibrium in solution simultaneously, with different reactivities, but since the catalyst is dissolved in the reacting medium, each molecule of a particular structure acts like any other. In many cases the structures have been well characterized and there are systematic correlations of the structure, the nature of the ligands, and the catalytic activity of the catalyst complex. A wide range of soluble metal complexes has proved to exert catalytic activity in hydrogenation of unsaturated molecules. Most attention, however, has focussed on Group VIII elements since they give rise to the most active catalytic systems.

Homogeneous catalysts have certain advantages: they contain only one type of active site and as a result are more specific. The selective ligand exchange, in contrast, thermal stablilty and suitable solvents are often limiting factors in homogeneous hydrogenations.[15]

Rhodium: The best known, most thoroughly studied, and most widely used catalyst for the reduction of a range of unsaturated compounds is chlorotris (triphenylphosphine) rhodium (I) [$RhCl(PPh_3)_3$], known as the Wilkinson’s catalyst.[16] Reduction is generally achieved under mild conditions (room temperature, atmosphereic or sub-atmospheric hydrogen pressure). Since aromatics are inert under these conditions, benzene is often used as solvent. The Wilkinson’s catalyst, just as many other soluble complexes, selectively catalyzes the reduction of unsaturated carbon-carbon double bonds in the presence of other reducible groups. In general, side reactions (hydrogenolysis, disproportionation) do not occur. Although carbonyl ligands usually tend to deactivate rhodium hydrogenation catalysts, [RhH (CO) $(PPh_3)_3$)], better known as a hydroformylation catalyst, also hydrogenates alkenes.

Iridium: An early and popular complex, [$IrCl(CO)(PPh_3)_3$], called the Vaska complex, and its derivatives can be used for the hydrogenation of unsaturated hydrocarbons.[10]

Ruthenium: Very high rates can be achieved for hydrogenations with dichlorotris(triphenylphosphine) ruthenium(II) [$RuCl_2(PPh_3)_3$, In catalytic hydrogenations it is transformed to [$RuHCl(PPh_3)_3$], which is the true catalyst.[17] In 2000, Abdur K. and his coworkers presented that $RuH_2Cl(PPh_3)_2$ *(R,R)-*

cyclohexyldiamine was used as catalyst in hydrogenation of ketones and imines, at 3 atm of H_2 and 20°C. The results showed high turnover numbers.[18]

Cobalt: Cyanide-containing cobalt catalysts, particularly potassium pentacyanocobaltate(II) $K_3[Co(CN)_5]$, are used in the reduction of activated alkenes (conjugated dienes). $Co_2(CO)_8$ is best known as a hydroformylation catalyst, but hydrogenation is also possible under specific conditions. Phosphine-substituted analogs are more successful.

Mechanism.[15] Both hydrogen and the organic substrate must be brought into the coordination sphere of the metal catalyst. The most important property of the homogeneous catalyst is a vacant coordination site, which may be occupied by a readily displaceable ligand.

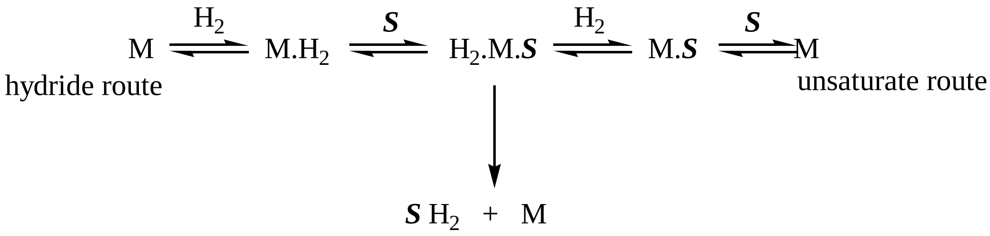
A common, quite general route for activation of hydrogen is the oxidative addition by homolytic cleavage to form a dihydride complex [Eq. (2.1)]. It involves an increase of two in the formal oxidation state of the metal. In turn, monohydrido complexes can be formed through both homolytic [Eq. (2.2)] and heterolytic [Eq. (2.3)] cleavages of hydrogen.[13]

$$\mathrm{M(I)} + \mathrm{H_2} \longrightarrow \mathrm{M(III)H_2} \qquad (2.1)$$

$$\mathrm{2M} + \mathrm{H_2} \longrightarrow \mathrm{2MH} \qquad (2.2)$$

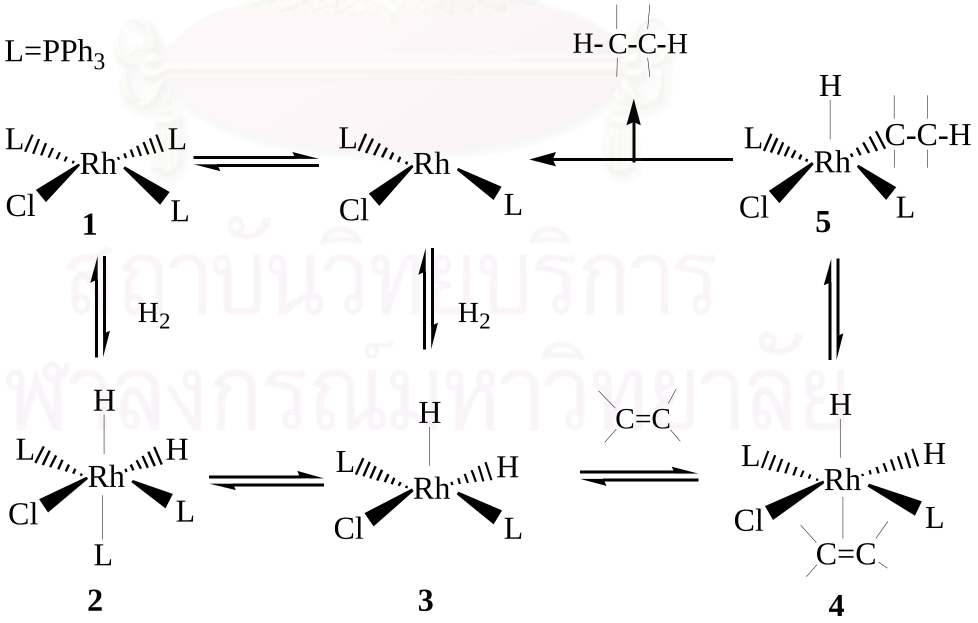
$$\mathrm{MX} + \mathrm{H_2} \longrightarrow \mathrm{MH} + \mathrm{H^+} + \mathrm{X^-} \qquad (2.3)$$

Catalytic cycles operating via the initial formation of a hydrido metal complex followed by coordination of the unsaturated compound (S) are termed the hydride route (Scheme 2.1). In contrast, the unsaturated route involves prior binding of the organic compound (Scheme 2.1). In many cases the hydride route was proven to be more efficient.



Scheme 2.1 Catalytic cycle of hydrido metal complex.

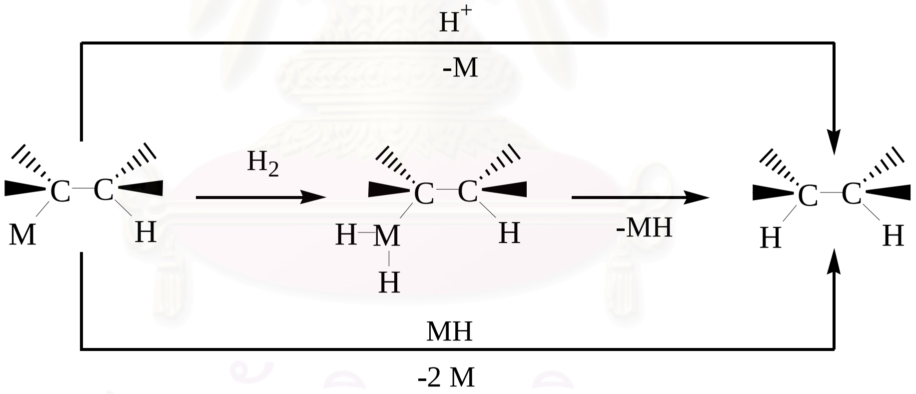
Activation of hydrogen through oxidative addition is best exemplified by the Wilkinson catalyst. The hydrogenation mechanism characteristic of dihydride complexes was originally suggested by Wilkinson and was later further elucidated.[14] The oxidative addition of hydrogen brings about the transformation of the coordinatively unsaturated square-planar rhodium (I) species (1) into a coordinatively saturated octahedral rhodium (III) *cis* dihydride complex (2). This then participates in a series of simple steps resulting eventually in the formation of the saturated end product. Of the several mechanistic pathways demonstrated for the Wilkinson catalyst, the kinetical dominant is shown in Scheme 2.2. The solvent, not shown, may also play an important role as a coordinating ligand. Dinuclear complexes also observed under reaction conditions were not found to be very effective.



Scheme 2.2 The mechanistic pathways for the Wilkinson's catalyst.

In the octahedral complex (2) the hydride ligand exerts a large *trans* effect labilizing the *trans* ligand. This ligand readily dissociates in solution, creating a vacant site (3) being able to form a π complex (4) with the alkene. This substrate association brings the alkene into suitable environment for addition. The next stage in the catalytic cycle is the migratory insertion of the alkene into rhodium-hydrogen bond. The σ-alkylrhodium hydride complex (5) thus formed undergoes a rapid reductive elimination. This leads to the saturated product and regenerates the catalytically active rhodium (I) species to complete the cycle.

There are many examples where monohydrido metal complexes are formed via homolytic or heterolytic hydrogen splitting. The basic difference between the mechanism demonstrated for the Wilkinson catalyst and the overall hydrogenation mechanism in the presence of a monohydride complex lies in the final product-forming step. The alkylmetal intermediate, in this case, can yield the saturated hydrocarbon via hydrogenolysis using H_2, or as a result of protolysis, or by reacting with a second hydrido complex (Scheme 2.3).



Scheme 2.3 The hydrogenation mechanism of a monohydride complex.

The formation of a metal-substrate bond of intermediate stability is of key important in a successful hydrogenation. If this bond is too strong, the subsequent migratory insertion may be hindered and hydrogenation does not take place. Strongly chelating dienes, such as 1,5-cyclooctadiene(COD) or cyclopentadiene, form stable complexes which, inturn, are used as catalysts in hydrogenation.

2.3 Heterogeneous catalysts

In general, the saturation of simple olefinic and acetylenic double bonds occurs readily in the presence of any typical hydrogenation catalyst. Platinum metals, mainly platinum, and rhodium, are active at high pressures and temperatures. Nickel, a cheap and frequently used substitute, usually requires elevated pressures and temperatures. These catalysts when used in hydrogenations are reduced to the metal form; thus, it is the metal that is the actual catalyst. Other catalysts, such as copper chromite (a specially prepared copper oxide- chromium oxide), zinc oxide, and metal sulfides, which are also active in hydrogenations, participate in the catalytic reaction in the oxide or sulfide form.

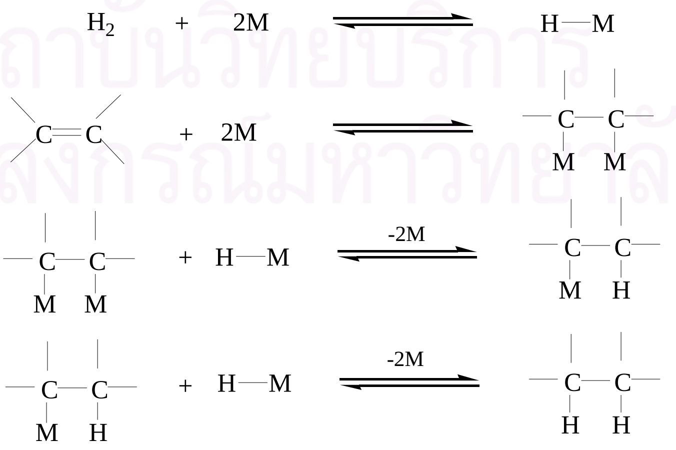
A major problem associated with most homogeneous catalyst systems is the separation and recycling of the expensive catalyst. A possible solution to this problem is to “heterogenize” a homogeneous catalyst, either by anchoring the catalyst on a solid support or by using a liquid-liquid two–phase system. Over the past two decades, the studies of insoluble polymer-supported catalysts have attracted much attention. Unfortunately, despite the advantage of easy separation, the use of insoluble polymer-supported catalysts suffered from lower catalytic activity and stereoselectivity due to the restriction of the polymer matrix which resulted in limited mobility and accessibility of the active sites. The leaching of the noble metal catalyst from the polymer support was also a significant problem.

Since hydrogenation over heterogeneous catalysts is a surface reaction, all these catalysts have a large surface area per unit weight. Metal catalysts are prepared from their salts, oxides, or hydroxides or the metal is deposited on a high surface area inert material (support) such as carbon, alumina, or silica. Another common technique to prepare a finely divided large-surface-area metal catalyst is the leaching of one component of a bimetallic alloy. Raney nickel is one of the oldest and most common hydrogenation catalyst.[15]

The choice of catalyst applied in hydrogenation of certain unsaturated hydrocarbon depends on several factors, such as the reactivity of the substrate and the experimental conditions (pressure, temperature, solvent, liquid- or gas-phase reaction). Multiple-unsaturated compounds may require the use of a selective catalyst attaining the reduction of only one multiple bonds.

Alkenes usually are reduced very easily. 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. Terminal olefins exhibit the highest reactivity, and the rate of hydrogenation decreases in the order: $RCH{=}CH_2 > R_2C{=}CH_2 > RCH{=}CHR > R_2C{=}CHR > R_2C{=}CR_2$. In these hydrogenations, *cis* isomers are hydrogenated in preference to the corresponding *trans* compounds. Since the rate of hydrogenation is sensitive to operating conditions, relative rates based on the measurements of competitive hydrogenation of binary mixtures are most often determined instead of measuring individual rates.

Mechanism. The generally accepted mechanism for the hydrogenation of double bonds over heterogeneous catalysts was first proposed by Horiuti and Polanyi and was later supported by results of deuteration experiments. It assumes that both hydrogen and alkenes are bound to the catalyst surface. The hydrogen molecule undergoes dissociative adsorption [Eq. (2.4)], while the alkene is adsorbed on metal surface [Eq. (2.5)]. Addition of hydrogen to the double bond occurs in a stepwise manner [Eqs. (2.6-2.7)].



(2.4)

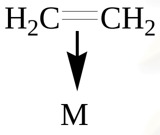
(2.5)

(2.6)

(2.7)

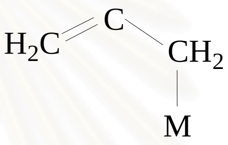
While the last step [Eq. (2.7)] is virtually irreversible under hydrogenation conditions, both the adsorption of alkene [Eq. (2.5)] and the formation of alkyl intermediate (half-hydrogenated state) [Eq. (2.6)] are reversible. The reversibility of these steps accounts for the isomerization of alkenes accompanying hydrogenation. Isomerizations, either double-bond migration or *cis-trans* isomerization, may not be observable unless the isomer is less reactive, or the isomerization results in other structure changes in the molecule, such as racemization.

Futher studies led to the suggestion of other types of surface species, such as the π-adsorbed intermediate (5) and dissociatively adsorbed alkenes [σ-vinyl (6), σ-allyl (7), and π-allyl (8)].

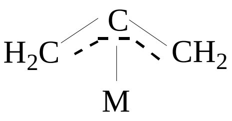


(5)

(6)

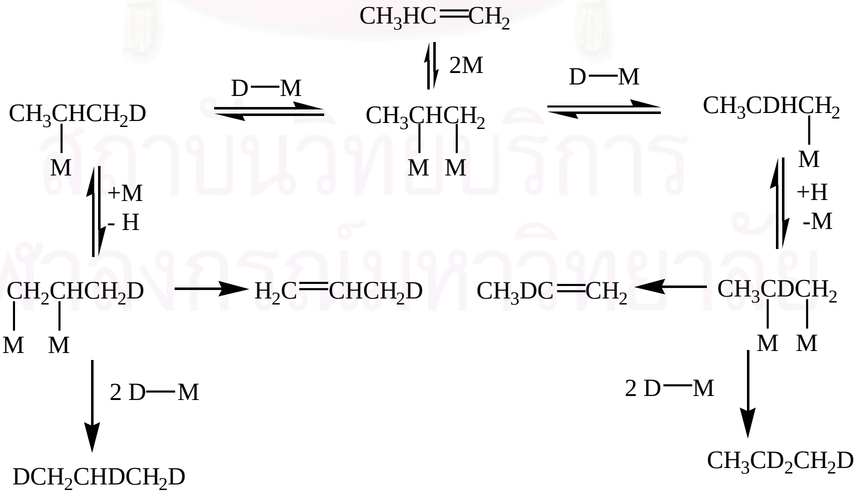


(7)



(8)

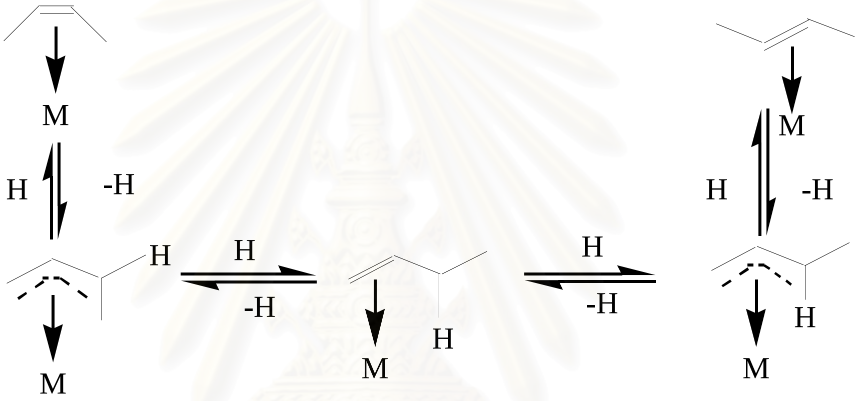
When deuterium instead of hydrogen is used, reversal of the half-hydrogenated intermediate accounts for deuterium exchange in alkenes and the formation of saturated hydrocarbons with more than two deuterium atoms in the molecule (Scheme 2.4).



Scheme 2.4 The half-hydrogenated intermediate accounts for deuterium exchange in alkenes.

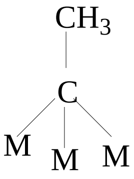
Metals differ in their ability to catalyze isomerization. Both the relative rate of transformation of the individual isomers and the initial isomer distribution vary with the metal. The order of decreasing activity of platinum metals in catalyzing the isomerization of alkenes was found to be Pd >> Rh, Ru, Pt > Os > Ir. Platinum is generally the preferable catalyst if isomerization is to be avoided. The most active Raney nickel preparations rival palladium in their activity of isomerization.

Another possible mechanism interprets *cis-trans* isomerization in combination with double-bond migration assuming the participation of π-allyl intermediates (Scheme 2.5).



Scheme 2.5 Possible mechanism of *cis-trans* isomerization.

Dissociatively adsorbed surface intermediates were also suggested to account for the self hydrogenation of ethylene. It occurs on most transition metals and yields ethane without added hydrogen. Highly dehydrogenated surface species may also be formed under normal hydrogenation conditions. The observation by Thomson and Webb showed that many different metal surfaces give nearly equal rate of alkene hydrogenation. They reasoned that a monolayer of adsorbed species represented as M-C_xH_y was involved as hydrogen transfer agent. Recent extensive surface science studies of ethylene adsorption on single crystals revealed the formation of ethylidyne moiety (9) on platinum. These results suggest that alkene hydrogenation reactions occur on metal surfaces covered with carbonaceous overlayer. Such hydrogen-deficient carbonaceous deposits seem to play an important role in hydrogenation reactions, serving as hydrogen source and providing desorption sites for intermediates and product molecules. Adsorption of reacting molecules, in turn, can lead to surface restructuring during catalytic reactions.[15]



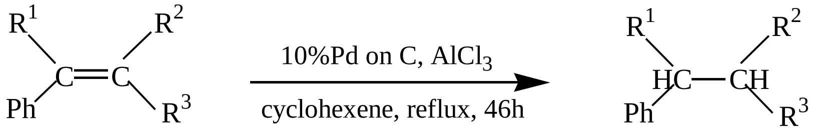
(9)

Transfer Hydrogenation

An interesting convenient, and useful alternative to conventional catalytic hydrogenation is transfer hydrogenation, named as such by Braude and Linstead. The process involves hydrogen transfer from a hydrogen donor, in most cases an organic molecule, to an unsaturated compound. Usually carried out at reflux temperature, it does not require an external hydrogen source nor a special apparatus. A special case is disproportionation, specifically, hydrogen transfer between identical donor and acceptor molecules.

Palladium is the most active and most frequently used catalyst in transfer hydrogenations.[19,20] Cyclohexene, a cheap, readily available, highly reactive molecule, is the preferred donor compound. Alternatively, tetralin and monoterpenes and, in general, any hydroaromatic compound may be used. Mainly alcohols are employed as the donor with Raney Ni.

According to a possible mechanism, transfer hydrogenation requires a catalyst-mediated formation of a donor-acceptor complex, followed by a direct hydrogen transfer. A unique example, the reduction via transfer hydrogenation of aryl-substituted alkenes, is facilitated by $AlCl_3$ [Eq. (2.8)]. The role of Lewis acid is to activate the substrate alkenes and initiate an acid-catalyzed hydride transfer from an allylic position.


(2.8)

R^1, R^2, R^3 = H, alkyl, Ph

2.4 Polymer supports

Polymer supports can be divided into three classes. The first class includes the highly crosslinked resin beads of large surface area called macroreticular or macroporous resins. For example, styrene-divinylbenzene resins with divinylbenzene contents of 5% to 60% of total monomer mixture. The attached catalysts lie mainly in a thin layer at the internal surface, where they are wet by solvents. The high crosslink density prevents rapid diffusion into the core of particle below the internal surface. Usually the surface region is not as highly crosslinked or as rigid as the core.

The second class is swellable, highly crosslinked, microporous (gel-type) resins. These resins swell in solvents and all of their internal volume is accessible to solvent and reagents. Therefore, they may be functionalized with catalyst sites, giving them the advantage of high capacity. Unlike macroreticular resins, they must be used with swelling solvent to permit access to this internal volume. Examples include styrene resins crosslinked with divinylbenzene 1% to 5% of total monomer mixture.

The third class is soluble polymers employed as supports. Reaction products may be continuously separated from polymer-supported catalysts by using membrane filtration or by addition of a non-solvent which precipitates the polymer.[17]

Typical organic supports include styrene polymers, poly(amino acid), acrylic polymers, and crosslinked dextrans. Among acceptable inorganic supports are glass, silica, alumina, zeolites, and clays. The active portion of the catalyst must be stable under reaction conditions while being solvated and soluble in the reaction medium.

Since crosslinked polymers are insoluble and non-volatile they are odorless and non-toxic. Most applications have used crosslinked polymer resins as the support, prepared by suspension copolymerization of styrene and divinylbenzene as the crosslinker. Crosslinked polystyrene, with various crosslink densities, surface and porosity, has received the most attention as an organic support. Variation of the percent crosslink in the support allows an almost continual change from solution chemistry to that of usual heterogeneous surface. The basic polymer backbone is chemically inert, the polar properties can be modified by controlled functionalization or by preparation of appropriate copolymer.[21]

Polymer supports offer several advantages over other catalyst supports. They are easily functionalized, especially when they incorporate aryl groups. Unlike surfaces of metal oxides, polymeric hydrocarbons are nearly inert and are not expected to interfere in catalysis, which may therefore be associated with a single kind of catalytic group and occur selectively.[22] Furthermore, the polymers obtain high densities of sites for binding catalytic groups, and therefore efficient use of reactor volume. Catalytic groups may be dispersed throughout the bulk of a polymer. Groups supported on metal oxides, in contrast, are restricted to surfaces. The polymer supports are unique in being flexible. They may therefore chelate organometallics, giving high ratios of ligands to metal.[23]

Several factors are important for selecting the type of polymer to be used to support a given reactive group. These include the ease of preparation of potentially suitable polymers with the appropriate functional groups and the ease with which these polymers can be obtained in a good physical form. It is also important that, apart from those groups that it is intended to react, the polymer should be chemically inert under the conditions of use. This is especially important if it is intended to recycle the reactive polymer, since after many reaction cycles even quite small and otherwise unimportant side reactions can seriously impair the capacities and/or physical properties of the polymer. The need for chemical inertness severely limits the use of polymers, which contain hydrolysable groups, active OH or NH groups, or easily oxidized or reduced groups. Polymers with such functional groups include poly (acrylate)s, polyesters, poly(acrylamid)s, polyamides (e.g. nylon and peptides), polyurethanes and polysaccharides.[23]

2.4.1 Functional polymers

Two approaches exist for the preparation of functional polymers, namely the polymerization or copolymerization of monomers which carry the desired functionality and the chemical modification of preformed polymers.

2.4.1.1 Preparation of functional polymers by copolymerization

Many functional linear polymers can be prepared by free radical, anionic, cationic, coordination and group transfer polymerizations. However, for the most purposes crosslinked polymers are more attractive than linear polymers. The preparation of crosslinked polymers in a good physical from is most readily achieved by suspension polymerization. This usually involves suspending droplets of a mixture of water-insoluble monomers in an aqueous medium and the use of an oil-soluble free radical initiator or, suspending droplets of a mixture of water-soluble monomers in a water-immiscible medium and the use of a water-soluble free radical initiator. The latter type of polymerization is usually termed inverse suspension polymerization including those shown in Fig. 2.2.

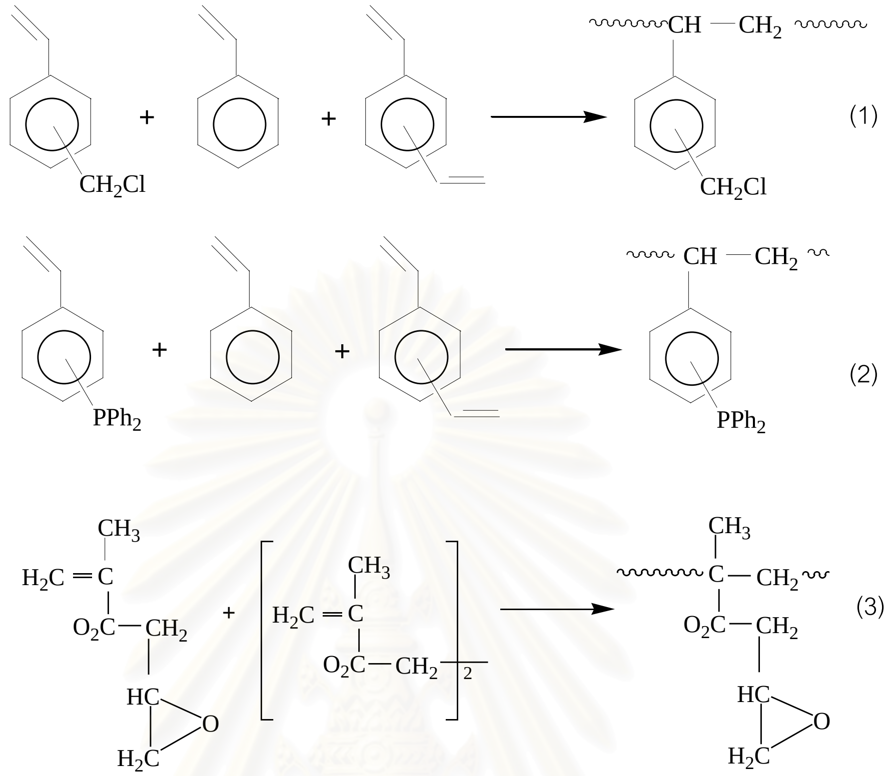


Figure 2.2 Crosslinked polymers prepared by suspension polymerization.[23]

The physical form of the products from suspension polymerization depends on the polymerization conditions. Including such details as the vessel shape, the stirrer size and shape, the stirring speed and the types and concentrations of suspending agents. The optimum conditions for a particular monomer mixture must often be determined by trial and error. By selecting appropriate conditions microporous or macroporous polymer beads can be obtained. The formers are prepared using low levels of crosslinking agent. When the product is dried the polymer matrix collapses to give beads with only very small pores (micropores). Macroporous polymers are usually prepared using relatively large amounts of crosslinking agent and additives called porogens. The latter could, for example, be toluene, certain alcohols or linear polymers. Macroporous polymers are relatively rigid. When they are dried the matrix does not collapse; the large pores remain.

2.4.1.2 Preparation of functional polymers by chemical modification of preformed polymers

It is attractive for using crosslinked polymers because one can start with commercially available microporous polymer beads of good physical size and form, with a known percentage of crosslinking and porosity. After chemical modification the final functional polymer generally has essentially the same physical form as the original polymer. However, the reaction conditions used must be carefully chosen to ensure that the reagents can penetrate the crosslinked matrix throughout the reaction. Ideally the reaction used should have no side reactions because it is not possible to remove the polymer-bound impurities resulting from such reactions.

Chemical modification will generally occur at the more accessible sites of the reactive functional groups. Depending on such factors as the rate of the chemical modification reaction relative to the rate diffusion of the reagent into the matrix, and whether the group introduced facilitates or hindered the introduction of further group in the vicinity, the functional groups in the final polymer may be clustered or well spaced. Of the many reactions which have been used to chemically modify polystyrenes those summarized in Figs. 2.3-2.5 are the most generally useful.[23]

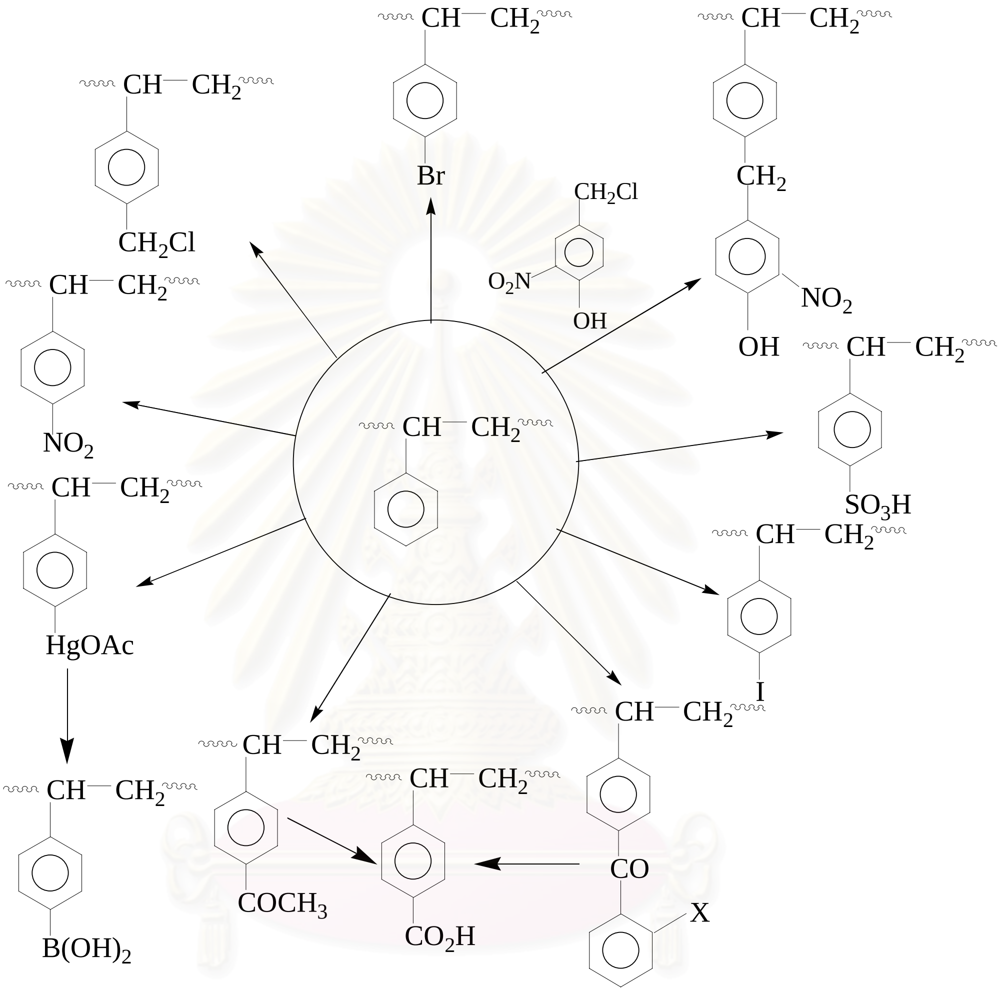


Figure 2.3 Electrophiles aromatic substitution reactions of polystyrene.[23]

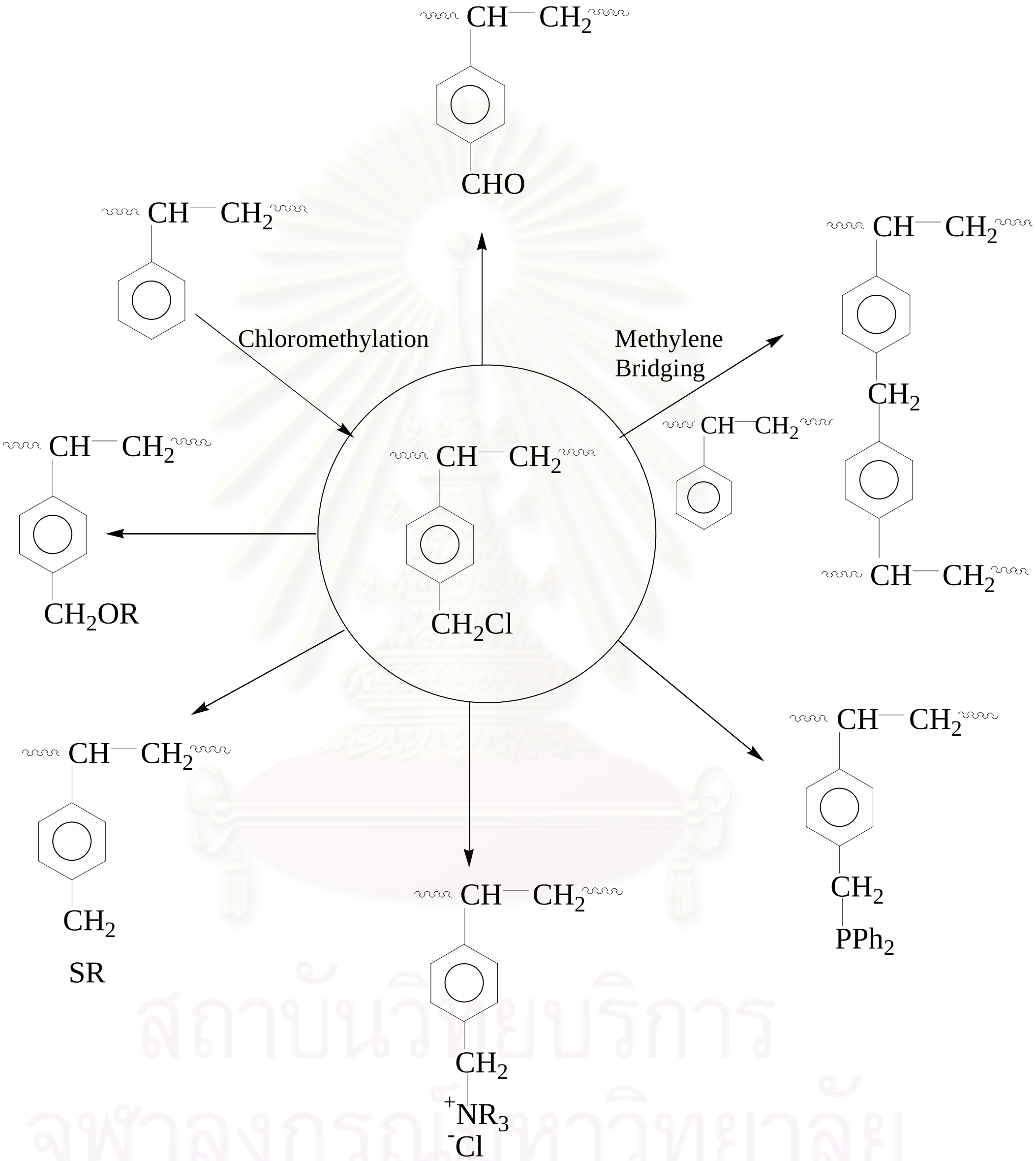


Figure 2.4 Chloromethylation of polystyrene and reactions of the product with nucleophiles.[23]

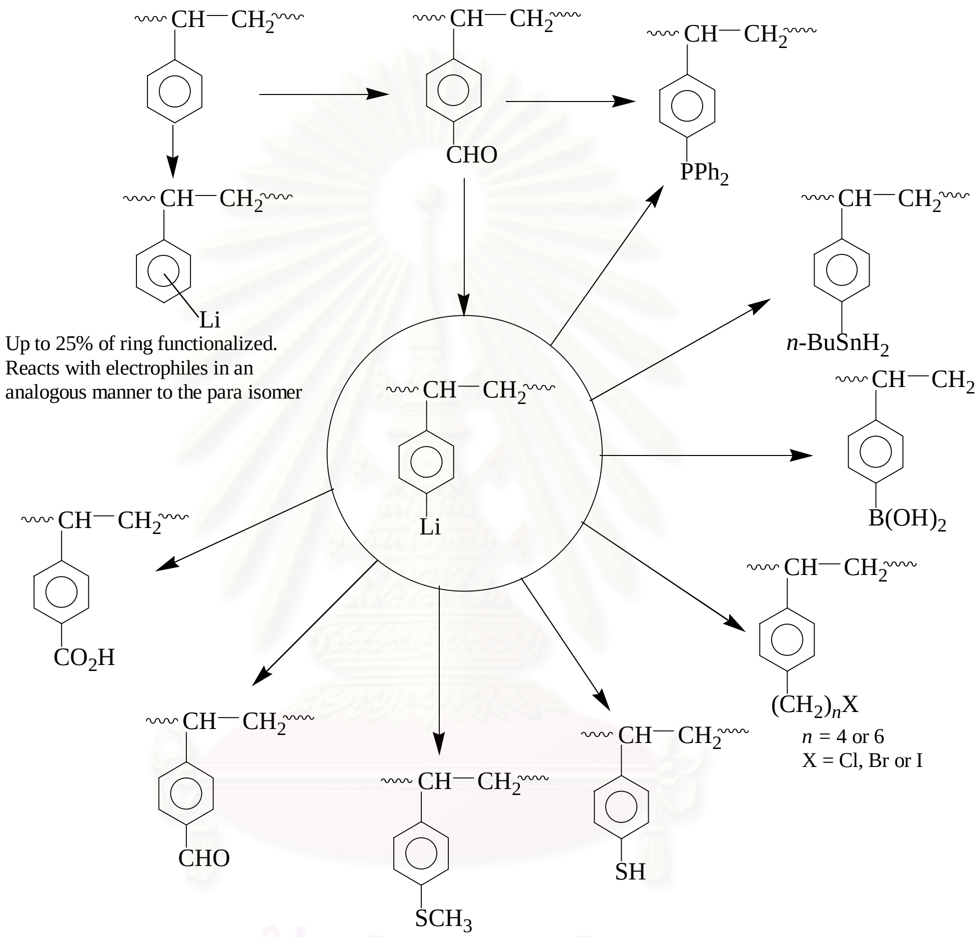


Figure 2.5 Lithiation of polystyrene and reaction of the product with electrophiles.[23]

Crosslinked polystyrene, which can be prepared in a various physical forms, is usually used as the catalyst support.[23] The ideal group used to bind a metal complex to a support should be chemically inert under the reactions conditions and form a nonlabile link between metal complex and the support. Numerous have been developed for functionalization of polystyrene with suitable ligands as shown in Fig. 2.6.

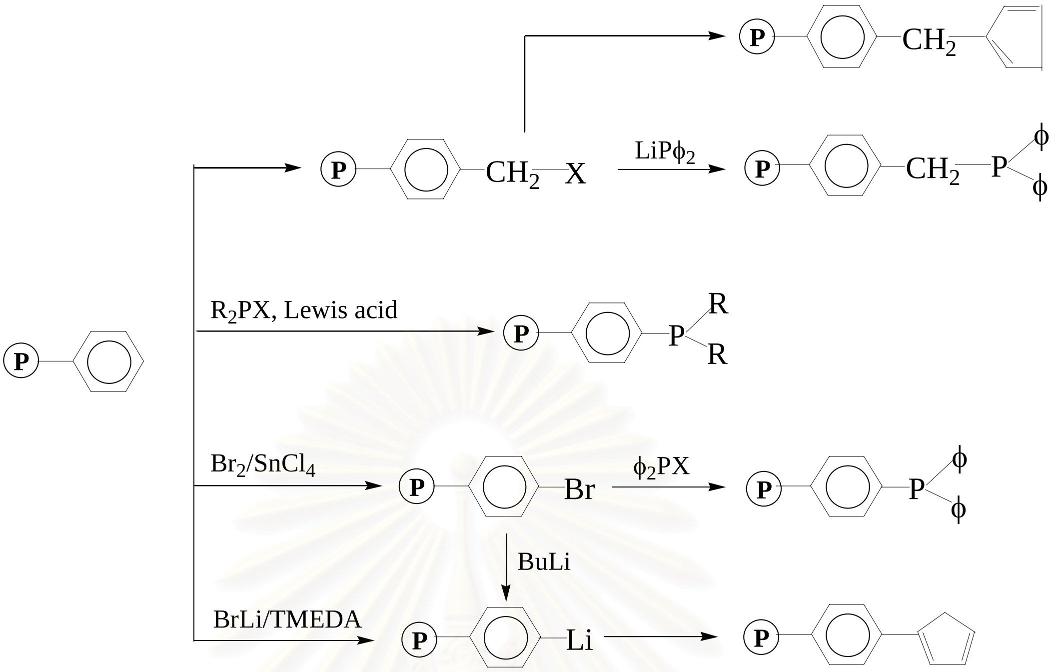


Figure 2.6 Functionalization of polystyrene with ligands.[23]

2.5 Polymer-supported catalyst[24]

Polymer-supported catalysts not only offer the potential to conserve energy inputs into the formation of chemical products, but also promise judicious use of metals. Expensive or precious species, such as optically active molecules or platinum group metal complexes, will be retained more efficiently when immobilised on a polymer support, which in turn might offer the prospect of efficient reuse or recycling.[24]

Corrosive, noxious or toxic species are generally rendered safe when bound to a macromolecule. Corrosive reagents are essentially encapsulated and do not make contact with apparatus or plant. Volatile hazardous species have their vapor pressures reduced almost at zero, and toxic low molecular weight compounds become extremely difficult to absorb through the lungs, skin or digestive systems, when thus immobilized. Supported systems have much to offer in the drive to develop more environmentally acceptable processes, and could make a significant contribution toward clean chemistry.

Some entirely chemical advantages might also arise. When a reactive species is attached to a polymer backbone, providing the number of groups attached (*the loading*) is kept low, the species will behave as though present in infinite dilution. Likewise one or more reactive species might be loaded in high concentration on the polymer, so that they are forced to be in constant proximity to each other.

These tricks may be used to reduce side reactions in the subsequent application or alternatively to enhance rates or selectivity. Indeed, reactive species with only a transilent existence in homogeneous solution can be stabilized for useful exploitation when attached to a polymer support.[25]

The following methods have been used to prepare polymeric catalyst:

(a) Functionalization of available crosslinked or non-crosslinked polymers and subsequent incorporation of transition metal complexes.
(b) Homopolymerization or copolymerization of functionalized monomers and subsequent incorporation of transition metal complexes.
(c) Homopolymerization or copolymerization of monomers already containing metal complexes.
(d) Homopolymerization and copolymerization of metal complexes containing polymerizable groups.

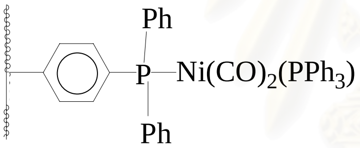
When a soluble catalyst is attached to an insoluble support through a covalently binding ligand, the complex becomes heterogeneous when considered at the bulk level but is essentially identical to a soluble analog or a molecular level. Consequently, the catalyst will show properties somewhere between the two major catalyst classes. Therefore a hybrid catalyst combines the best properties of both systems while minimizing their inherent deficiencies, for example, increased substrate size selectivity, increased activity, easier catalyst recovery and recycle, and protection of catalyst sites from water.[26]

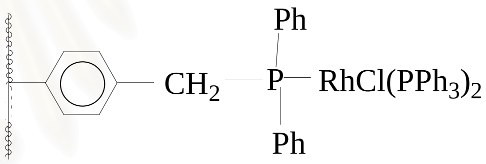
Anchoring ligands to insoluble polymeric supports, followed by complexation with transition metals, results in polymers having catalytic potential. These metal complexes, hybrids of homogeneous and heterogeneous approaches, are attractive because they often permit the activity of soluble catalysts and the ease of product separation inherent in heterogeneous catalysts. In referring to this class of catalysts the names “polymer-anchored”, “polymer-bound”, “hybrid phase”, or “polymer-supported” are common.[27]

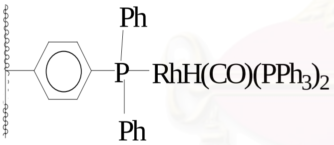
It seemed that all homogeneous catalysts could be bound, the decreases in activity were minimal and the catalysts could be filtered off and recycled indefinitely with little or no loss in activity. There appeared to be no reason why commercialization would not be just around the corner. Polymer-bound catalysts have shown as Table 2.2.

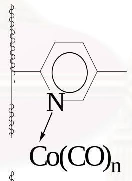
Table 2.2 Some examples of polymer-supported metal complexes[23]

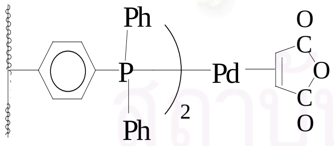
Cross-linked polystyrene as the polymer

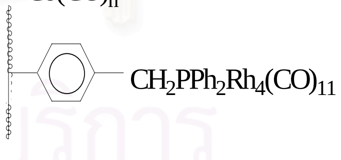


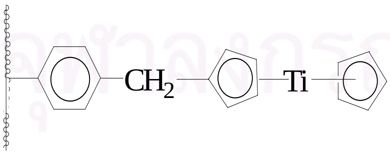


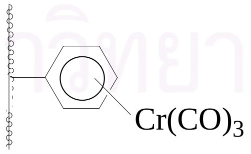




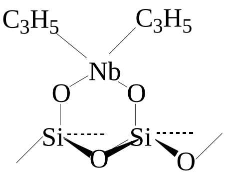


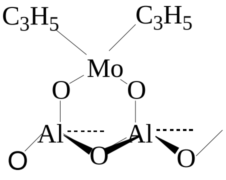


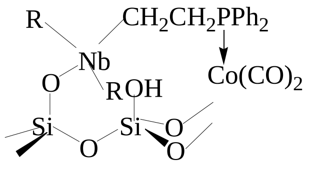




Silica or alumina as the polymer







The percent substitution, determined by elemental analysis, indicates the moles of ligand per gram of support. Local concentration of the ligand is important and elemental concentrations are rapidly determined by electron microprobe in a 1-10 micron surface area. By examining a polymer bead half section, it is easily found the distribution of a non-carbon ligand inside the polymer. A completely random distribution throughout the polymer is easiest for model studies; however, for practical applications it may be advantageous to functionalize only the outer polymer volume.[23]

The selectivity of the polymer-bound catalyst towards substrates with different sizes can be controlled by the loading of the catalyst on the polymer support and also by the solvent used to swell the polymer. The selectivity increases with decreasing swelling ratio of the polymer in the solvent and, in the more polar solvent, it depends on the separation of the functionality.

2.5.1 Characterization of polymer-supported catalysts[23]

The mechanical behavior of gel or macroporous supports might limit the use. For instance, gel particles with very low crosslink density, which might be desirable in order to limit the diffusion control of the reactions inside the polymer, are too soft to be handled and cannot be used in a column reactor. On the other hand, macroporous resins with large pore volumes are very brittle and will disintegrate into very fine particles upon attrition in a stirred reactor. In other cases, the swelling-deswelling process which may occur during the life of the supported reagent may cause it to disintegrate into smaller particles.

Determination of the organometallic structures present in a polymer-supported catalyst is best carried out spectroscopically and, if the supported species are uniform in structure, they can often be characterized quite well by comparison of their spectra with the spectra of molecular analogues. The most easily and widely applied technique continues to be infrared spectroscopy.[28]

NMR spectroscopy is used to characterize organometallic structure in polymers. ^{31}P-NMR spectroscopy has been used to characterize polymer-supported rhodium complexes. The supports were made by homopolymerization of *p*-styryldiphenylphosphine or *p*-styryldicyclohexylphosphine. Each ring of the highly swelled polymer was functionalized with a phosphine ligand, giving a sample with a high signal strength and a nearly uniform environment of phosphorus in the polymer.

X-ray photoelectron spectroscopy (XPS) has been used to characterize metals in polymers. The data often provide clear evidence of changes in metal oxidation state resulting from catalyst treatment.

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 functionalization of the chloromethylated polymer.

2.5.2 Catalytic reactions of polymer-supported catalysts[23]

Catalytic reactions of polymer-supported catalysts include hydrogenation, hydrosilylation, hydroformylation, acetoxylation, polymerization, and oligomerization. The practical advantages of using polymer-supported catalysts are the fact that they are generally prepared from crosslinked polymers. Such polymers are insoluble in all solvents and, with the sizes of bead commonly used, more than 99% of the reactive groups are within the beads, for the reactions to take place the low-molecular weight reactants must diffuse into the polymer beads. With microporous polymers diffusion will be very slow unless the reaction solvent swells the beads. The beads must not only be swollen initially but throughout the reaction.

Hydrogenation

With one of the triphenylphosphine ligands replaced by phosphenated polystyrene, the activity of the complex as a hydrogenation catalyst is much more sensitive to the size of the alkene substrate. This is attributed to restriction of movement of the solution within the cross-linked polymer, indicating that most of the reaction is taking place inside the polymer bead. These supported complexes are still somewhat less reactive than related unsupported complexes in homogeneous solution.

Hydroformylation

During hydroformylation of a terminal alkene the aldehyde group can add to the end carbon atom giving a linear aldehyde, or to the internal carbon atom giving a branched aldehyde. The amount of each aldehyde is dependent on the catalyst. Rh-BINAPHOS-catalyzed asymmetric hydroformylation in the presence of dense and sc CO_2 phase has been recently reported. Under the conditions used it is shown that at 60^oC increasing the CO_2 density diminishes the enantioselectivity of styrene hydroformylation. The sulfonated ligands BDPPTS, and sulfonated 1,2-bis (diphenylphosphinomethyl)cyclobutane have also been used for Rh-catalyzed asymmetric hydroformylation of styrene with modest results. The ratio of branched to linear aldehyde product is 3:1, and the best e.e. value of 2-phenylpropane is only 17%.[29]

Hydrosilylation

Hydrosilylation is a reaction of some considerable interest and potential to the organosilicon industry. The usual homogeneous hydrosilylation catalyst is chloroplatinic acid, and its use necessitates the reaction being carried out in inconvenient alcoholic solvents to obtain a homogeneous reaction mixture. Unsupported chloroplatinic acid is a good hydrosilylation catalyst, and rhodium trichloride shows little activity. However, putting these two compounds onto polymer supports has a marked effect on their activity.

2.6 Literature reviews

2.6.1 Polymer supports

In 1982, Balakrishnan T. and Ford W. T. studied the particle size distribution of poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) by suspension copolymerization using gelatin and poly(diallyldimethylammonium chloride) as suspending agent and AIBN as an initiator. The particle size was controlled by stirring speed (300-400 rpm), suspending agent, the relative of monomer and aqueous phase.[23]

In 1984, Poinescu Ig. C. and coworkers studied the formation of the permanent porosity in the classical matrix, styrene-divinylbenzene copolymers, using cyclohexane, cyclohexanol, or cyclohexanone as diluent. The data concerning porous networks were confirmed with the solvent-polymer interaction and the cohesive energy density, which are important in the prediction of copolymer porosity. The diluent volume and the divinylbenzene percent strongly influence the porous structure of the network. Cyclohexanol was the most efficient diluent for building up the highest porosity even at low percents of divinylbenzene.[24]

In 2000, Carre E. L. and coworkers reported the preparation of chloromethylated polystyrene resins (Merrifield type), Fig. 2.7, and used for polymer-supported metal catalysts. 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 butyrate and 11-bromoundecanol producing the desired product, 11-bromoundecyl butylrate in 86% yield. It can be reused twice (79% yield).[25]

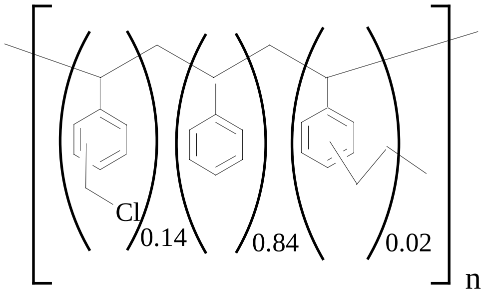


Figure 2.7 Crosslinked chloromethylated polystyrene (Merrifield resin).

2.6.2 Polymer-supported catalysts for hydrogenation

In 1981, Pertici P. and coworkers reported that polystyrene-ruthenium complexes could be prepared by reacting (η^6-cycloocta-1,3,5-triene) (η^4-cycloocta-1,5-diene) ruthenium (0), [(η^6-cycloocta-1,3,5-triene) (COT)], [(η^4-cycloocta-1,5-diene) (COD)] with polystyrene under hydrogen pressure atmosphere at room temperature. Then were used for hydrogenation of unsaturated substrate under rather mild conditions (25-80^{o}C, P_{H_2} 50 atm). The catalysts were easily separated from products, allowing the reuse of them without appreciable loss of activity.[33]

In 1981, Nicolaides C. P. and Coville N. J used poly(styrene-*co*-divinylbenzene)-supported $RuCl_2(PPh_3)_3$ (Fig.2.8) as a catalyst in kinetic study of olefins hydrogenation. The ratio of Ru to Cl ~1/2 and Ru to P ratio is ~1/3. The supported catalyst was analysed by X-ray fluorescence and gave a Ru/Cl/P ratio of 1/1/3. It was found that hydrogenation of olefins could be performed at 30^{o}C with benzene/ethanol as solvent. The rate of reaction depends on amount of catalyst, ratio of solvent mixture (benzene/ethanol = 1/1), concentration of olefin and hydrogen pressure of 0.82 atm. The effect of catalyst and olefin concentrations on the reaction rate of 1-hexene hydrogenation is shown in Table 2.3. The results indicate that an increase in olefin concentration results in a rate enchancement, however the rate reaches a limiting value at high olefin concentration. [34]

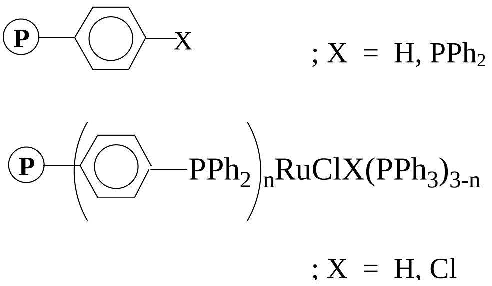


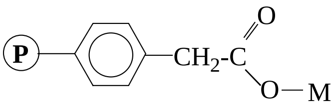
Figure 2.8 Structures of the polymer supports and polymer-supported ruthenium (phosphine) catalysts.

Table 2.3 Hydrogenation of 1-hexene: Effect of varying catalyst and olefin concentrations using polymer-supported ruthenium (phosphine) catalyst[34]

Catalyst (mg)	Olefins (ml)	Rate (ml/min)
100	0.30	0.44
	0.40	0.58
	0.60	0.76
	0.80	0.90
150	0.30	1.38
	0.40	1.00
	0.60	0.83
	0.80	0.90
300	0.25	1.58
	0.40	1.91
	0.80	2.37

Reaction conditions: temperature 30 ^{o}C, hydrogen pressure of 0.82 atm, solvent ~ 20 ml (benzene/ethanol =1/1) and stirring rate 500 rpm

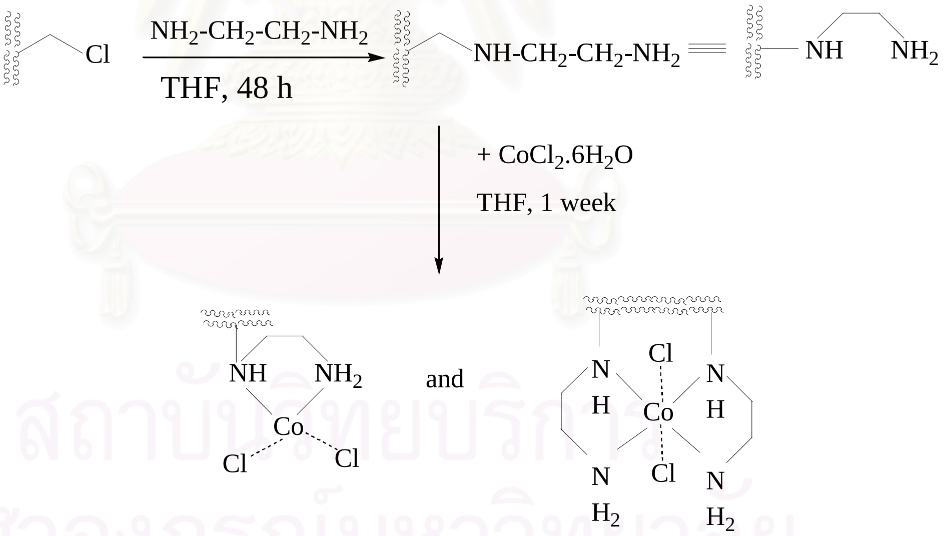
In 1984, Nicolaides C. P. and Coville N. J. presented that poly(styrene-*co*-divinylbenzene)-supported ruthenium (acetate) as catalyst was used in the hydrogenation of olefins at 80^{o}C, hydrogen pressure of 1 atm. It was found that the reaction rates follow the order: terminal olefin > cyclic olefin > alkynes. The metal complex was coordinated to polymer predominantly via a unidentate acetate coordination mode, Fig. 2.9.[35]



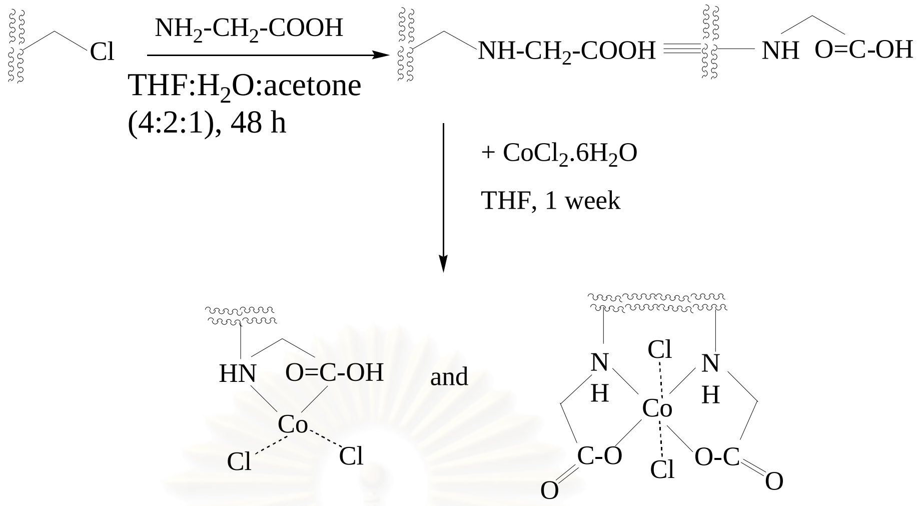
P = poly(styrene-*co*-divinylbenzene)
M = ruthenium complex

Figure 2.9 Unidentate metal-carboxylate on polymer.

In 1988, Gokak D. T. and coworkers 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 2.6-2.7. The catalysts were used for hydrogenation of 1-octene at 25-55^oC, hydrogen pressure of 1-5 atm. The conversion was low (15% of 1-octene).[36]



Scheme 2.6 The structures of polymer-supported cobalt (ethylenediamine) complexes.



Scheme 2.7 The structures of polymer-supported cobalt (glycine) complexes.

In 1989, Gokak D. T. and Ram R. N. synthesized polymer-supported rhodium (I) catalyst, prepared by reacting 2, 5% poly(styrene-*co*-divinylbenzene) beads with ethylenediamine as ligand and $RhCl_3(PPh_3)_3$. It was used for hydrogenation of 1-octene in THF at 35-50^{o}C and atmospheric pressure. The results are summarised in Table 2.4. It was found that the rate of reaction depends on 1-octene and catalyst concentration and temperature.[37]

Table 2.4 Hydrogenation of 1-octene using polymer-supported rhodium (ethylenediamine) catalyst[37]

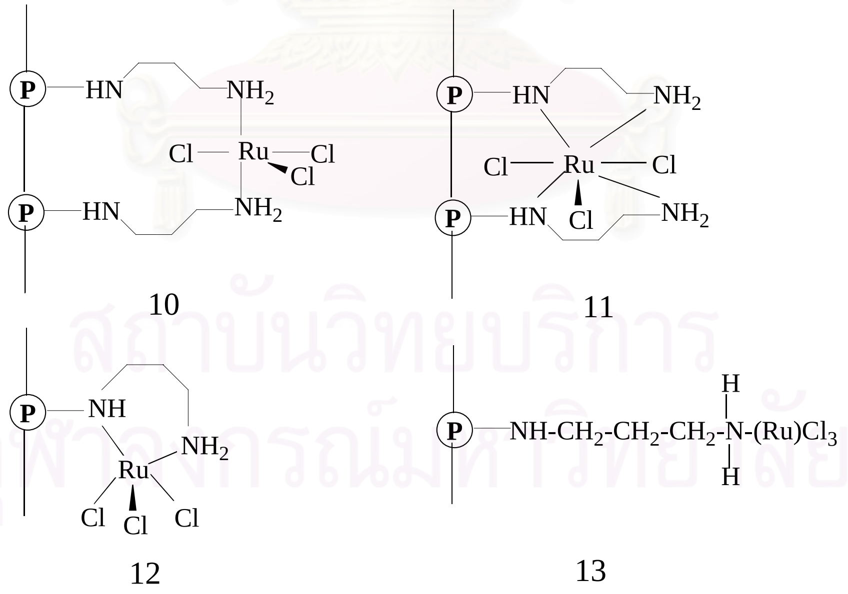
Temperature (^{o}C)	Rh present ($Mml^{-1}x10^9$)	1-Octene ($Mml^{-1}x10^6$)	Rate of reaction ($Mmin^{-1}x10^6$)
30	2.18	6.38	0.48
30	8.75	6.38	0.66
30	8.75	12.76	0.73
30	8.75	19.15	0.94
30	8.75	25.53	1.12
30	13.10	6.38	0.82
35	2.18	6.38	0.66
35	8.75	6.38	0.87
35	8.75	12.76	1.07
35	8.75	19.15	1.86

Table 2.4 (cont.)

Temperature (^oC)	Rh present ($Mml^{-1}x10^9$)	1-Octene ($Mml^{-1}x10^6$)	Rate of reaction ($Mmin^{-1}x10^6$)
35	8.75	25.53	1.92
40	8.75	12.76	4.50
50	8.75	12.76	7.27

Reaction conditions: time 2 h, hydrogen pressure of 1 atm, and stirring rate 650 rpm

In 1990, Shan J. N. and Gokak D. T. prepared the polymer-supported ruthenium (trimethylenediamine) complex, by reacting 3 and 10% poly(styrene-*co*-divinylbenzene) porous beads with bifunctional ligand (trimethylenediamine) and $RuCl_3.xH_2O$, for hydrogenation of cyclohexene at 30-50°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 (10-13) were proposed as shown in Scheme 2.8.[38]



Scheme 2.8 Possible structures of polymer-supported ruthenium (trimethylenediamine) complexes.

In 1993 Shan J. N. and Ram R. N. studied kinetic of cyclohexene hydrogenation using polymer-supported ruthenium (trimethylenediamine) complex in methanol. The polymer-supported metal catalyst was active and stable. The rate of hydrogenation was calculated from the slope of the plots of volume of H_2. A summary of the results is given in Table 2.5. It was found that the rate of reaction depends on the amount of catalyst, cyclohexene concentration, hydrogen pressure and temperature.[39]

Table 2.5 Summary of the kinetics of hydrogenation of cyclohexene for polymer-supported ruthenium (trimethylenediamine) at atmospheric pressure[39]

Catalyst (Ru mol $l^{-1}x10^5$)	Cyclohexene (mol $l^{-1}x10^3$)	Temperature (^oC)	Methanol (ml)	Rate of reaction (ml min^{-1} $x10^2$)
0.544	1.38	35	25	1.25
0.544	3.94	35	25	2.13
0.544	6.82	35	25	2.59
0.277	3.94	35	25	1.75
0.831	3.94	35	25	2.25
1.385	3.94	35	25	2.55
1.360	9.86	30	10	1.45
1.360	9.86	35	10	1.75
1.360	9.86	40	10	2.15
1.360	9.86	45	10	2.37
1.360	9.86	50	10	2.60
0.544	3.94	35	10	1.75
0.544	3.94	35	20	1.92
0.544	3.94	35	40	2.45

In 1995, Li H. and He B. used polystyrene-supported transition metal (Ru, Rh, Pd) as catalyst in hydrogenation of polyunsaturated cycloolefins and unsaturated carbonyl compounds. The complexes of polymer-supported metal catalyst were prepared by using phosphine or amine as a ligand. The structures of polymer-supported metal catalysts were shown in Fig. 2.10. The results show that the catalysts produce products in high conversion and selectivity. Moreover, the pore size, crosslinkage of polymer support, donor atom (P or N) for the tailoring of support and ligand were important factor. Pore sizes of supports are appropriate 200 A^o. If it is too large or too small, the catalyst's selectivity will decrease. The selectivity of polymeric phosphine-supported rhodium catalyst is higher than that of the polymeric amine-supported catalyst.[11]

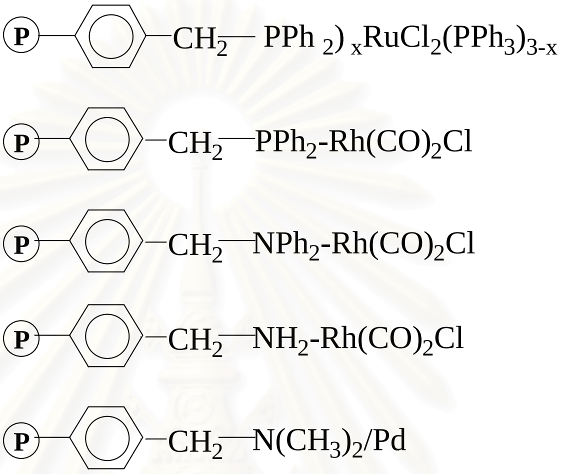
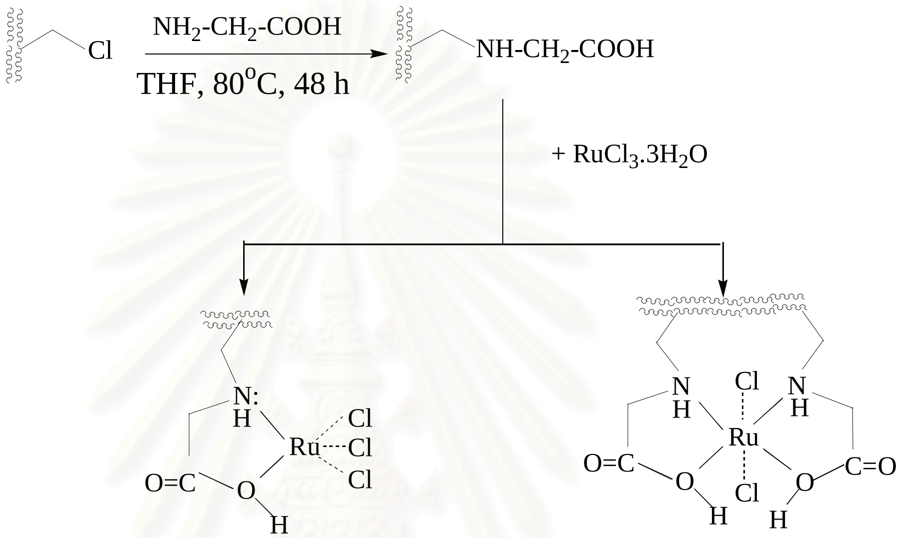


Figure 2.10 The structures of polymer-supported metal catalysts (Ru, Rh, Pd).

In 1996, Giannandrea R. and coworkers reported the use of isocyanide polymer-bound Rh(PPh$_3$)$_3$Cl (Fig. 2.11) as a catalyst in hydrogenation of organic substrates (alkenes, alkynes, aldehydes, nitriles and nitro compounds) under mild conditions (temperature at room temperature to 50^{o}C). The conversion was high (80-100%). Unsaturated aldehydes are converted into saturated aldehydes whereas nitriles are selectively converted into the corresponding imines or secondary amines depending on the reaction conditions. The catalyst was recycled six times with negligible loss of activity.[40]

Figure 2.11 The structure of polymer-supported rhodium (isocyanide) catalyst.

In 1996, Patel D. R. and coworkers reported the preparation of 8% chloromethylated poly(styrene-*co*-divinylbenzene) support with $RuCl_3.3H_2O$. The catalytic study of hydrogenation of nitrobenzene in methanol was shown that the rate of reaction is slow in atmospheric pressure and 30-45°C. A probable structure of the catalyst is shown in Scheme 2.9.[41]



Scheme 2.9 Probable structures of the polymer-supported ruthenium (glycine) complexes.

In 2000, Bianchini C. and coworkers presented that $[(sulphos)Ru(NHMe)_3]$ $(OSO_2CF_3)/SiO_2$ (Fig 2.12) was used as a supported hydrogen-bounded ruthenium catalyst in hydrogenation of benzylideneacetone and benzonitrile. It was found that benzylideneactone and benzonitrile could be transformed to benzylacetone and benzylidebenzylamine, respectively, in high yield and selectivity.[42]

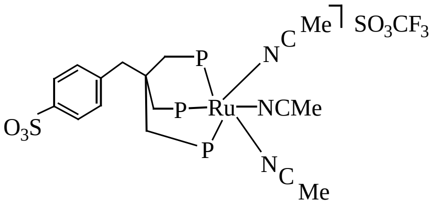


Figure 2.12 The structure of $[(sulphos)Ru(NHMe)_3]$ $(OSO_2CF_3)/SiO_2$.

In 2002, Ros T.G. and coworkers prepared rhodium complexes by reacting $RhCl_3.2H_2O$ with *N*-phenyl anthranilic acid (PAA) and anthranilic acid (AA) ligands (Fig 2.13) and used for hydrogenation of cyclohexene in DMF as solvent. It appears that rhodium interacts with PAA and AA *via* the carboxyl and amine groups. The catalytic activities of RhPAA and RhAA are comparable in cyclohexene hydrogenation.[43]

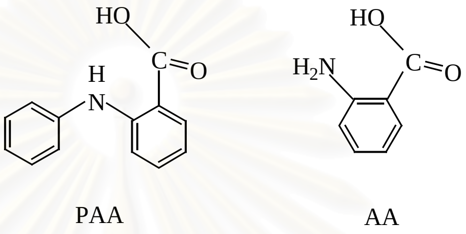


Figure 2.13 The structures of PAA and AA.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The used chemicals in this experiment were analytical grade.

Chemicals	Supplier
Acetone	Merck KGaA., Germany
2-Aminopyridine	Merck KGaA., Germany
Benzoyl peroxide	Aldrich Chemical Co., Inc., USA
Calcium hydride	Merck KGaA., Germany
Cyclohexanone	Merck KGaA., Germany
Cyclooctene	Fluka Chemie A.G., Switzerland
Chloromethyled polystyrene bead (2%DVB, ~4.3 mmolCl/polymer)	Fluka Chemie A.G., Switzerland
Chloromethyled polystyrene bead (5%DVB, ~5.5 mmolCl/polymer)	Fluka Chemie A.G., Switzerland
1,3-Diaminopropane	Merck KGaA., Germany
Dimethyl sulfoxide (DMSO)	Fluka Chemie A.G., Switzerland
Dioxane	Aldrich Chemical Co., Inc., USA
Divinyl benzene monomer	Fluka Chemie A.G., Switzerland
Ethanol	Merck KGaA., Germany
Methanol	Merck KGaA., Germany
Poly(vinyl pyrrolidone)	Aldrich Chemical Co., Inc., USA
Ruthenium trichloride hydrate ($RuCl_3.xH_2O$)	Aldrich Chemical Co., Inc., USA
Rhodium trichloride ($RhCl_3$)	Aldrich Chemical Co., Inc., USA
Sodium hydrogen carbonate ($NaHCO_3$)	Merck KGaA., Germany
Sodium hydroxide	Aldrich Chemical Co., Inc., USA

Chemicals	Supplier
Sodium sulfate anhydrous	Aldrich Chemical Co., Inc., USA
Styrene monomer	Fluka Chemie A.G., Switzerland
Toluene	Fluka Chemie A.G., Switzerland
Triphenylphosphine (PPh_3)	Fluka Chemie A.G., Switzerland
Tris(triphenylphosphine) ruthenium dichloride ($Ru(PPh_3)_3Cl_2$)	Fluka Chemie A.G., Switzerland
Ultra high purity nitrogen gas (99.99%)	Thai Industry Gas Co., Ltd., Thailand
Vinyl benzyl chloride monomer	Fluka Chemie A.G., Switzerland

3.2 Equipment

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

3.2.1 Schlenk line

Schlenk line consists of nitrogen and vacuum line. The vacuum line was equipped with the solvent trap and pump, respectively. The nitrogen line was connected to the moisture trap and oil bubbler. The Schlenk line was shown in Fig. 3.1.

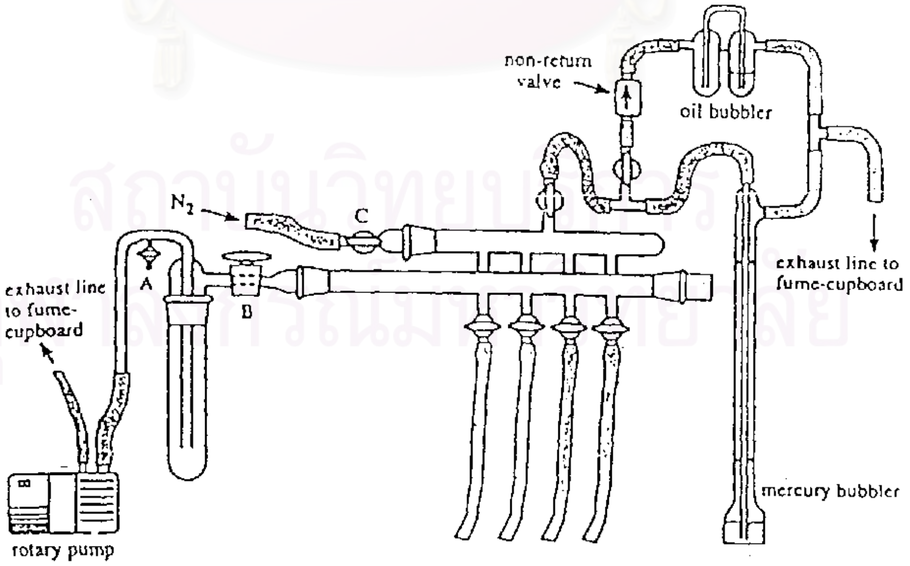


Figure 3.1 Schlenk line.

3.2.2 Schlenk flask

A flask with a side-arm for use with inert gas. The standard requirements of a joint to connect to other items of glassware provide access to the contents for connection to the manifold. Some typical examples are shown in Fig. 3.2.

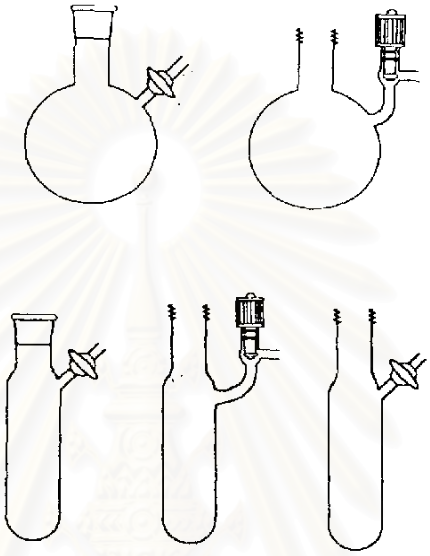


Figure 3.2 Schlenk flask.

3.2.3 Heating bath

The heating oil bath with thermometer was used for high polymerization reaction.

3.2.4 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.

3.2.5 Inert gas supply

The inert gas (nitrogen) was passed through drying column with 4^{o}A molecular sieves. The inert gas was used to feed in the nitrogen line of Schlenk line and polymerization reactor.

3.2.6 Hydrogen gas supply

The hydrogen gas was used to feed in hydrogenation reactor.

3.2.7 Parr reactor

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

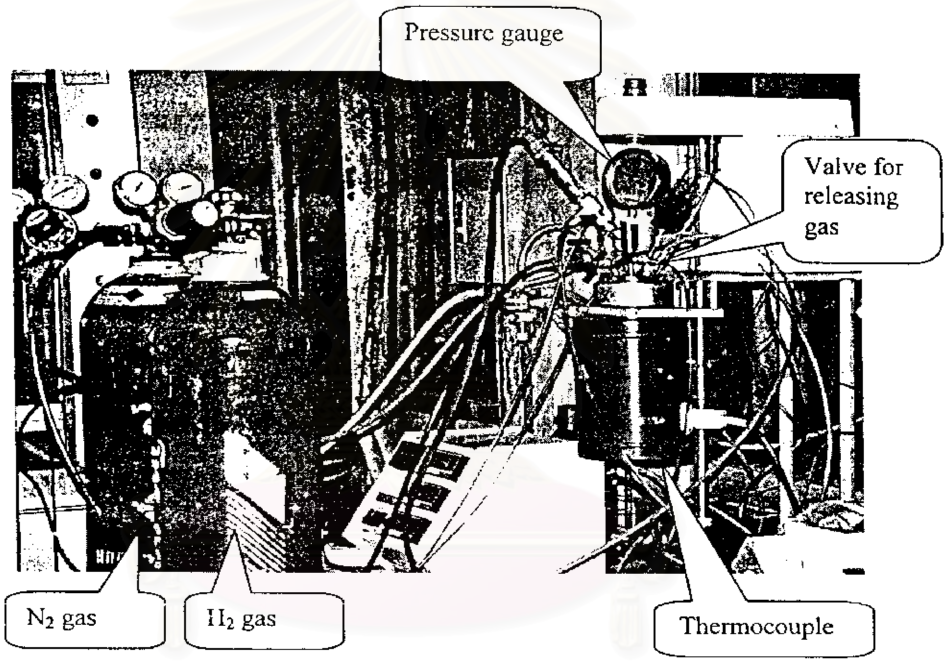


Figure 3.3 Parr reactor.

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 cm^{-1} 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 products. The conditions are as follows:

Column : DB wax
Programmed temperature : 50^{O}C for 5 min, increased at 10^{O}C/min to 120 ^{O}C
Detector temperature : Flame ionization (FID)
Detector temperature : 220 ^{o}C
Injector temperature : 220 ^{o}C
Carrier gas : N_2
Flow rate : 1

3.3.3 UV-visible spectrophotometry (UV-vis)

UV-visible spectra were recorded on Milton Roy Spectronic 3000 in range of 200-700 nm.

3.3.4 Thermogravimetric analysis (TGA)

Thermogravimetric measurements were performed on a Netzsch thermogravimetric analyzer (STA 409C) at the heating rate of 10°C/min under air/nitrogen (30/20) atmosphere.

3.3.5 X-ray fluorescence spectrometry (XRF)

XRF was performed on a Phillips P.W. 1410 X-ray fluorescence spectrometer.

3.3.6 Scanning electron microscopy (SEM)

The polymer beads were coated with a thin layer of gold in vacuum and photographed using scanning electron microscopy on the Joel JSM-6400 to characterize surface morphology of the polymer beads.

3.3.7 Elemental analysis (EA)

The carbon, hydrogen and nitrogen content were measured by CHN elemental analyzer at Science and Technological Research Equipment Centre Chulalongkorn University or Department of Chemistry, Faculty of Science, Chiangmai University. The polymers were weighed by ultramicrobalance and then were placed in a sample holder. They were oxidized in combustion zone under pure oxygen gas atmosphere. The carbon, hydrogen and nitrogen were oxidized to carbon dioxide, vapor and nitrogen gas, respectively. All of gases were passed to gas control zone where the pressure, temperature and volume were determined. Each gas was separated and detected quantitatively by thermal conductivity detector in separation zone and detector zone, respectively.

3.4 Procedure

3.4.1 Purification of chemicals

3.4.1.1 Styrene and other monomers

Styrene monomer of 99 % purity containing 40-50 ppm *p-tert*-butylcatechol was purified by washing with an equal volume of 10 % aqueous solution of sodium hydroxide until liquid became clear, followed by deionized water until the litmus paper showed that all the base had been removed, and dried several hours with anhydrous sodium sulfate. Then it was distilled before use under reduced pressure.

3.4.1.2 Solvents

-Anhydrous diethyl ether was dried in 4 A^o molecular seives.

-Toluene was dried with sodium metal and benzophenone. Freshly cut sodium (1g) was added into the solvent (650 ml) and benzophenone (4g) was added. After swirling to dissolve benzophenone, a blue color should form at the metal surface. This localized color will initially disappear but, on refluxing, the bulk of the solvent should gradually turned green and then blue as all of water and oxidizing impurities were removed.

-Ethanol and methanol were dried with magnesium ethoxide, prepared by placing 5 g of clean dry magnesium turnings and 0.5 g of iodine in a 2 l flask, followed by 50-75 ml of absolute ethanol, and warmed the mixture until a vigorous reaction occurs. When this subsides, heating was continued until all the magnesium was converted to magnesium ethoxide. Up to 1 l of ethanol was added and, after an hour reflux, it was distilled off.

3.4.2 Synthesis of polymer-supported catalysts

3.4.2.1 Preparation of polymer support

Crosslinked poly(styrene-co-DVB-co-VBC) (10% DVB)

10% Crosslinked poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) was prepared by suspension polymerization, in 500 ml four-necked-round-bottom flask with water-cooled condenser and mechanical stirrer. Poly(vinyl pyrrolidone) was previously dissolved in 200 ml of deionized water in a beaker at 50^{o}C to obtain 80^{o}C, clear aqueous solution was added carefully to the flask.

For monomer phase, the following monomers: styrene (30 ml, 80 %wt/v), divinylbenzene (3 ml, 10 %wt/v), vinylbenzyl chloride (3 ml, 10 %wt/v) and cyclohexanol (6 ml) were mixed in another flask. Then the monomer phase was added slowly to the above mentioned aqueous phase. This was followed by addition of benzoyl peroxide (0.2 g, 0.2%wt). Nitrogen was swept through the flask for 30 min, and a slight positive pressure of nitrogen was maintained throughout the polymerization. Heating was switched off 7 hours after the introduction of the reaction mixture.

The beads were washed with water and methanol and dried for 24 hours at 60^{o}C under vacuum. Polymer beads were sieved and measured morphology by scanning electron microscope.

3.4.2.2 Preparation of functionalised polymer by anchoring ligands

2% Polymer bound 2-aminopyridyl ligand [2P-2AP] [44]

2-Aminopyridine (1.43 g, 15.2 mmol) was added slowly to a suspension of 2% chloromethylated poly(styrene-*co*-divinylbenzene) beads (1.08 g) in 20 ml dioxane. The contents were heated to 120°C for 24 h while continuously stirring. The solution was cooled and the 2-aminopyridyl-bound polymer was filtered, washed successively with dioxane, water, alcohol and finally with petroleum ether (60-80°C). The yellow colored functionalised polymer was dried under reduced pressure at 70°C for 12 h.

5% Polymer bound 2-aminopyridyl ligand [5P-2AP] [44]

This complex was prepared by the same methodology as that described for 2P-2AP but replaced 2% chloromethylated poly(styrene-*co*-divinylbenzene) beads with 5% chloromethylated poly(styrene-*co*-divinylbenzene) beads.

10% Polymer bound 2-aminopyridyl ligand [10P-2AP] [44]

This complex was prepared by the same methodology as that described for 2P-2AP but replaced 2% chloromethylated poly(styrene-*co*-divinylbenzene) beads with 10% chloromethylated poly(styrene-*co*-divinylbenzene) beads.

5% Polymer bound Schiff base-2-aminopyridyl ligand [5P-SB-2AP] [45]

5% Chloromethylated poly(styrene-*co*-divinylbenzene) beads (2.02 g) were oxidized to the aldehyde by reaction with 20 ml dimethylsulfoxide and sodium hydrogen carbonate (0.516 g) at 155^{o}C for 6 h. The dried aldehyde bearing polymer was allowed to swell for 1 h in methanol (20 ml). To this a solution of 2-aminopyridine (2.25 g; 0.024 mole) in methanol was added dropwise over a period of 45 min with constant stirring. The contents were refluxed for 6 h. After cooling to room temperature the pale yellow colored polymer beads were filtered, washed thoroughly with methanol, petroleum ether (40-60^{o}C) and dried in vacuo at 70 ^{o}C for 24 h.

5% Polymer bound Schiff base-1,3-diaminopropane ligand [5P-SB-DP] [45]

This complex was prepared by the same methodology as that described for 5P-SB-2AP but replaced 2-aminopyridine with 1,3-diaminopropane (2 ml, 0.024 mole).

3.4.2.3 Preparation of polymer-supported ruthenium catalysts

2% Polymer-supported Ru(III)-2-aminopyridyl [2P-Ru-2AP] [44]

The loading of the metal onto the polymer was carried out as follows: 0.5092 g of 2% DVB functionalised polymer beads were kept in contact with dry ethanol 20 ml for 45 min. To this was added hydrated ruthenium(III) chloride (0.0273g, 0.132 mmol) and stirred for 10 days at room temperature. The color of the beads changed from pale yellow to dark brown during this period indicating the formation of the metal complex on the polymer matrix. After 10 days the dark brown colored polymer was filtered, washed thoroughly with ethanol to ensure the removal of any unreacted metal chloride and dried in vacuum.

5%Polymer-supported Ru(III)-2-aminopyridyl [5P-Ru-2AP] [44]

This complex was prepared by the same methodology as that described for 2% polymer-supported ruthenium-2-aminopyridyl but replaced 2%DVB polymer beads with 5%DVB polymer beads. The gray solid of 5% polymer-supported ruthenium-2-aminopyridyl was obtained.

10% Polymer-supported Ru(III)-2-aminopyridyl [10P-Ru-2AP] [44]

This complex was prepared by the same methodology as that described for 2% polymer-supported ruthenium-2-aminopyridyl but replaced 2%DVB polymer beads with 10%DVB polymer beads. The brown solid of 10% polymer-supported ruthenium-2-aminopyridyl was obtained.

5% Polymer-supported Ru(III)-Schiff base 2-aminopyridyl [5P-Ru-SB-2AP][39]

This complex was prepared by the same methodology as that described for 2% polymer-supported ruthenium-2-aminopyridyl but replaced polymer bound 2-aminopyridyl with polymer bound Schiff base-2-aminopyridyl. The gray solid of polymer-supported ruthenium Schiff base 2-aminopyridyl was obtained.

5% Polymer-supported Ru(III)- Schiff base 1,3-diaminopropane [5P-Ru-SB-DP] [45]

This complex was prepared by the same methodology as that described for 2% polymer-supported ruthenium-2-aminopyridyl but replaced polymer bound 2-aminopyridyl with polymer bound Schiff base-1,3-diaminopropane. The gray solid of polymer-supported ruthenium- Schiff base 1,3-diaminopropane was obtained.

3.4.2.4 Preparation of polymer-supported rhodium catalyst

2% Polymer-supported Rh(III)-2-aminopyridyl [2P-Rh-2AP][44]

This complex was prepared by the same methodology as that described for 2% polymer-supported ruthenium-2-aminopyridyl but replaced ruthenium chloride with rhodium chloride. The orange solid of polymer-supported rhodium-2-aminopyridyl was obtained.

3.4.3 Synthesis of homogeneous catalysts

Ruthenium-2-aminopyridyl complex [Ru-2AP]

2-Aminopyridine (0.14 g, 1.5 mmol) was added an ethanolic solution of hydrated ruthenium(III) chloride (0.10 g, 0.5 mmol) and stirred for 10 days at room temperature. The color of solution changed from dark red color to dark green during this period indicating the formation of metal complex. After 10 days the complex was washed thoroughly with ethanol and dried in vacuum.

Ruthenium-1,3-diaminopropane complex [Ru-DP]

This complex was prepared by the same methodology as that described for Ru-2-aminopyridyl but replaced 2-aminopyridine with 1,3-diaminopropane (0.125 g, 1.5 mmol).

Ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane [Ru-DA]

1,3-Di(2,6-diisopropylphenyl)aminopropane (0.53 g, 1.36 mmol) was dissolved in acetonitrile 10 ml. Then, *tris*-(triphenylphosphine) ruthenium(II) dichloride (1.01g, 1.05 mmol) was added to a solution of diamine. The mixture was continuously stirred and refluxed for 48 h. After that, the mixture was removed the solvent by vacuum. Then, dichloromethane was added onto yellow solid. It was filtered. The filtrate was pumped off solvent to obtain yellow solid.

3.5 Hydrogenation of cyclooctene with catalysts

The hydrogenation of cyclooctene was catalyzed by supported catalysts in Parr reactor. The mixture of clooctene (1.3 ml, 10 mmol), supported catalyst (0.025 g) and methanol (50 ml) were introduced into the reactor, flushed with hydrogen. Then the hydrogen gas pressure, temperature and stirring speed was set as follows:

-Hydrogen pressure 1, 3, 5 and 10 atm
-Temperature at 35, 60 °C
-Stirring speed at 600 rpm

3.6 Test of catalyst leaching of metal from polymer support

Polymer-supported ruthenium (2-aminopyridyl) catalyst (0.03 g) and ethanol (5 ml) were added into 50 ml round-bottom flask, stirred at 60 °C, reaction time 24 h. Then, it was filtered, washed thoroughly with methanol and dried. It was used for hydrogenation of cyclooctene at 60 °C, reaction time 5 h and hydrogen pressure of 5 atm.

3.7 Recycling catalyst for cyclooctene hydrogenation

After being used in cyclooctene hydrogenation, the catalyst was separated from the reaction mixture by filtration, washed with methanol and dried. Then it was reused for hydrogenation by charging fresh cyclooctene at 60 ^{o}C, reaction time 5 h and hydrogen pressure of 5 atm.

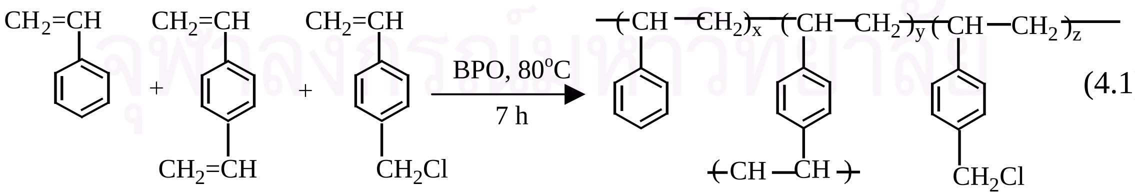
CHAPTER IV

RESULTS AND DISCUSSION

4.1 The formation of crosslinked polymer beads

In the polymerization, the aqueous phase composed of poly(vinyl pyrrolidone) was gently mixed in order to prevent foam forming. Styrene monomer, divinylbenzene monomer, vinylbenzyl chloride monomer and benzoyl peroxide in the organic phase should be mixed well before adding into the aqueous phase. The spherical beads could be obtained.

Poly(vinyl pyrrolidone), suspending agent, was added in order to hinder the coalescence of monomer droplets and sticking together of the beads during the course of polymerization. Reproducibility of this polymerization was obtained. It was observed that poly(vinyl pyrrolidone) affected on the formation of the polymer beads. If the amount of poly(vinyl pyrrolidone) was more than 2 g, the organic phase would become sticky yellowish solution when the polymerization was completed. These events could be explained that both reagents acted as suspending agent to stabilize the charge around the polymer beads. Polymer supports with different percentage of crosslinks were made under the same condition. Polymerization was carried out with 2%, 5% and 10% DVB as shown below.



(4.1)

The FT-IR spectrum of poly(styrene-*co*-divinyl benzene-*co*-vinylbenzyl chloride) exhibited the characteristic absorption peaks and are presented in Appendix A and shown in Table 4.1.

Table 4.1 The assignment for the FT-IR spectra of 2, 5, 10 % DVB crosslinked polymeric support

Wave number (cm^{-1})			**Assignment**
2%DVB	**5%DVB**	**10%DVB**	
3024	3024	3024	C-H aromatic st.
2921	2921	2921	C-H aliphatic st.
1625	1625	1625	C=C aromatic st.
763	763	763	C-Cl st.

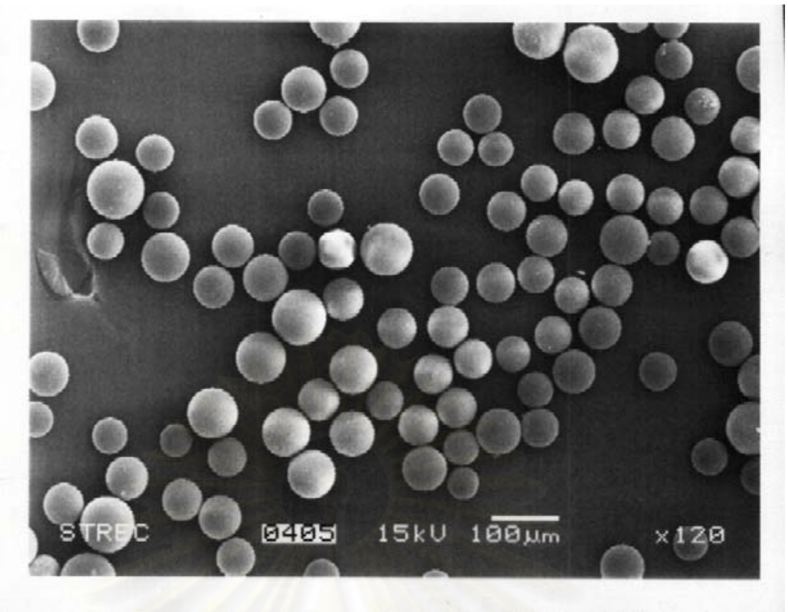
The absence of bands at 900-990 cm^{-1} (terminal double bond) and the presence of C-H stretching vibration at 2921 cm^{-1} indicated the polymerization and the benzene C=C stretching appeared at 1625 cm^{-1} and the C-Cl stretching vibrations appeared at 763 cm^{-1}.

Table 4.2 The elemental analysis of poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride)

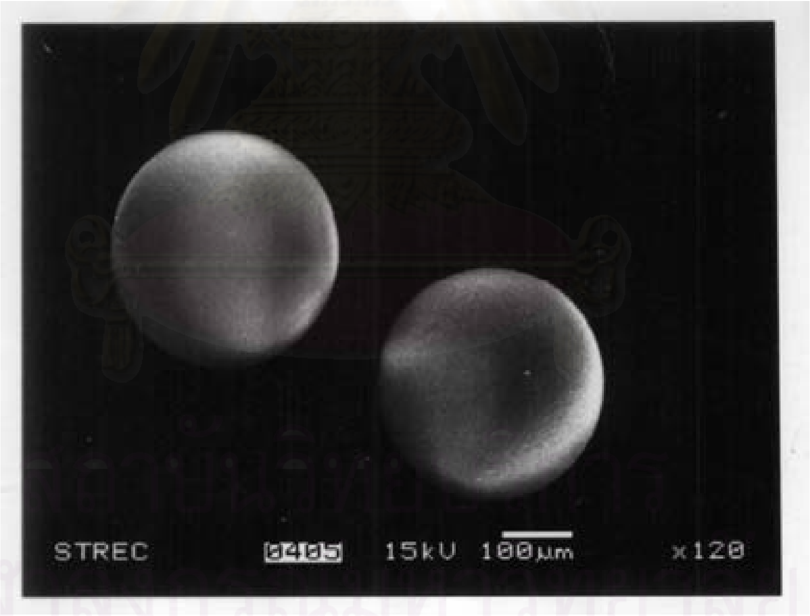
Polymer support	Elemental			
	%C (Found)	%H (Found)	%Cl (Found)	%Cl (Calculated)
2%DVB	88.70	6.75	4.30	4.55
5%DVB	88.67	6.03	5.50	5.30
10%DVB	80.79	6.46	ND	12.75

ND = not determined

In Table 4.2, the chloride content of polymeric supports could be calculated by substracting %C and %H. Although the monomer feed ratios of styrene and divinylbenzene were varied, all polymer supports had similar structure.

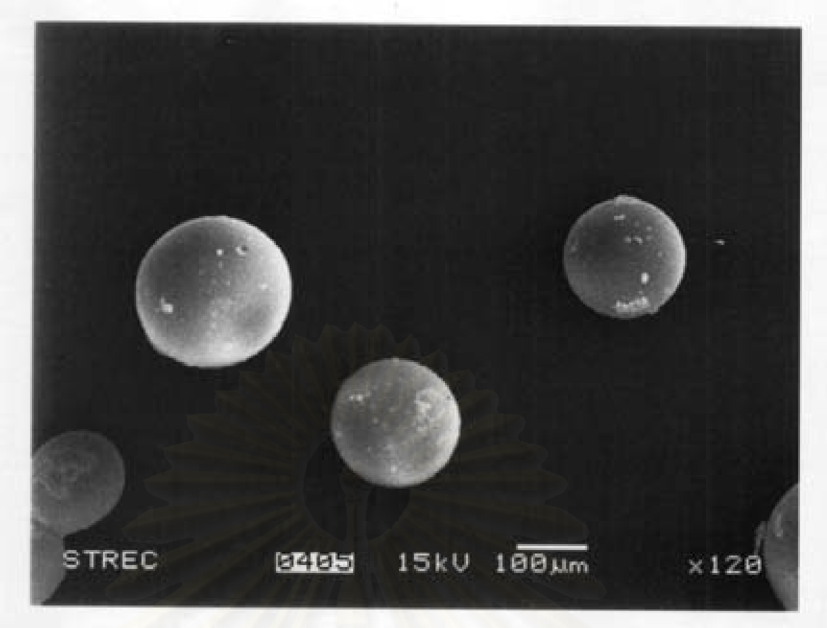


(a) 2%DVB



(b) 5%DVB

Figure 4.1 Scanning electron micrographs of poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl cholride) with (a) 2%DVB, (b) 5%DVB and (c) 10%DVB.



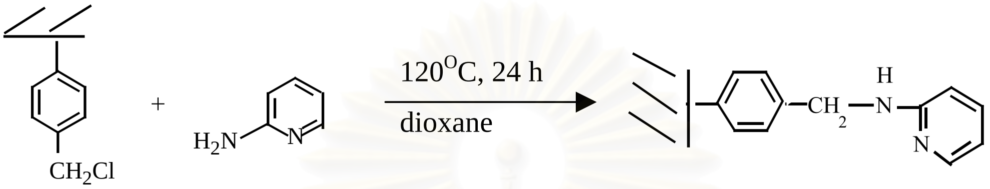
(c) 10% DVB

Figure 4.1(cont.) Scanning electron micrographs of poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl cholride) with (a) 2%DVB, (b) 5%DVB and (c) 10%DVB.

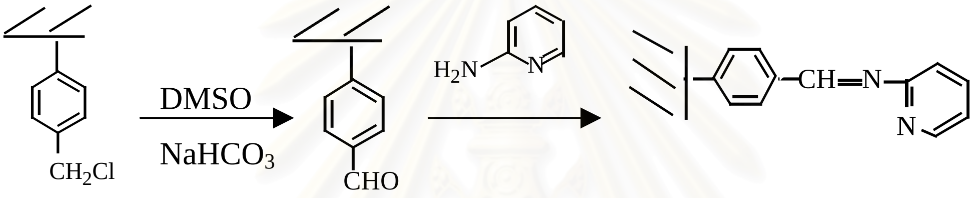
From the scanning electron micrographs of poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl cholride), it can be seen that 2% DVB and 5% DVB which obtained commercially have bead size (diameter) of 0.58 μm (200-400 mesh) and 2.61 μm (40-60 mesh), respectively, while 10% DVB which was synthesized in this work has bead size of 1.52 μm (100-120 mesh). The difference in size depends on stirred speed (rpm), suspending agent and time.

4.2 Anchoring ligand to polymer supports

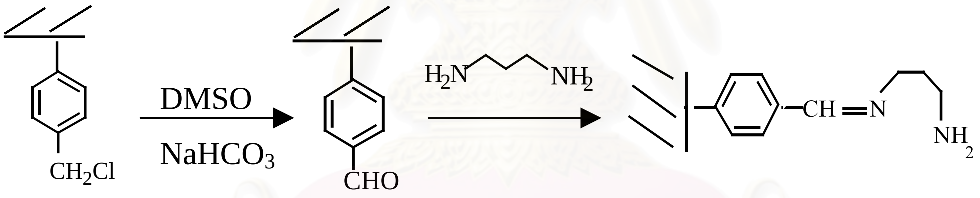
2-Aminopyridine and 1,3-diaminopropane are bidentate ligands, which can bind the metal through the amino and pyridyl ring. Anchoring bidentate ligand to poly (styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) was accomplished through the reaction sequence shown in the following equations (4.2)-(4.4).[44,45]



(4.2)



(4.3)



(4.4)

The FT-IR spectra of poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) anchoring ligand exhibited the characteristic absorption peaks as assignments shown in Table 4.3.

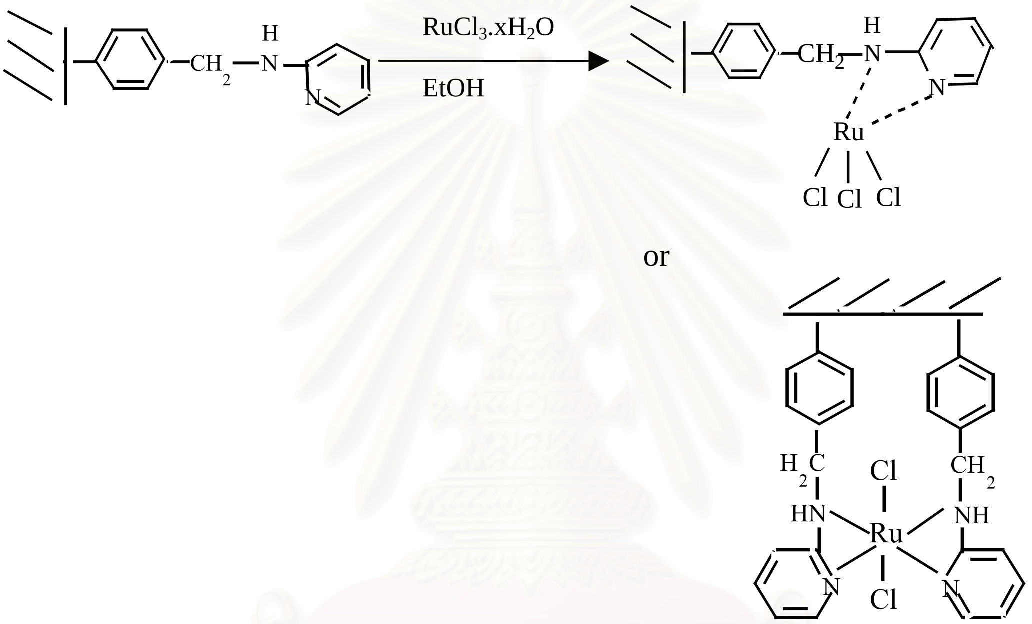
Table 4.3 The assignment for the FT-IR spectra of poly(styrene-*co*-divinyl benzene-*co*-vinylbenzyl chloride) anchoring 2-aminopyridyl, Schiff base 2-aminopyridine and Schiff base 1,3-diaminopropane ligands

Wave number (cm^{-1})			**Assignment**
5P-2AP	5P-SB-2AP	5P-SB-DP	
3343	-	3409	N-H st.
3137	3016	3090	C-H aromatic st.
2920	2924	2921	C-H aliphatic st.
1672	1690	1658	C=N st.
1621	1644	1630	C=C aromatic st.
1442	1444	1442	C-N aromatic amine st.
700	702	699	C-Cl st.

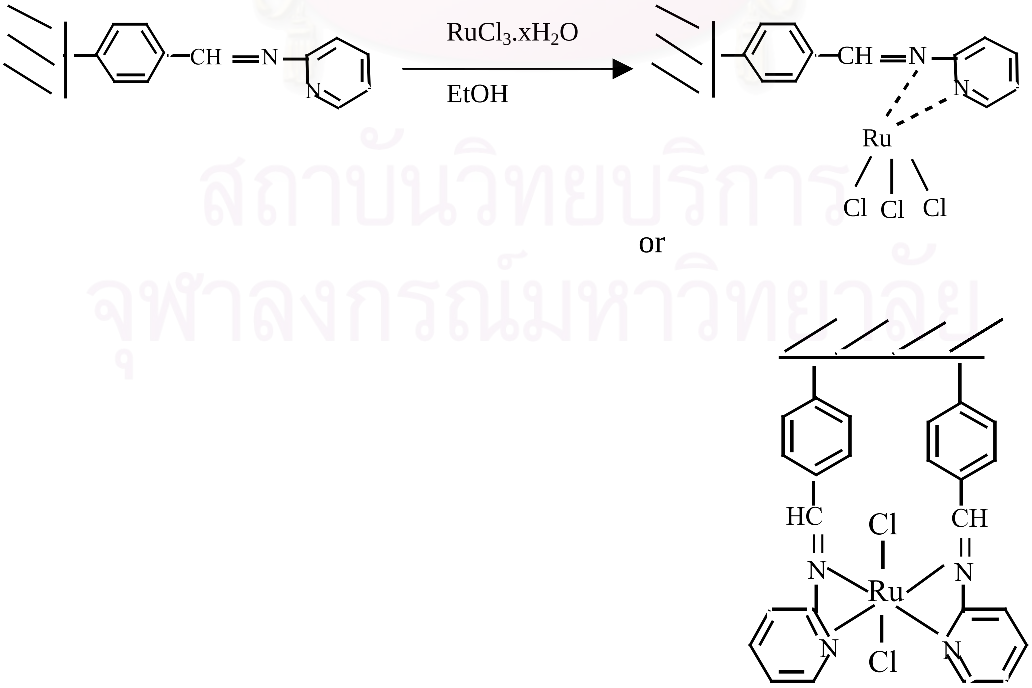
The N-H stretching vibration of ligands was present around 3340-3409 cm^{-1}. The C-H stretching vibration appeared at 2921-2924 cm^{-1}. The C=N stretching vibration appeared around 1658-1690 cm^{-1} and the C-N stretching vibration appeared around 1442 cm^{-1}, indicating that chloride group was replaced by amino group from 2-aminopyridyl and 1,3-diaminopropane ligands. The benzene C=C stretching appeared around 1621-1644 cm^{-1}. The C-Cl stretching vibration appeared around 699-702 cm^{-1}, indicating remaining chloride. Therefore, the replacement was not complete.

4.3 Preparation of polymer-supported ruthenium catalysts

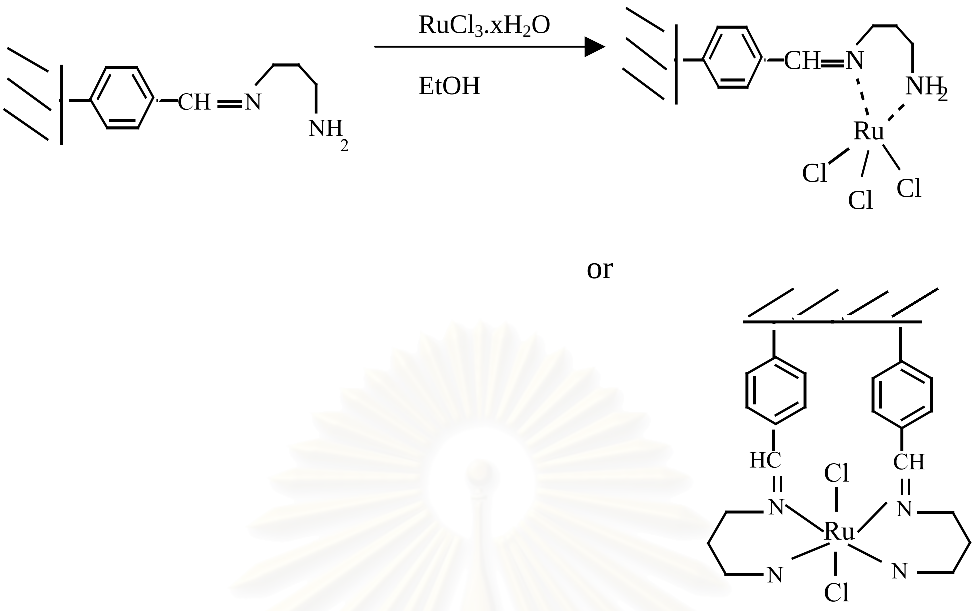
Poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) anchoring either 2-aminopyridyl ligand or 1,3-diaminopropane ligand was reacted with ruthenium trichloride hydrate to obtain polymer-supported Ru(III) catalyst. The possible structures are proposed as shown in equations (4.5), (4.6) and (4.7), respectively.[44,45]



(4.5)



(4.6)



(4.7)

The ruthenium metal was attached to functionalized polymer. It was observed that the yellowish reactants of 5P-Ru-2AP, 5P-Ru-SB-2AP and 5P-Ru-SB-DP became gray colored products and the yellowish reactants of 2P-Ru-2AP and 10P-Ru-2AP became dark brown colored products.

The FT-IR spectra of polymer-supported ruthenium catalysts exhibited the characteristic absorption peaks as assignments shown in Table 4.4.

Table 4.4 The assignment for the FT-IR spectra of polymer-supported ruthenium complexes

Wave number (cm^{-1})			**Assignment**
5P-Ru-2AP	5P-Ru-SB-2AP	5P-Ru-SB-DP	
3400	-	3452	N-H st.
2921	2919	2924	C-H aliphatic st.
1678	1690	1690	C=N st.
1658	1645	1644	C=C aromatic st.
1510	1516	1521	C-N st.
700	707	707	C-Cl st.

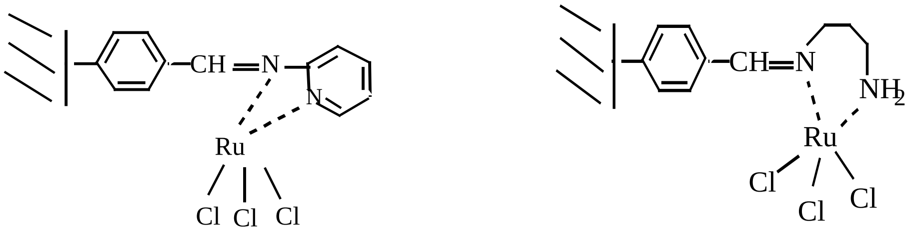
The N-H stretching vibration of ligands was present around 3400-3452 cm^{-1}. The C-H stretching vibration appeared around 2919-2924 cm^{-1}. The C=N stretching vibration appeared at 1678-1690 cm^{-1} and the C-N stretching vibration appeared around 1510-1521 cm^{-1}. The C-Cl stretching vibration appeared around 700-707 cm^{-1}. In the case of Schiff base bearing polymer, a strong band of C=N stretching at 1690 cm^{-1} undergoes a position shift from 1658 cm^{-1}. The results show that coordination of the ligand nitrogen to the ruthenium (III) metal ion was occurred.[45]

The ruthenium content in polymer-supported catalysts was determined by X-ray fluorescence spectroscopy (XRF) as shown in Table 4.5 and the elemental analysis is shown in Table 4.6.

Table 4.5 The ruthenium content in the polymer-supported ruthenium catalysts

Polymer-supported catalyst	Ruthenium content (%wt of polymer)
2 P-Ru-2AP	3.2
5 P-Ru-2AP	3.9
10 P Ru-2AP	0.8
5 P-Ru-SB-2AP	2.1
5 P-Ru-SB-DP	1.0

From Table 4.5, it was found that the different degree of crosslinking of polymer beads affects the ruthenium content. At 10% crosslinked polymer-supported ruthenium catalyst, the ruthenium content was low, this might be due to the fact that the highly crosslink was more porous and had smaller size, so the attaching of ruthenium on polymer support decreased. For the same degree of crosslink of polymer beads, it was found that the content of ruthenium on polymer support was different with the different ligand. In Fig. 4.2, the Schiff base 2-aminopyridyl ligand forms complex with ruthenium better than 1,3-diaminopropane.



(a) (b)

Figure 4.2 Polymer-supported ruthenium catalysts (a) 5P- Ru-SB-2AP
(b) 5P-Ru-SB-DP

Table 4.6 The elemental analysis of polymer-supported ruthenium catalysts

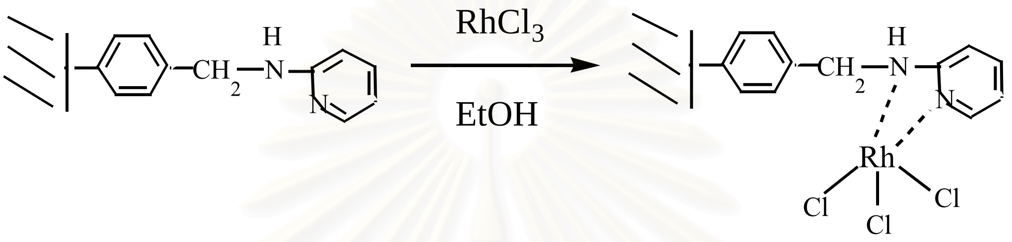
Polymer support	Elemental			
	%C (Found)	%H (Found)	%N (Found)	%Cl (Calculated)
2P-Ru-2AP	63.03	6.73	6.95	20.09
5P-Ru-2AP	62.10	6.00	8.77	19.23
10P-Ru-2AP	72.05	6.03	1.66	19.46
5P-Ru-SB-2AP	72.70	6.85	3.05	15.30
5P-Ru-SB-DP	68.77	5.38	1.85	23.00

The attachment of 2-aminopyridyl ligand on the polymer was confirmed by elemental analysis. The %C, %H and %N were obtained by elemental analysis, %Cl of polymeric supports could be calculated by substracting %C, %H and %N.

The higher percentage of nitrogen found in 2% and 5% polymer-supported ruthenium catalysts compared to that in 10% polymer-supported ruthenium catalyst is attributed to the surface characteristic. For the polymer support with a higher degree of crosslinking (10%), the network has a dense, relatively larger number of inaccessible larger size domains, so that porous sizes are small, as a result, less functionalization is achieved.[29]

4.4 Preparation of polymer-supported rhodium catalyst

In this work, rhodium complex was also tested for comparison. Polymer-supported Rh catalyst was synthesized as in equation (4.8) from the reaction of poly (styrene-*co*-divinyl benzene-*co*-vinylbenzyl chloride) anchoring 2-aminopyridyl ligand with rhodium trichloride.



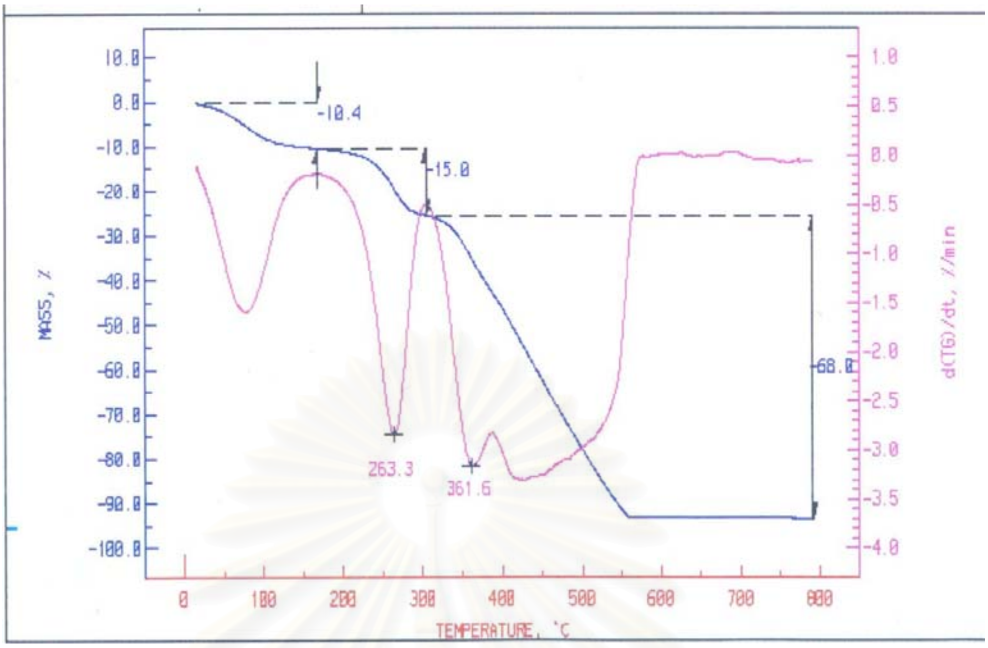
(4.8)

The rhodium content in polymer-supported rhodium catalyst determined by X-ray fluorescence spectroscopy. The content of rhodium on polymer support was 0.18%wt.

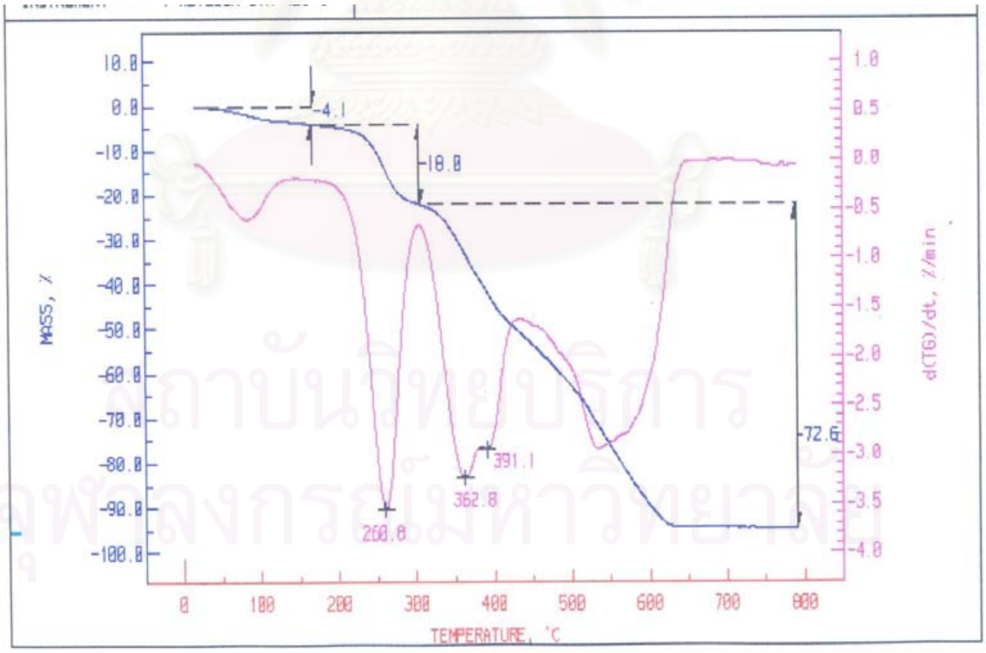
From FT-IR spectrum the N-H stretching vibration of ligand was present at 3437 cm^{-1}. The C=N stretching vibration of ligand appeared at 1654 cm^{-1} and the C-N stretching vibration appeared at 1522 cm^{-1}.

4.5 Thermal stability of polymer-supported catalysts

Thermal stability of poly(styrene-*co*-divinyl benzene-*co*-vinylbenzyl chloride)-supported ruthenium and rhodium catalysts were determined by thermogravimetric analysis. Representative thermogravimetric analysis was depicted in Fig. 4.3 and Table 4.7.



(a) Polymer-supported ruthenium catalyst.



(b) Polymer-supported rhodium catalyst.

Figure 4.3 TGA of polymer-supported Ru (a) and Rh (b) catalysts.

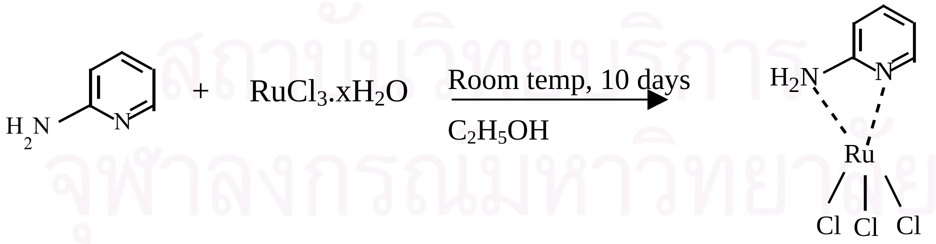
Table 4.7 TGA data of polymer-supported catalysts

Sample	**Degradation temp. (^oC)**	**Weight loss (%)**
5P-Ru-2AP	362	68
	263	15
2P-Rh-2AP	391	52
	363	23
	260	18

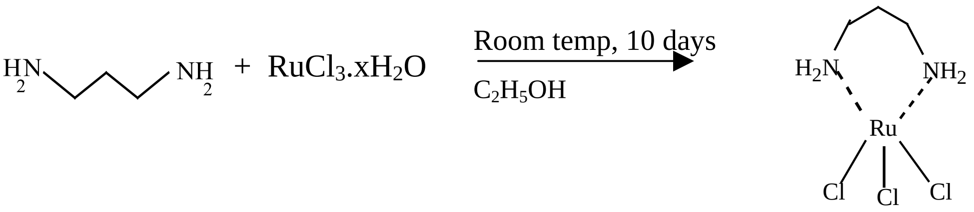
From Fig.4.3 and Table 4.7, it was found that polymer-supported catalysts were degraded around 360-390 ^oC. However, at around 260 ^oC a weight loss of about 15-18%was clearly observed. It was possible that either the 2-aminopyridyl moiety or the chlorides might dissociate at this temperature from the catalyst surface.

4.6 Homogeneous catalysts

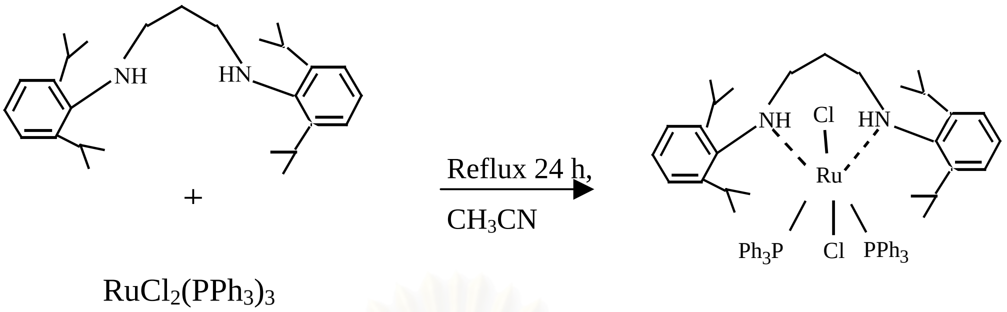
Ruthenium complexes were prepared by reacting 2-aminopyridyl and 1,3-diaminopropane ligands with rutheniun chloride hydrate as shown in equations (4.9)-(4.10). Ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane complex was synthesized as shown in equation (4.11).



(4.9)



(4.10)



(4.11)

Ruthenium complexes were characterized by UV-visible and FT-IR. Fig. 4.4 shows a representative UV-visible spectrum of ruthenium-2-aminopyridyl. The various frequencies are assigned in Tables 4.8-4.9.

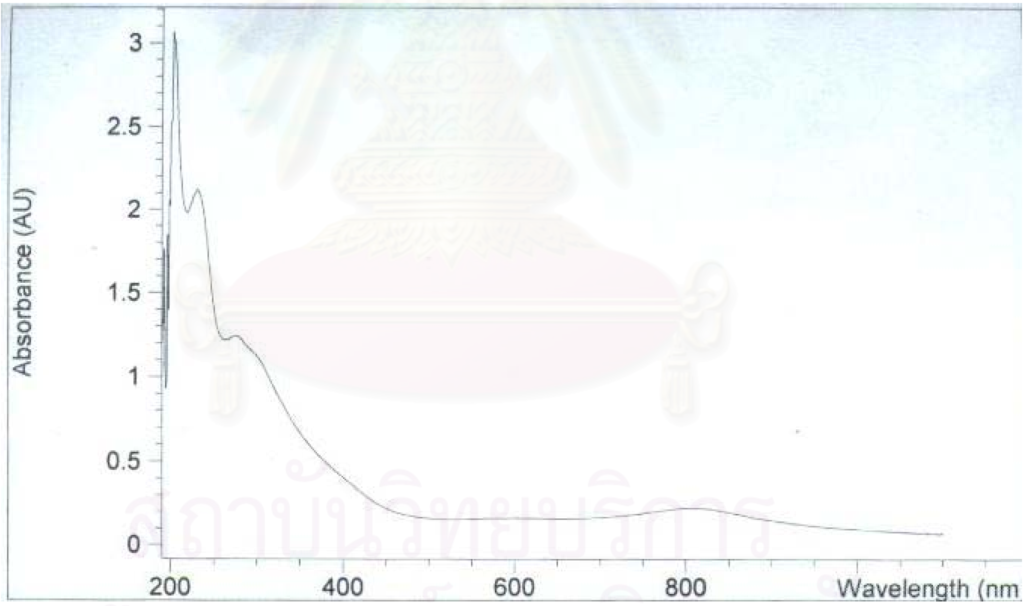


Figure 4.4 The UV-visible spectrum of ruthenium-2-aminopyridyl complex.

Table 4.8 The assignment for the UV-visible spectra of ruthenium complexes

Wavelength (nm)			**Assignment**
Ru-2AP	**Ru-DP**	**Ru-DA**	
231	231	226	N-H
275	275	265	Ru-N

The band at λ_{max} 231 nm was assigned to N-H of ligand. Furthermore, the band at λ_{max} 275 nm was assigned to Ru-N. The results show complex formation of ruthenium with ligand via N-atom.[38]

Table 4.9 The assignment for the FT-IR spectra of ruthenium complexes

Wave number (cm^{-1})			**Assignment**
Ru-2AP	**Ru-DP**	**Ru-DA**	
3306	3400	3410	N-H st.
3100	3016	3090	C-H aromatic st.
2920	2921	2950	C-H aliphatic st.
1663	-	-	C=N st.
1621	1613	1630	C=C aromatic st.
1484	1449	1480	C-N st.

The N-H stretching vibration of ligands was presented around 3306-3410 cm^{-1}. The C=N stretching vibration appeared at 1663 cm^{-1}, the benzene C=C stretching appeared around 1613-1630 $cm^{-1}$and the C-N stretching vibration appeared around 1449-1484 cm^{-1}. From the results shown above, it was confirmed that the ruthenium attached to the ligand.[38]

4.7 Hydrogenation of cyclooctene by homogeneous catalysts

Rutheium complexes synthesized and tested catalytic activity in homogeneous hydrogenation were: ruthenium-2-aminopyridyl [Ru-2AP], ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane [Ru-DA] and ruthenium-1,3-diaminopropane [Ru-DP]. In this work, the activity of catalyst was reported as %conversion, which is the same as %yield, since only one product (cyclooctane) was detected.

4.7.1 Ruthenium-2-aminopyridyl [Ru-2AP]

The reaction conditions: 35- 60 °C, hydrogen pressure of 1-10 atm, reaction time of 1-5 h and catalyst concentration 0.020 mmole have been studied. The results of hydrogenation of cyclooctene catalyzed by ruthenium-2-aminopyridyl complex are presented in Appendix A1 and shown in Fig. 4.5.

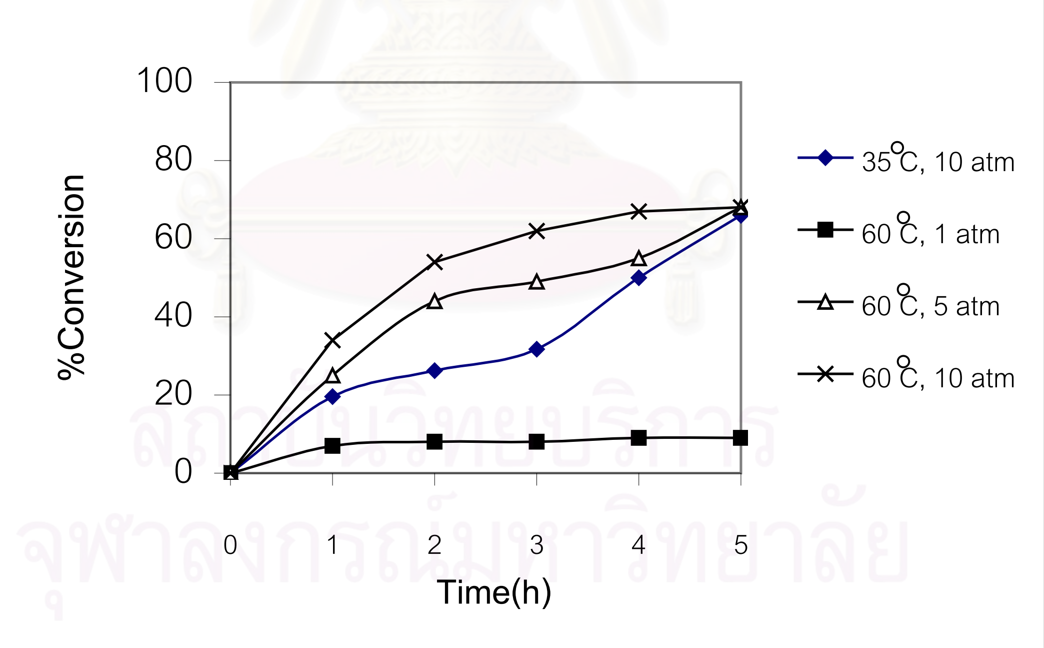


Figure 4.5 Hydrogenation of cyclooctene catalyzed by ruthenium-2-aminopyridyl.

From Fig. 4.5, it can be seen that within 1-4 hours, at hydrogen pressure of 10 atm, %conversion at 60°C is higher than that at 35°C. This is due to the faster rate of hydrogenation.[46]

At low hydrogen pressure (1 atm), yield was low, hydrogen may be not enough to complete the hydrogenation. At higher pressure (5 atm), more hydrogen transfer to ruthenium and then to substrate results in higher %conversion. % Conversion was not significantly increased when pressure was increased to 10 atm.

4.7.2 Ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane [Ru-DA]

The same condition as in 4.7.1 was used for ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane complex, except that only pressure 1 and 5 atm was tried. The results of cyclooctene hydrogenation are presented in Appendix A2 and shown in Fig. 4.6.

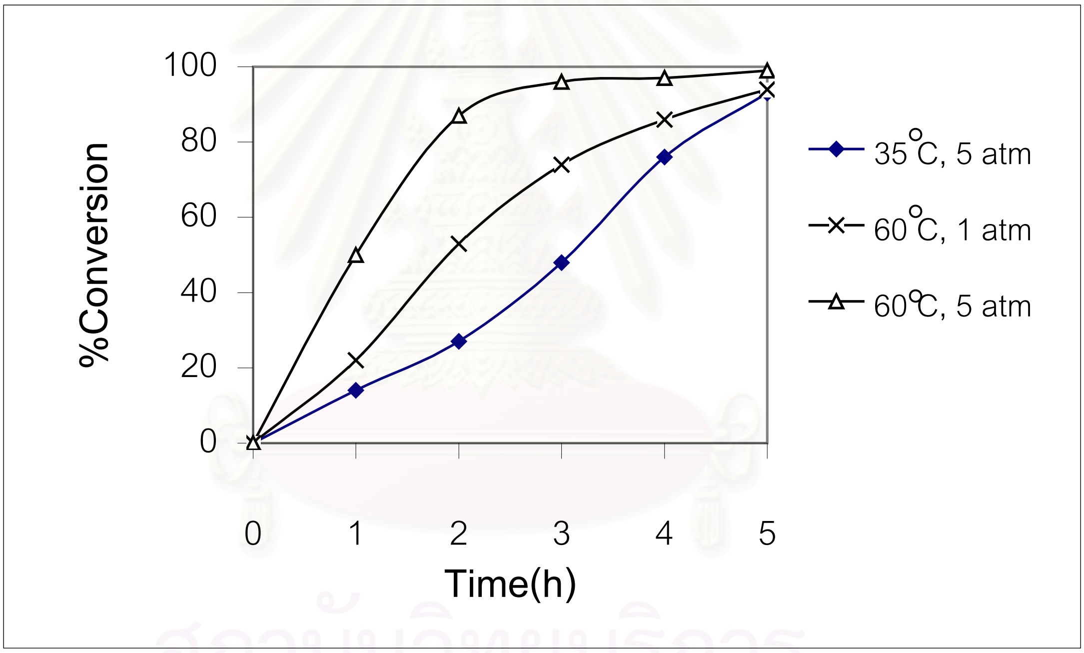


Figure 4.6 Hydrogenation of cyclooctene catalyzed by ruthenium-1,3-di (2,6-diisopropylphenyl)aminopropane complex.

From Fig 4.6, the effects of temperature and pressure are same as in ruthenium-2-aminopyridyl [Ru-2AP]. It was found that at 60 ^{o}C and hydrogen pressure of 5 atm, %conversion reached 100% in 3 h. The experimental result shows that 1 atm is adequate for achieving almost 100%conversion. This can be explained that ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane [Ru-DA] has phosphine ligand which is a good leaving group and bulky. It dissociates and creates a vacant site for the incoming substrate.[40, 47]

4.7.3 Ruthenium-1,3-diaminopropane [Ru-DP]

The same condition as in 4.7.1 was used for ruthenium-1,3-diaminopropane complex, except that only pressure 5 atm was tried. The results of cyclooctene hydrogenation are presented in Appendix A3 and shown in Fig. 4.7.

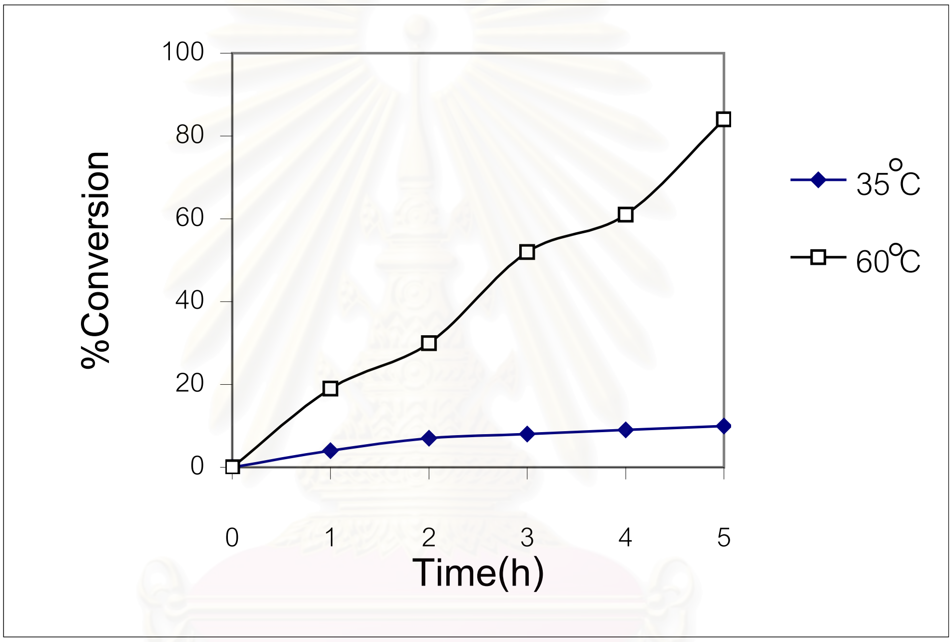


Figure 4.7 Hydrogenation of cyclooctene catalyzed by ruthenium -1,3-diaminopropane complex.

From Fig. 4.7, the effect of temperature is more pronounced than in the above catalysts.[46]

In conclusion, it was found that order of catalytic activity is:

Ru-DA > Ru-2AP ~ Ru-DP

In ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane [Ru-DA], oxidation state of Ru is II, it was more active than Ru (III). It is an efficient catalyst even at mild condition (1 atm, 35 ^{o}C), In comparison between ruthenium-2-aminopyridyl [Ru-2AP] and ruthenium-1,3-diaminopropane [Ru-DP] with the same condition, the result showed that the initial rate of reaction of Ru-2AP catalyst was faster than Ru-DP catalyst.

4.8 Cyclooctene hydrogenation with heterogeneous catalysts

Heterogeneous ruthenium catalysts used in hydrogenation of cyclooctene were:

2P-Ru-2AP = 2%polymer-supported ruthenium-2-aminopyridyl
5P-Ru-2AP = 5%polymer-supported ruthenium-2-aminopyridyl
10P-Ru-2AP = 10%polymer-supported ruthenium-2-aminopyridyl
5P-Ru-SB-2AP = 5%polymer-supported ruthenium- Schiff base 2-aminopyridyl
5P-Ru-SB-DP = 5%polymer-supported ruthenium Schiff base 1,3-diaminopropane
2P-Rh-2AP = 2%polymer-supported rhodium-2-aminopyridyl

4.8.1 Cyclooctene hydrogenation with polymer-supported ruthenium-2-aminopyridyl catalyst [P-Ru-2AP]

To investigate the optimum condition for heterogeneous hydrogenation, polymer-supported ruthenium-2-aminopyridyl was chosen to be a representative catalyst. The parameters studied in this reaction are effect of %DVB of polymer-support, effect of type of catalyst, type of metal, temperature, hydrogen pressure, the amount of catalyst and substrate.

4.8.1.1 Effect of % DVB of polymer support

The polymer-supported ruthenium-2-aminopyridyl catalysts with different percentage of divinylbenzene in polymer support: 2% DVB, 5%DVB and 10%DVB, were used to hydrogenate cyclooctene at 60^{o}C and hydrogen pressure of 5 atm. The results are presented in Appendix B1-B3 and shown in Fig. 4.8.

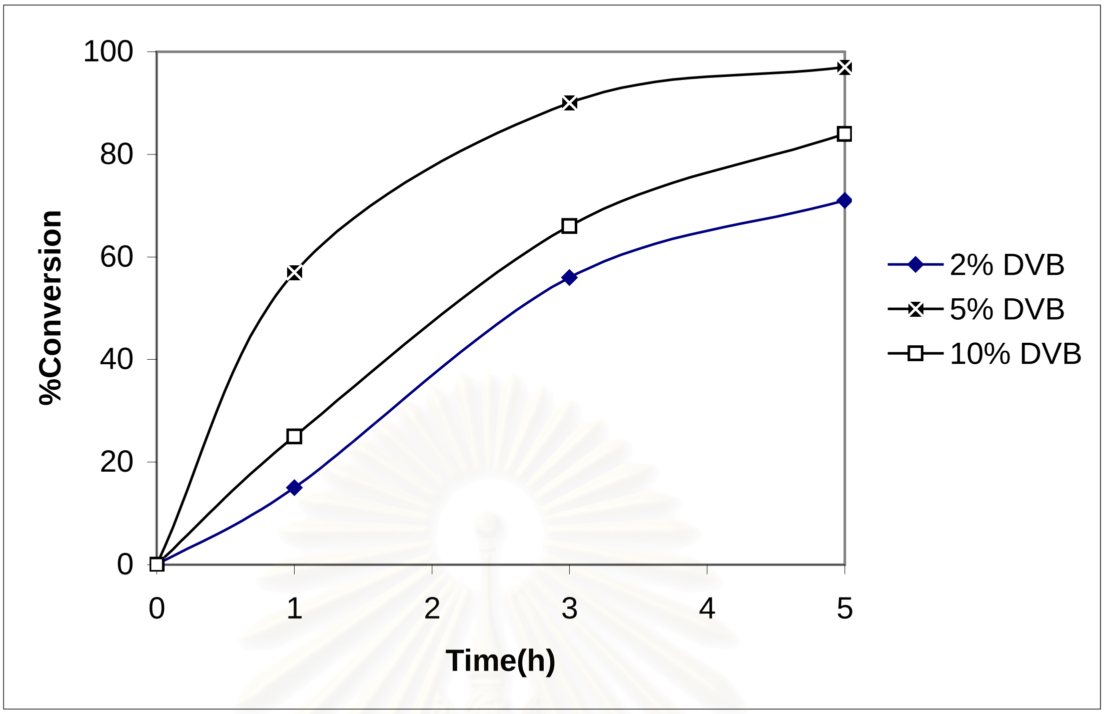


Figure 4.8 Effect of %DVB of polymer support on cyclooctene hydrogenation.

From Fig. 4.8, it was found that 5%polymer-supported ruthenium-2-aminopyridyl [5P-Ru-2AP] catalyst gave higher conversion than 2% and 10% polymer-supported ruthenium-2-aminopyridyl catalysts. 5%Polymer-supported ruthenium-2-aminopyridyl [5P-Ru-2AP] has large size bead, more surface area and more chloride content, so that more ruthenium could attach on polymer support.[36] Therefore, 5%polymer-supported ruthenium-2-aminopyridyl [5P-Ru-2AP] was chosen to study other parameters in the next experiments.

4.8.1.2 Effect of amount of catalyst

The amount of 5%polymer-supported ruthenium-2-aminopyridyl catalyst in reaction was varied from 0.005, 0.010, and 0.020 mmol of Ru in order to find the appropriate amount of catalyst. The results are presented in Appendix B2 and shown in Fig.4.9.

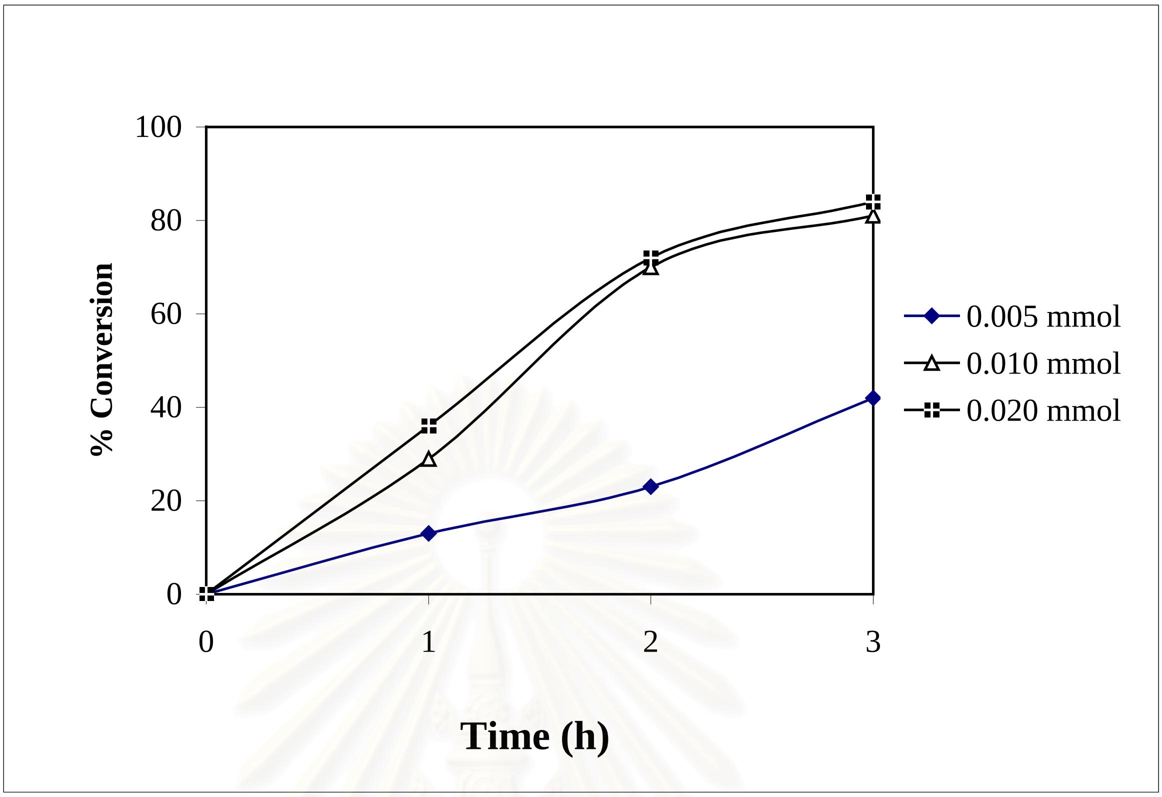


Figure 4.9 Effect of amount of catalyst on cyclooctene hydrogenation.

From Fig.4.9, when the amount of catalyst in hydrogenation increased, it was observed that the yield of product was increased.[39] When the amount of catalyst was further increased from 0.010 to 0.020 mmol of Ru, % conversion reached constant Thus, 0.010 mmol of Ru was sufficient in this reaction.

4.8.1.3 Effect of amount of cyclooctene

The amount of cyclooctene in reaction was varied from 5, 10 and 20 mmol in order to find the appropriate amount of substrate. The reaction condition was same as in 4.8.1.2. The results are presented in Appendix B2 and shown in Fig.4.10.

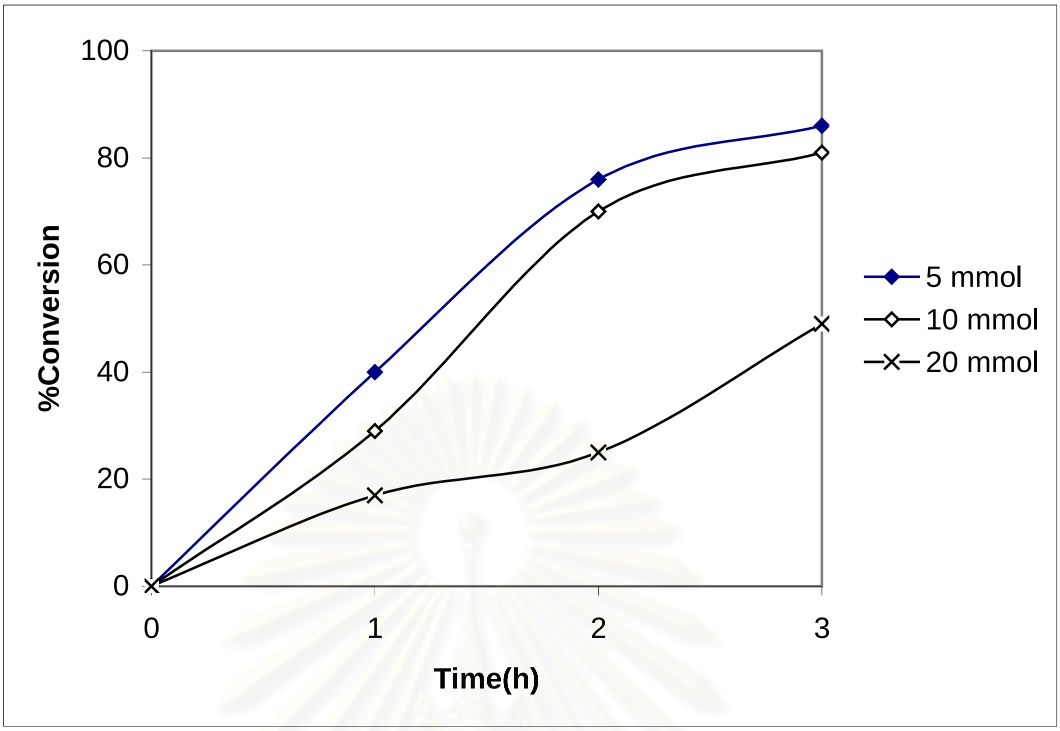


Figure 4.10 Effect of amount of substrate on cyclooctene hydrogenation.

From Fig.4.10, when increasing the amount of cyclooctene in hydrogenation from 5 to 10 and 20 mmol, it was observed that the yield of product was decreased. When the amount of cyclooctene in hydrogenation increased to 20 mmol, the conversion was clearly decreased to 40%. This might be caused by inadequate amount of catalyst. When comparing the amount of cyclooctene at 5 mmol with 10 mmol, % conversions are comparable. Lower amount of catalyst will be more attractive for industrial process.

4.8.1.4 Effect of temperature

Temperature is another important parameter for hydrogenation condition. The temperature examined was 35^{o}C and 60^{o}C by fixing hydrogen pressure at 5 atm and 5%polymer-supported ruthenium-2-aminopyridyl catalyst [5P-Ru-2AP] 0.010 mmol of Ru. The results are presented in Appendix B2 and shown in Fig. 4.11.

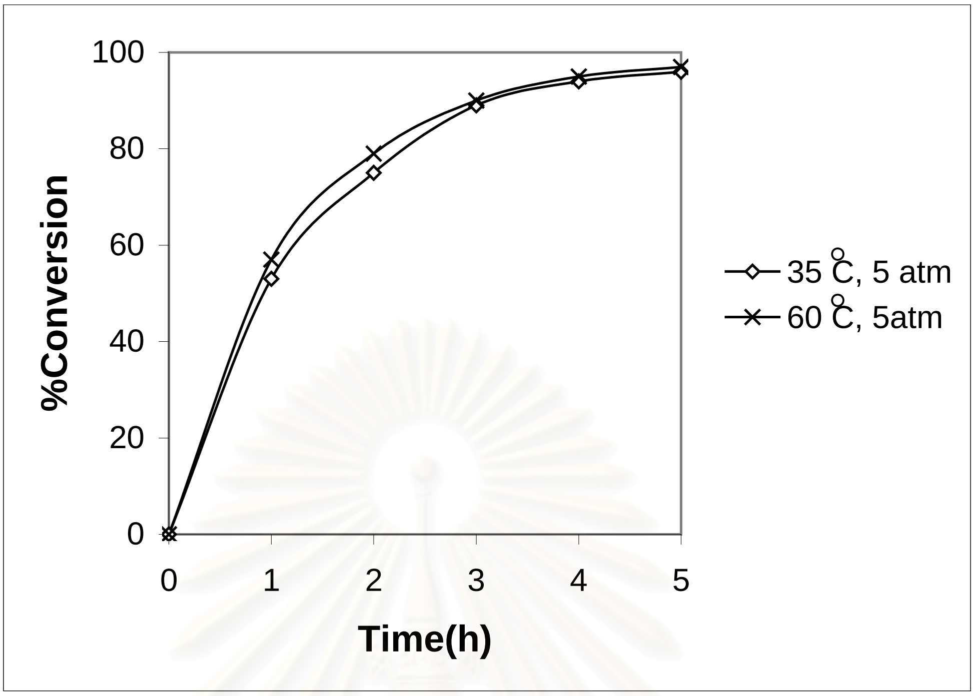


Figure 4.11 Effect of temperature on cyclooctene hydrogenation .

From Fig.4.11, it was found that %conversions at 35 °C and 60 °C are the same. The temperature used in this experiment might be not high enough to see any difference, as a result, there is no or less effect on the activity. Another reason is that in the heterogeneous system, the metal catalyst was supported on polymer so it can withstand high temperature than homogeneous catalyst. This is in contrast to the results obtained from homogeneous system. Therefore, the temperature at 35 °C was chosen for the next reactions.

4.8.1.5 Effect of hydrogen pressure

Hydrogen pressure is another important parameter for hydrogenation condition. The hydrogen pressure examined was 1, 5 and 10 atm by fixing temperature at 60°C and 5%polymer-supported ruthenium-2-aminopyridyl catalyst [5P-Ru-2AP] 0.010 mmol of Ru. The results are presented in Appendix B2 and shown in Fig.4.12.

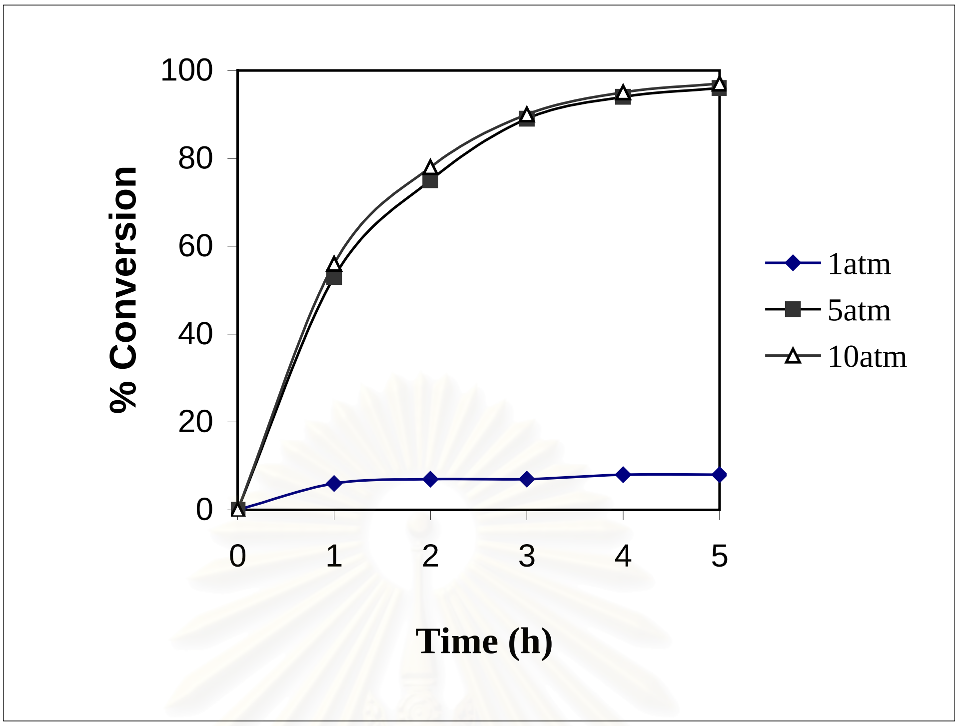


Figure 4.12 Effect of hydrogen pressure on cyclooctene hydrogenation.

From Fig.4.12, the same explanation as in the homogeneous system in 4.7 is used.[46]

The results from the investigation of parameters show that 35 ^{o}C and hydrogen pressure of 5 atm, 5% DVB and 10 mmol of cyclooctene was an optimum condition and so this condition was used for next reactions. It should be noted that the weight of catalyst is 0.025 g (0.010 mmol of Ru). This same weight was used for other catalysts.

4.8.2 Cyclooctene hydrogenation by polymer-supported ruthenium Schiff base ligand complexes

The above reaction condition was chosen to study hydrogenation for polymer-supported ruthenium Schiff base ligand complexes: 5% Polymer-supported ruthenium Schiff base 2-aminopyridyl [5P-Ru-SB-2AP] and 5% Polymer-supported ruthenium Schiff base 1,3-diaminopropane [5P-Ru-SB-DP].

4.8.2.1 5% Polymer-supported ruthenium Schiff base 2- aminopyridyl [5P-Ru-SB-2AP]

Hydrogenation of cyclooctene catalyzed by 5%polymer-supported ruthenium Schiff base 2-aminopyridyl catalyst [5P-Ru-SB-2AP] 0.025 g (0.005 mmol of Ru) at 35 ^{o}C, 60 ^{o}C, hydrogen pressure of 5 atm and reaction time of 1-5 h. The results of cyclooctene hydrogenation are presented in Appendix B4 and shown in Fig. 4.13.

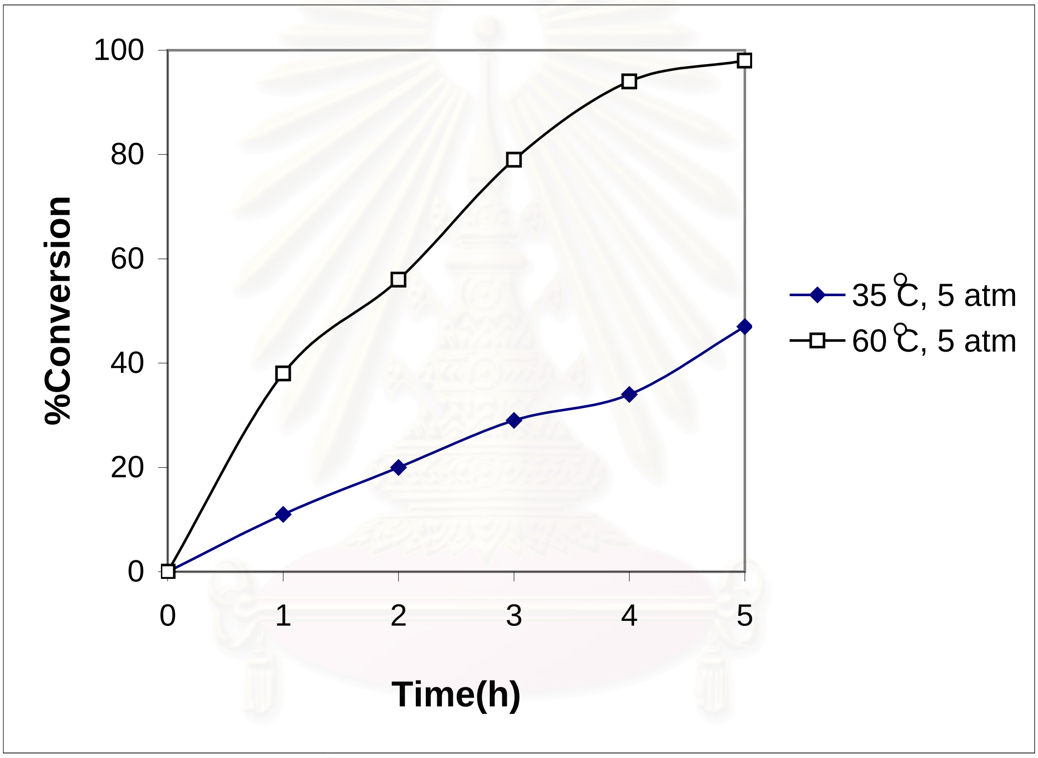


Figure 4.13 Hydrogenation of cyclooctene catalyzed by 5%polymer- supported ruthenium Schiff base 2-aminopyridyl catalyst.

4.8.2.2 5% Polymer-supported ruthenium Schiff base 1,3-diaminopropane) [5P-Ru-SB-DP]

The same condition as in 4.8.2.1 was used for 5% Polymer-supported ruthenium Schiff base 1, 3-diaminopropane [5P-Ru-SB-DP] 0.025 g (0.0025 mmol of Ru). The results of cyclooctene hydrogenation are presented in Appendix B5 and shown in Fig. 4.14.

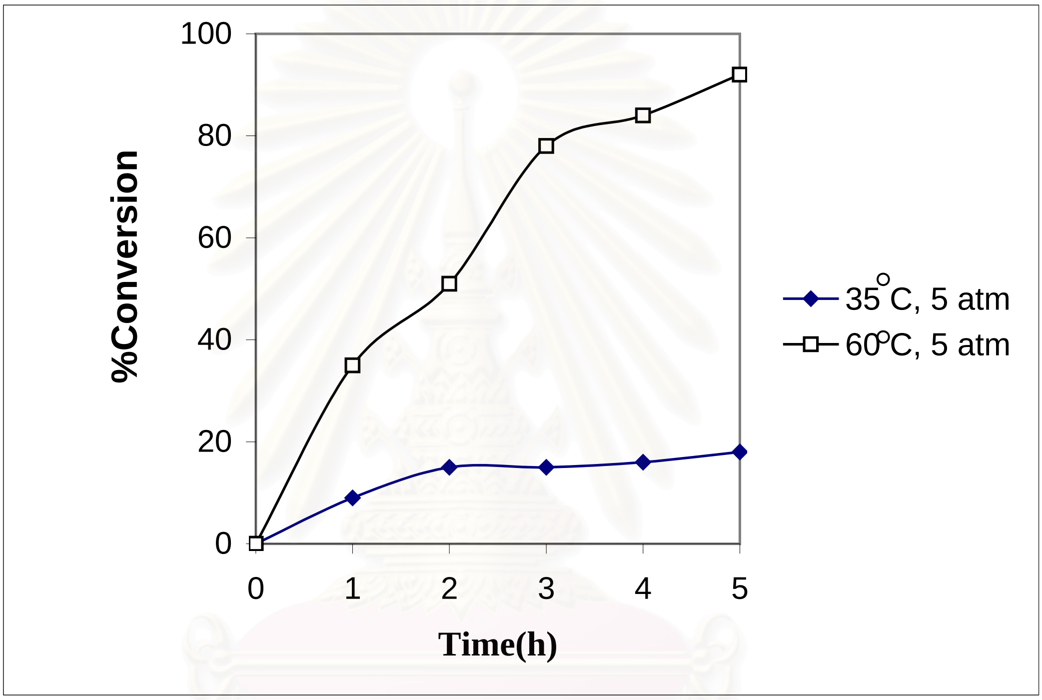


Figure 4.14 Hydrogenation of cyclooctene catalyzed by 5%polymer-supported ruthenium Schiff base 1,3-diaminopropane catalyst.

From Figs 4.13 and 4.14, it showed that for polymer-supported ruthenium Schiff base ligand catalysts, temperature showed pronounced effect on the activity of catalyst. At 35 °C, the conversion was low (~20%). When temperature increased to 60 °C, the conversion was higher, since the rate of hydrogenation increased.

Proposed mechanism for homogeneous and heterogeneous systems is presented in equations (4.12)-(4.14).

$$[P\text{-}L\text{-}RuCl_2]Cl + H_2 \longrightarrow [P\text{-}L\text{-}Ru(H)Cl]Cl + HCl \qquad (4.12)$$

$$[P\text{-}L\text{-}Ru(H)Cl]Cl + S \longrightarrow [P\text{-}L\text{-}Ru(HS)Cl]Cl \qquad (4.13)$$

$$[P\text{-}L\text{-}Ru(HS)Cl]Cl + H_2 \longrightarrow [P\text{-}L\text{-}Ru(H)Cl]Cl + \text{alkane} \qquad (4.14)$$

Where P is polymer-supported, L is ligand and S is substrate (cycclooctene).

The mechanism of cyclooctene hydrogenation over a ruthenium catalyst has been extensively studied.[37] First, hydrido species was formed from the heterolytic cleavage of hydrogen (Eq. 4.12). Cyclooctene (S) was adsorbed on catalyst surface while the hydrogen migrated to add to the double bond of S. (Eq. 4.13). Another molecule of hydrogen was adsorbed, the alkene was hydrogenated to alkane. (Eq. 4.14). A similar mechanism for heterogeneous catalyst (polymer-supported ruthenium (III) trimethylenediamine catalyst) was reported. [39]

4.8.3 Cyclooctene hydrogenation by polymer-supported rhodium complex [P-Rh-2AP]

Rhodium was also attached to the polymer support for the comparison with ruthenium support catalysts using 2% DVB of polymer support anchoring with 2-aminopyridyl. Hydrogenation of cyclooctene catalyzed by 2%polymer- supported rhodium-2-aminopyridyl catalyst (0.0005 mmol of Rh) at 35 ^oC, 60 ^oC, hydrogen pressure of 1 and 5 atm and reaction time of 1-5 h has been studied. The results of cyclooctene hydrogenation are presented in Appendix B6 and shown in Fig. 4.15.

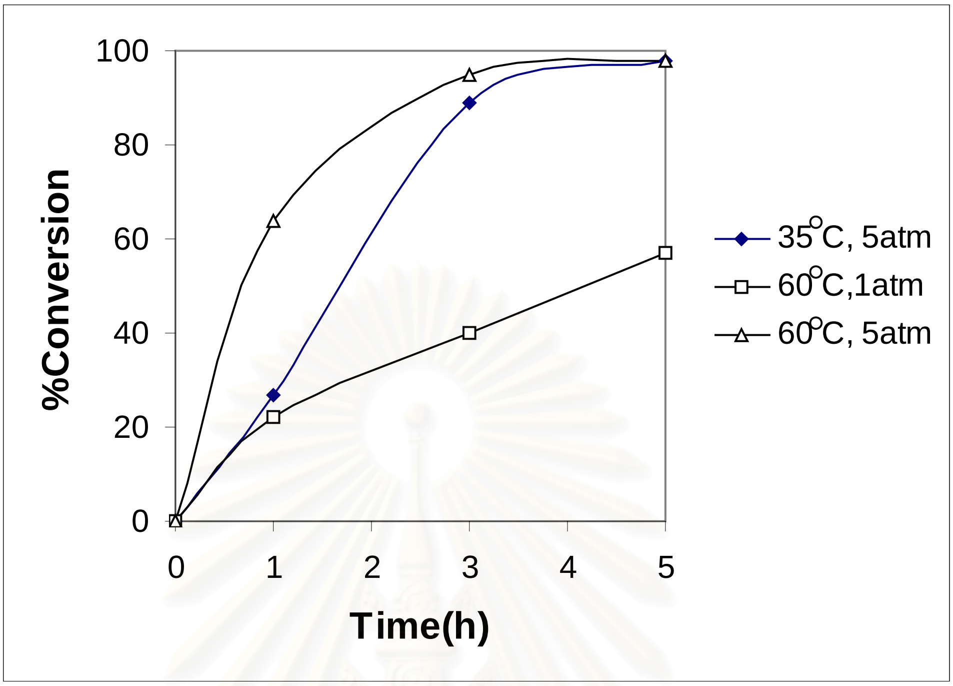


Figure 4.15 Hydrogenation of cyclooctene catalyzed by 2%polymer-supported rhodium-2-aminopyridyl catalyst.

From Fig. 4.15, temperature and hydrogen pressure affect on hydrogenation of cyclooctene with polymer-supported rhodium as same as polymer-supported ruthenium catalyst.

Cyclooctene hydrogenation with 2% polymer-supported rhodium (2-aminopyridyl) catalyst gave high conversion (~99%) and reaction rate was fast, although the amount of catalyst was only 0.0005 mmol of Rh. Polymer-supported rhodium catalyst has higher catalytic activity than polymer-supported ruthenium catalyst because rhodium catalyst was more active than ruthenium catalyst in hydrogenation.[48]

4.9 Test of catalyst leaching from polymer support

The leaching of metal from the polymer support was tested by following: polymer-supported ruthenium-2-aminopyridyl catalyst (0.01 mmol of Ru) and ethanol (5 ml) were added into 50 ml round-bottom flask, stirred at 60 ^{o}C and reaction time 24 h. Then, polymer-supported ruthenium-2-aminopyridyl catalyst was filtered, washed thoroughly with methanol and dried. Finally, it was used for hydrogenation of cyclooctene at 60^{o}C, reaction time 5 h and hydrogen pressure of 5 atm. The results from leaching test and none leaching test showed that the % yield of cyclooctane was not different. % Yield of cyclooctane at 1 h, 3 h and 5 h was 67, 90 and 97 respectively. This means that the metal attached well on the support.

4.10 Recycling catalyst for hydrogenation

The recycling catalysts: polymer-supported ruthenium catalyst and polymer-supported rhodium catalyst were studied for reuse in hydrogenation. The results are presented in Table 4.10.

Table 4.10 % Conversion of recycled catalysts

Catalyst	**T (^{o}C)**	**%Conversion**
5P-Ru-2AP	60	97
5P-Ru-2AP*	60	83
2P-Rh-2AP	35	90
2P-Rh-2AP*	35	74

Reaction condition: cyclooctene 10 mmol, catalyst 0.0025 g, P_{H2} 5 atm and 5 h
* recycled catalyst

The results of reusing catalyst were shown in Table 4.10. After being used once, %conversion was lower than that from fresh catalyst, however these catalysts were still efficient to be reused for hydrogenation.

CHAPTER V

CONCLUSION AND SUGGESTIONS

In this research, polymer-supported ruthenium catalysts were prepared by following steps: (I) Copolymerization of styrene, divinylbenzene and vinylbenzyl chloride with 2%, 5% and 10%DVB were used as polymer support. (II) Prepared polymer was attached ligand (2-aminopyridyl, Schiff base 2-aminopyridyl and Schiff base 1,3-diaminopropane) to obtain functional polymer. (III) The ruthenium catalyst was immobilized on functionalized polymer. These catalysts were characterized by FT-IR, XRF, TGA and EA techniques. From FT-IR spectra peak in the region around 3400 cm^{-1} corresponded to N-H stretching vibration of ligand on polymer. The C=N stretching vibration of ligands appeared around 1600 cm^{-1}. The complexation of polymer-supported ruthenium catalyst was occurred through ‘N’ atom of amino group and pyridine ring to the ruthenium metal. It was found from TGA that polymer-supported catalysts have high thermal stability. The content of metal on polymer support was determined by XRF spectroscopy, it was found that 5% polymer-supported ruthenium (2-aminopyridyl) catalyst has more Ru content than the other heterogeneous catalysts. All catalysts were used to catalyze hydrogenation of cyclooctene, it was found that all prepared catalysts were efficient, giving high yield of cyclooctane (>95%) at 60^{o}C, hydrogen pressure of 5 atm in 5 h. The ruthenium complex on the polymer support did not leach out even after 24 h of immersion in methanol. In addition, it was proved to be able to be reused.

Some homogeneous ruthenium catalysts were synthesized and tested catalytic activity. These catalysts were also used for hydrogenation of cyclooctene, the results showed the order of catalytic activity: ruthenium-1,3-di(2,6-diisopropylphenyl) aminopropane > ruthenium-2-aminopyridyl ~ ruthenium-1,3-diaminopropane.

Suggestions

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

1. The catalytic activity for hydrogenation should be increased by changing ligand to polydentate such as porphyrin, *N*,*N*-bis(2-pyridyl)ethylamine.
2. Copolymerization using monomer containing suitable functional group to obtain functional polymer should be attempted. This route could control the content of functionalized group on polymer and also decreased preparation steps.
3. The prepared polymer-supported ruthenium catalyst should be used in other reactions such as oligomerization of olefin or hydroformylation.

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APPENDICES

APPENDIX A

Hydrogenation of cyclooctene with homogeneous ruthenium catalysts

A. 1 Hydrogenation of cyclooctene catalyzed by ruthenium-2-aminopyridyl [Ru-2AP]

T (^oC)	**P (atm)**	**% Conversion**					**Turnover number**
		1 h	**2 h**	**3 h**	**4 h**	**5 h**	**5 h**
35	10	20	26	32	49	66	330
60	1	7	8	8	9	9	45
60	5	25	44	49	55	68	340
60	10	34	54	62	67	68	340

Reaction condition: catalyst 0.020 mmol of Ru and cyclooctene 10 mmol.

A. 2 Hydrogenation of cyclooctene catalyzed with ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane [Ru-DA]

Catalyst (mmol of Ru)	**T (^{o}C)**	**P (atm)**	**% conversion**					**Turnover number**
			1 h	**2 h**	**3 h**	**4 h**	**5 h**	**5 h**
0.036	35	5	14	27	48	76	93	258
0.036	60	1	22	53	74	86	94	261
0.036	60	5	50	87	96	97	99	275
0.072	60	10	95	-	97	-	99	138

Reaction condition: cyclooctene 10 mmol.
- not determined

A. 3 Hydrogenation of cyclooctene catalyzed with ruthenium-1,3-diaminopropane [Ru-DP]

T (^{o}C)	**P (atm)**	**%conversion**					**Turnover number**
		1 h	**2 h**	**3 h**	**4 h**	**5 h**	**5 h**
35	5	4	7	8	9	10	50
60	5	19	30	52	61	84	420

Reaction condition: catalyst 0.020 mmol of Ru and cyclooctene 10 mmol

APPENDIX B

Hydrogenation of cyclooctene with heterogeneous catalysts

B. 1 Hydrogenation of cyclooctene with 2%polymer-supported ruthenium-2-aminopyridyl catalyst [2P-Ru-2AP]

T (^oC)	**P (atm)**	**% conversion**					**Turnover number**
		1 h	**2 h**	**3 h**	**4 h**	**5 h**	**5 h**
35	5	11	12	14	17	24	300
35	10	15	51	56	66	71	888
60	5	19	69	83	87	89	1113
60	10	60	79	88	91	97	1213

Reaction condition: catalyst 0.008 mmol of Ru and cyclooctene 10 mmol

B. 2 Hydrogenation of cyclooctene with 5% polymer-supported ruthenium-2-aminopyridyl catalyst [5P-Ru-2AP]

Catalyst (mmol of Ru)	**Cyclooctene (mmol)**	**T (^{o}C)**	**P (atm)**	**%yield**					**Turnover number**
				1 h	**2 h**	**3 h**	**4 h**	**5 h**	**5 h**
0.010	10	35	1	6	7	7	8	8	80
0.010	10	35	5	53	75	89	94	96	960
0.010	10	35	10	56	78	90	95	97	970
0.010	10	60	3	29	70	81	92	96	960
0.010	10	60	5	57	79	91	95	97	970
0.010	10	60	10	63	83	93	96	98	980
0.005	10	60	3	13	23	42	-	-	840(3h)
0.020	10	60	3	36	72	84	-	-	860(3h)
0.010	5	60	3	40	76	86	-	-	860(3h)
0.010	20	60	3	18	25	49	-	-	840(3h)

- not determined

B. 3 Hydrogenation of cyclooctene with 10%polymer-supported ruthenium-2-aminopyridyl catalyst [10P-Ru-2AP]

T (^{o}C)	**P (atm)**	**% conversion**					**Turnover number**
		1 h	**2 h**	**3 h**	**4 h**	**5 h**	**5 h**
60	5	26	38	66	79	85	4250

Reaction condition: catalyst 0.002 mmol of Ru and cyclooctene 10 mmol

B. 4 Hydrogenation of cyclooctene with 5% polymer-supported ruthenium- Schiff base 2-aminopyridyl catalyst [5P- Ru-SB-2AP]

T (°C)	**P (atm)**	**% conversion**					**Turnover number**
		1 h	**2 h**	**3 h**	**4 h**	**5 h**	**5 h**
35	5	11	20	28	34	47	940
60	5	38	56	79	94	98	1960

Reaction condition: catalyst 0.005 mmol of Ru and cyclooctene 10 mmol

B. 5 Hydrogenation of cyclooctene with 5% polymer-supported ruthenium- Schiff base 1,3-diaminopropane catalyst [5P- Ru-SB-DP]

T (^oC)	**P (atm)**	**% conversion**					**Turnover number**
		1 h	**2 h**	**3 h**	**4 h**	**5 h**	**5 h**
35	5	9	15	15	16	18	720
60	5	35	51	78	84	92	3680

Reaction condition: catalyst 0.0025 mmol of Ru and cyclooctene 10 mmol

B. 6 Hydrogenation of cyclooctene with 2%polymer-supported rhodium-2-aminopyridyl catalyst [2P-Rh-2AP]

T (°C)	**P** (atm)	**% conversion**			**Turnover number**
		1 h	**3 h**	**5 h**	**5 h**
35	5	27	89	98	19600
60	1	22	40	57	11400
60	5	64	95	98	19600

Reaction condition: catalyst 0.001 mmol of Rh and cyclooctene 10 mmol
- not determined

APPENDIX C

FT-IR spectra

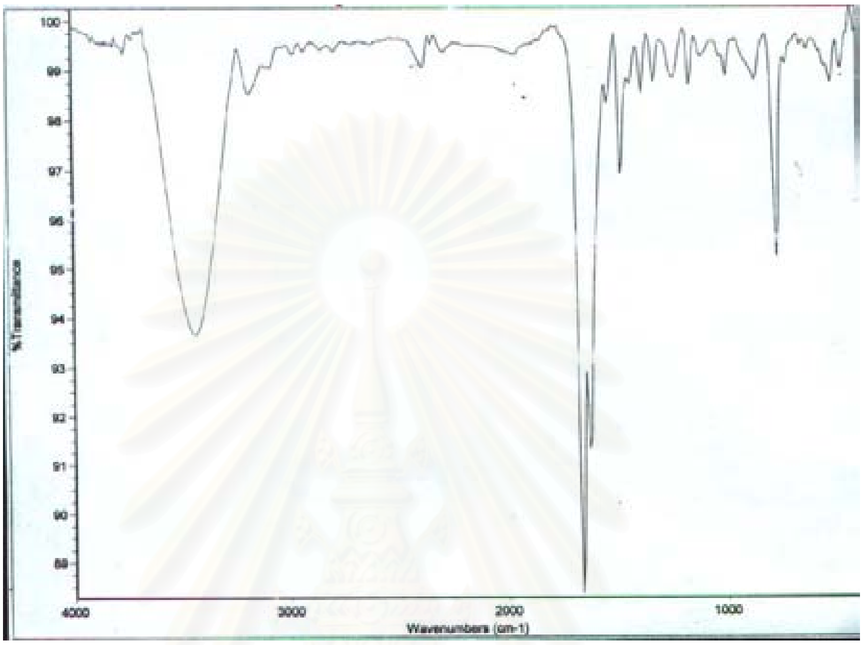

Figure C1 Ruthenium-2-aminopyridyl [Ru-2AP].

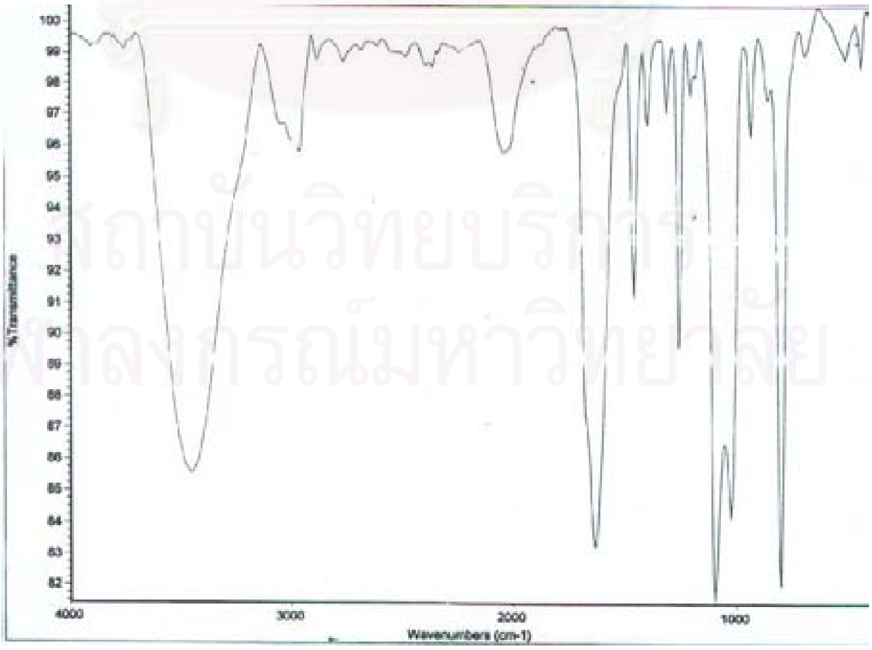

Figure C2 Ruthenium-1,3-diaminopropane [Ru-DP].

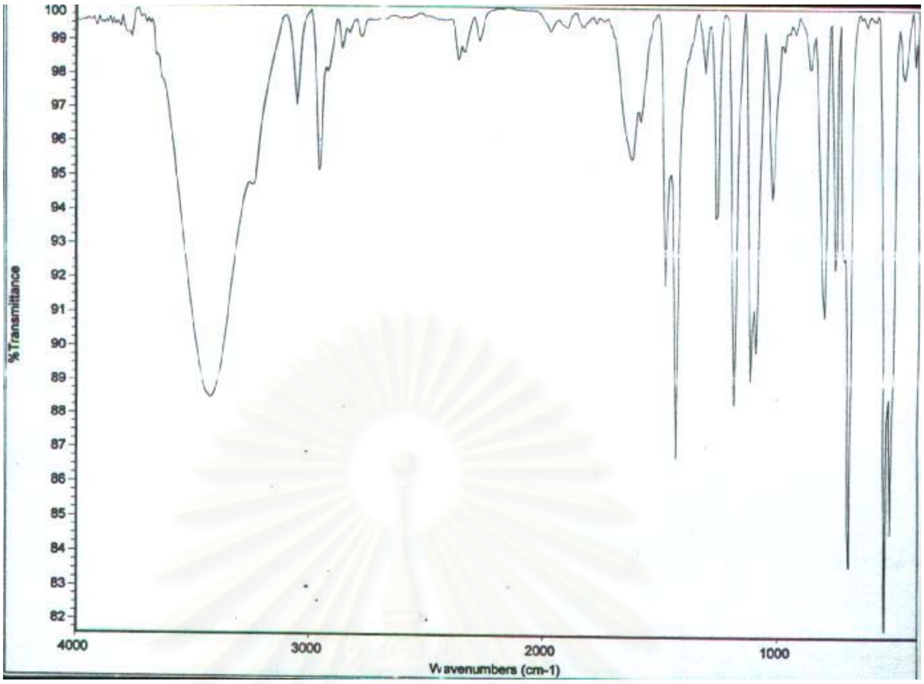

Figure C3 Ruthenium-1,3-di(2,6-diisopropylphenyl)aminopropane [Ru-DA].

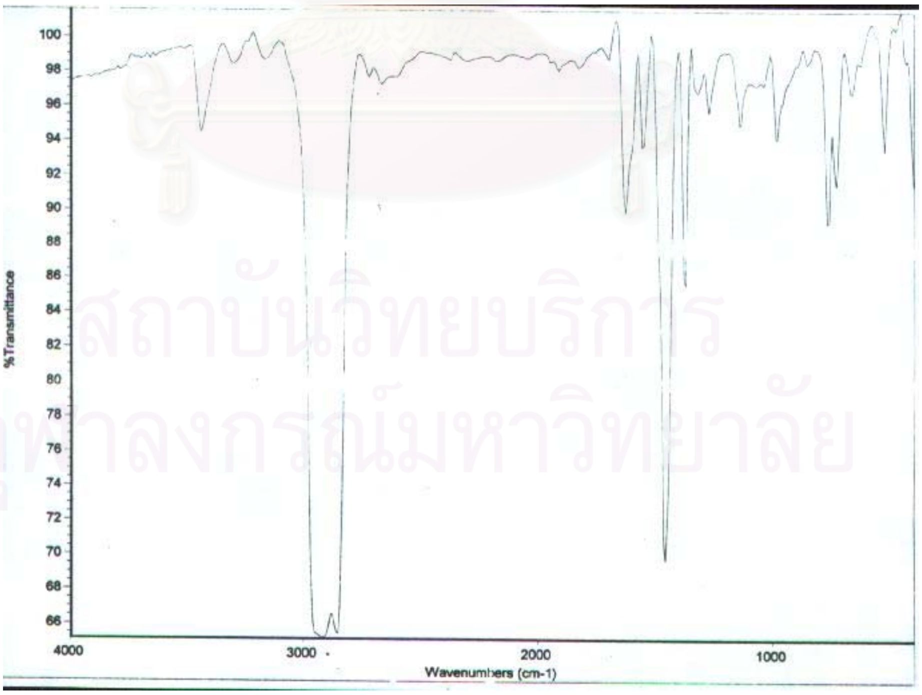

Figure C4 2% Chloromethylated poly(styrene-*co*-divinylbenzene).

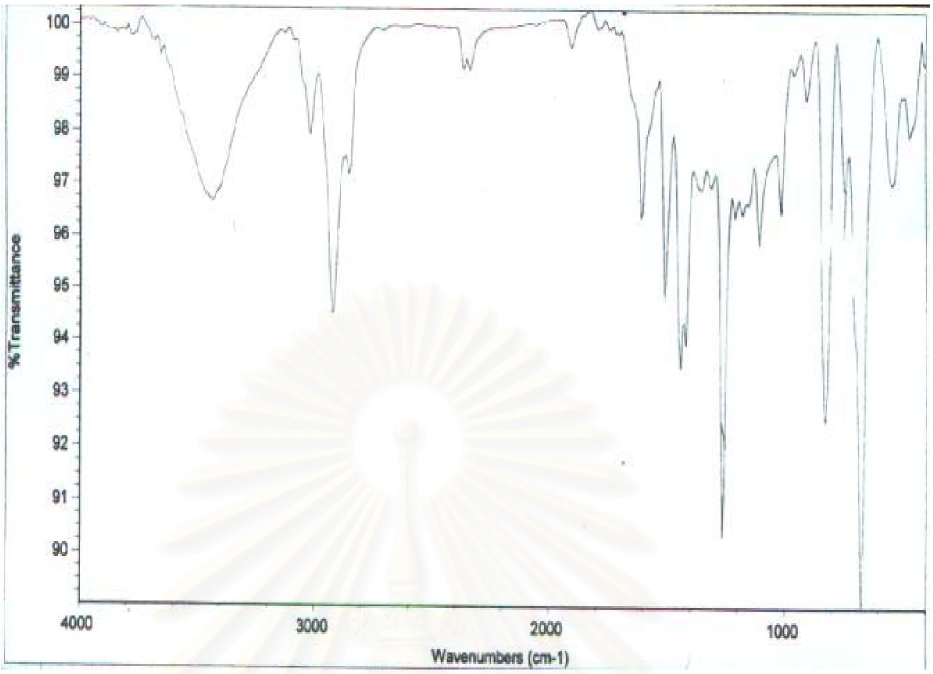

Figure C5 5% Chloromethylated poly(styrene-*co*-divinylbenzene).

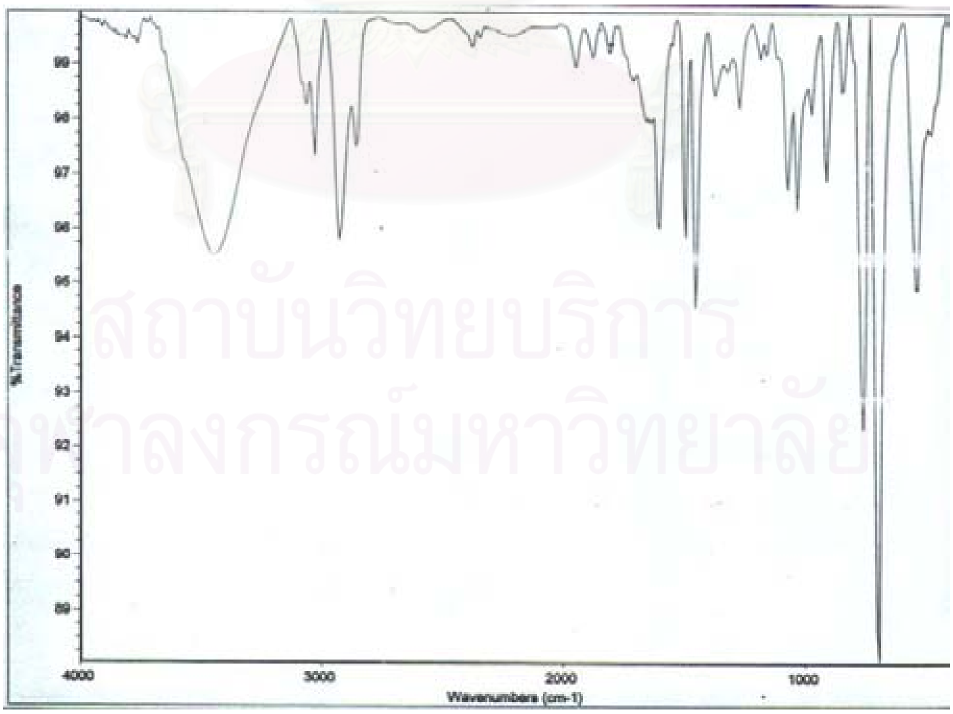

Figure C6 10% Chloromethylated poly(styrene-*co*-divinylbenzene).

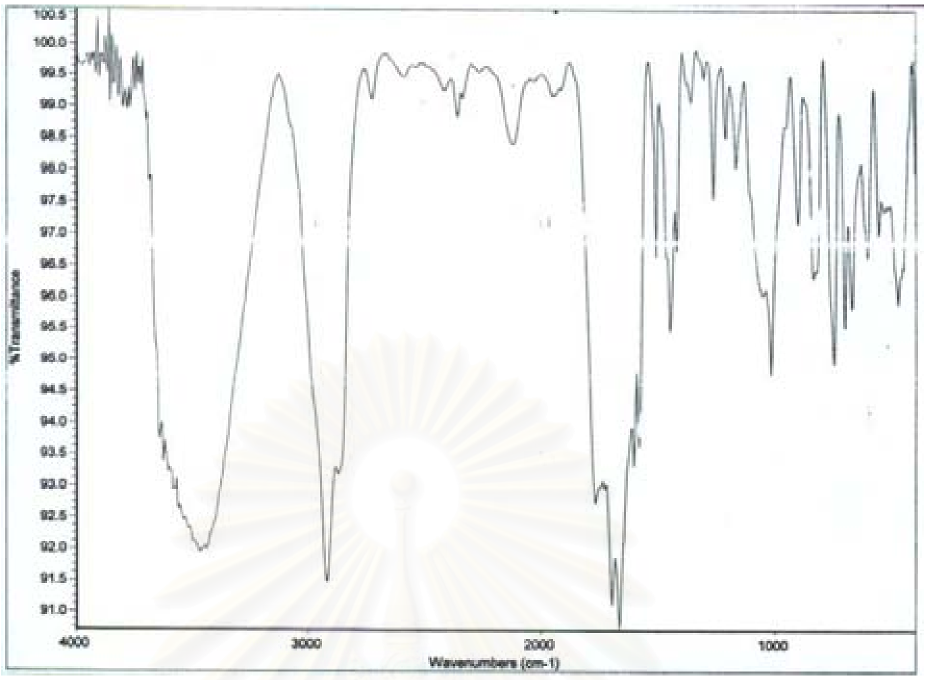

Figure C7   5% Polymer bound 2-aminopyridyl ligand [5P-2AP].

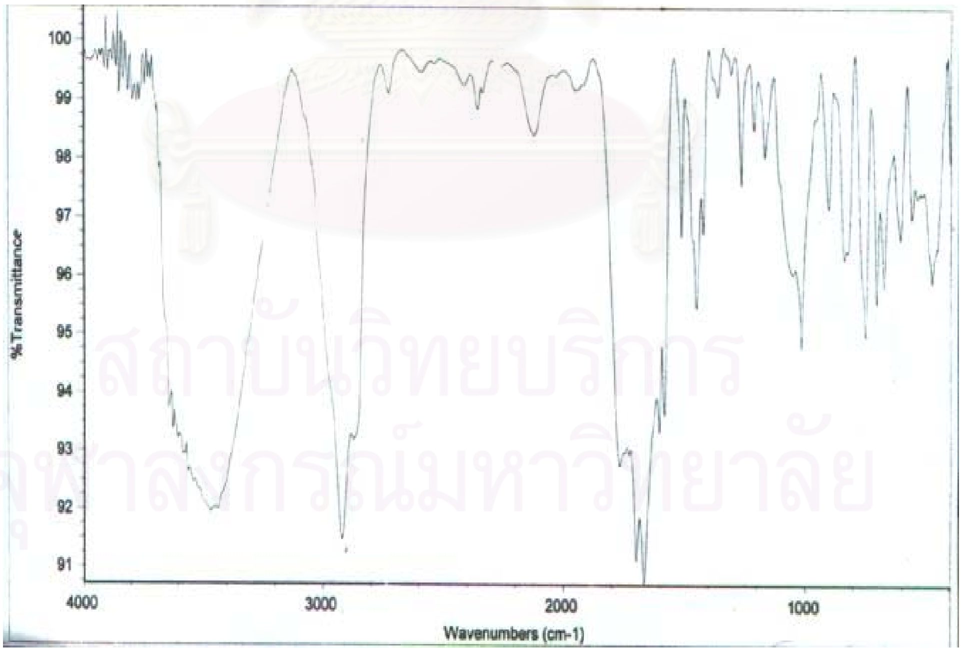

Figure C8   5% Polymer bound Schiff base 2-aminopyridyl [5P-SB-2AP].

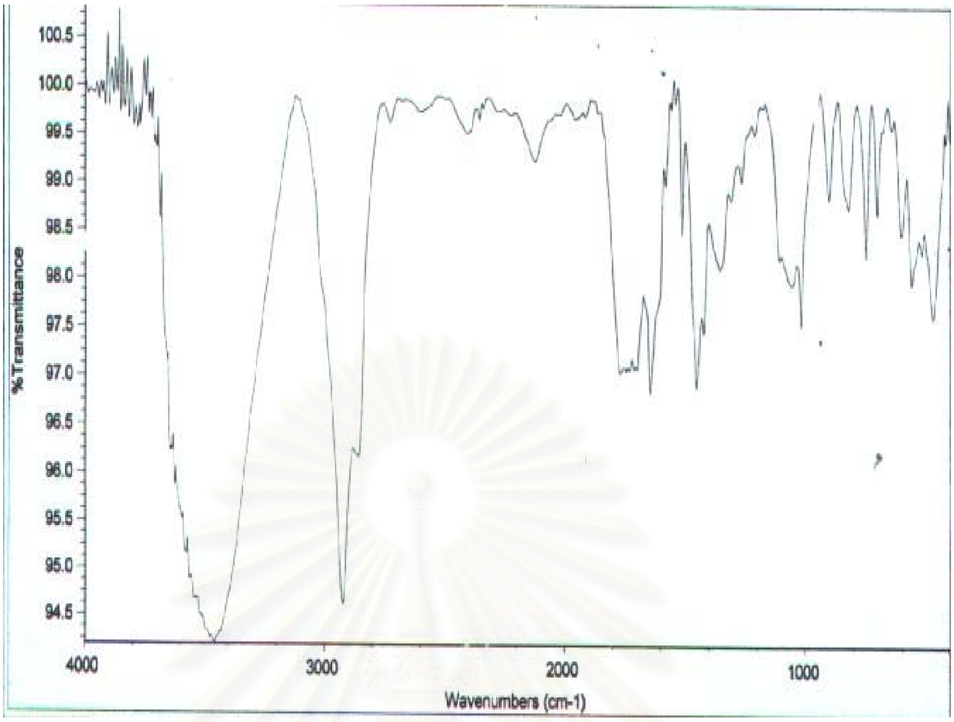

Figure C9 5% Polymeric support bound Schiff base 1,3-diaminopropane [5P-SB-DP].

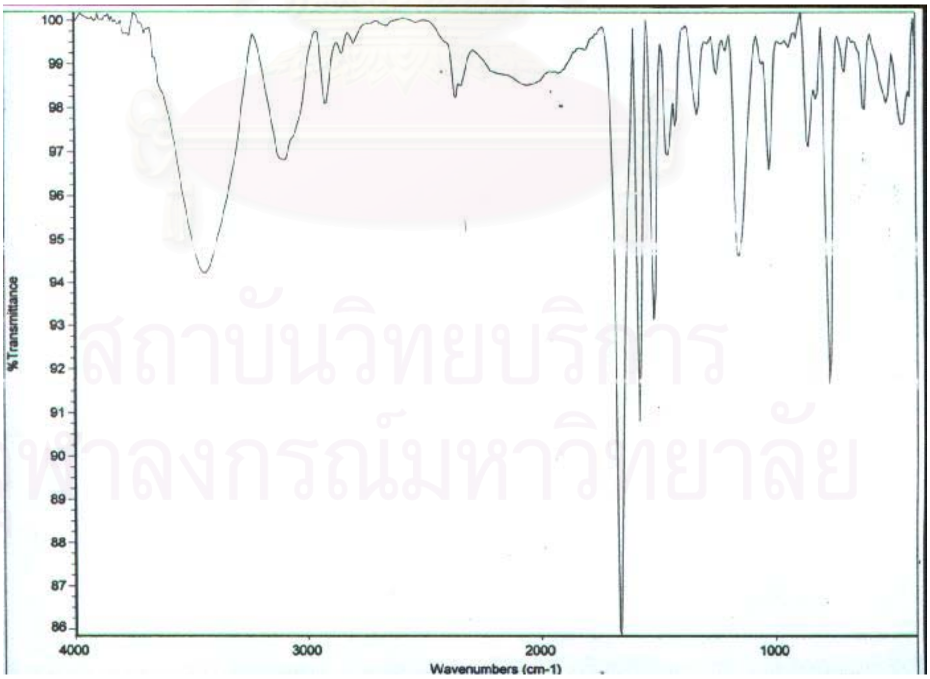

Figure C10 2%Polymer-supported ruthenium-2-aminopyridyl [2P-Ru-2AP].

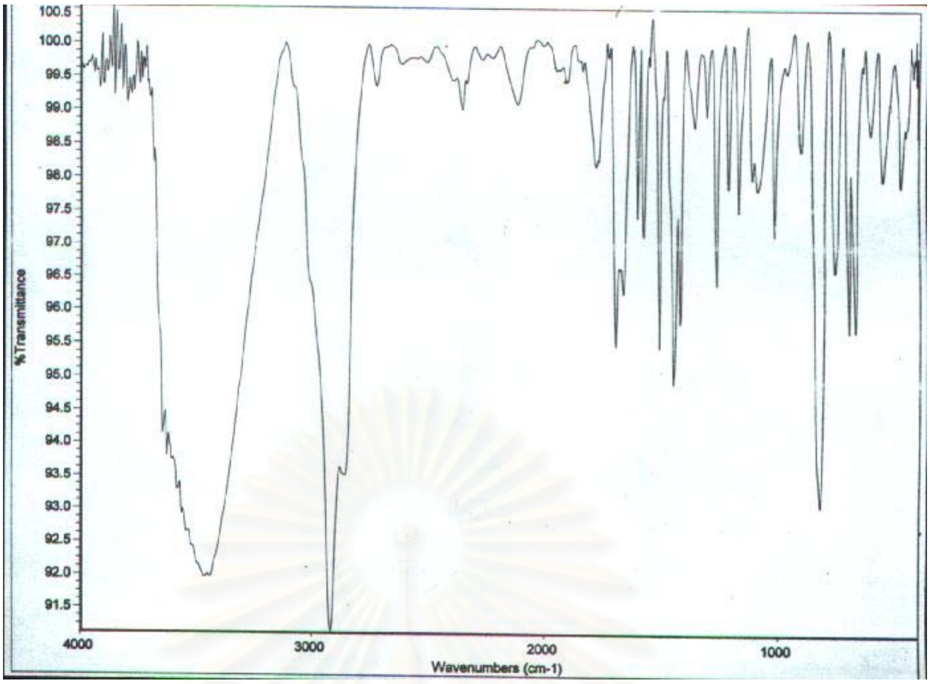

Figure C11 5%Polymer-supported ruthenium-2-aminopyridyl [5P-Ru-2AP].

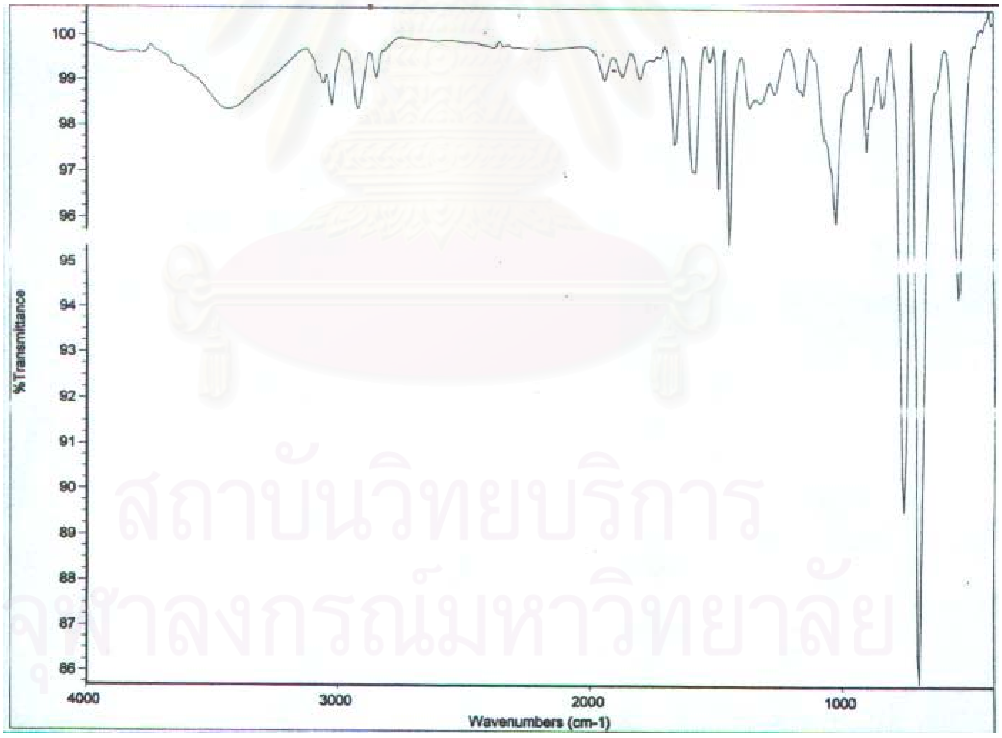

Figure C12 10%Polymer-supported ruthenium-2-aminopyridyl [10P-Ru -2AP].

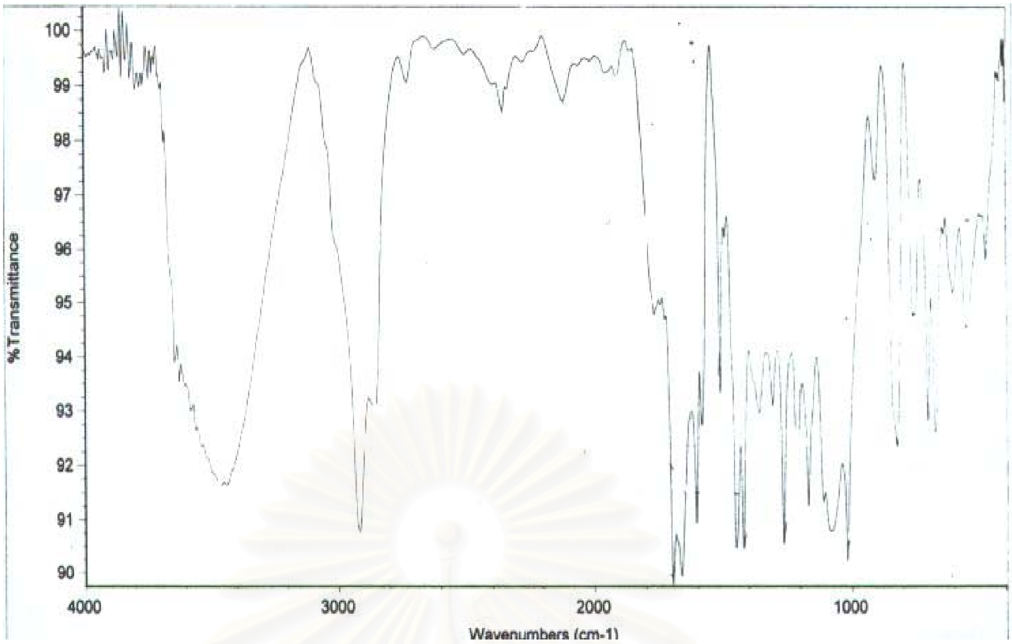

Figure C13 5%Polymer-supported ruthenium-Schiff base 2-aminopyridyl [5P-Ru-SB-2AP].

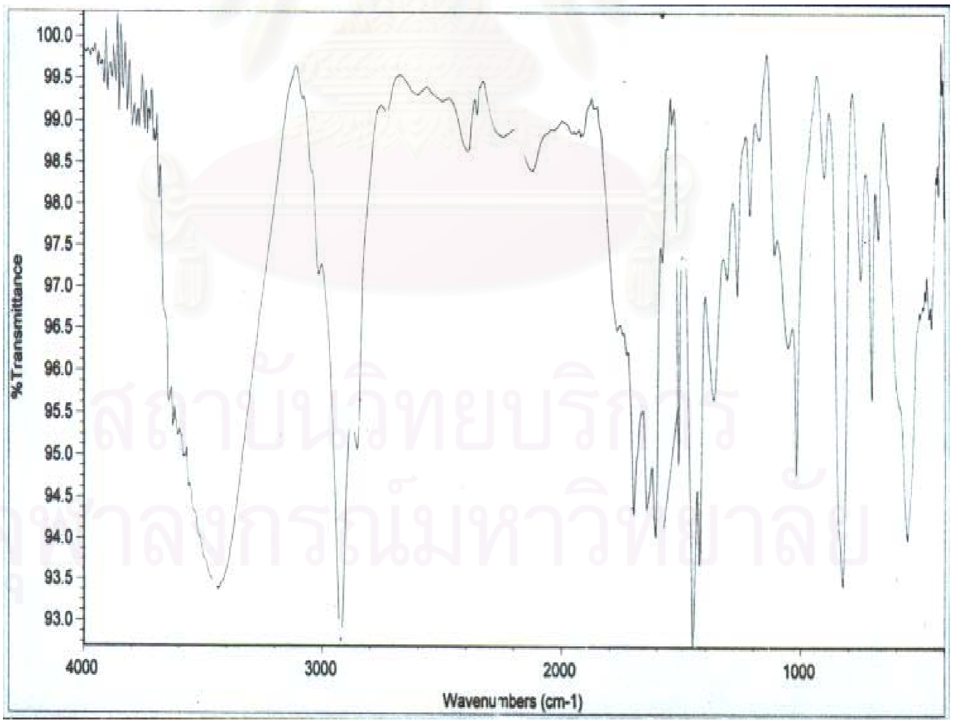

Figure C14 5%Polymer-supported ruthenium-Schiff base 1,3-diaminopropane [5P-Ru-SB-DP].

VITA

Miss Sirindhorn Bunchongsiln was born on July 8, 1977 in Sakonnakhon, Thailand. She received a Bachelor Degree of Science, major in Chemistry from Mahidol University in 2000. Since 2000, she has been a graduate student in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and graduated in 2003.

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