ไฮโดรจิเนชันของไดอีนอิลาสโทเมอร์โดยใช้ตัวเร่งปฏิกิริยาแพลเลเดียมบน
ตัวรองรับเส้นใยคาร์บอน

นายทศพร ตั้งทองกูร
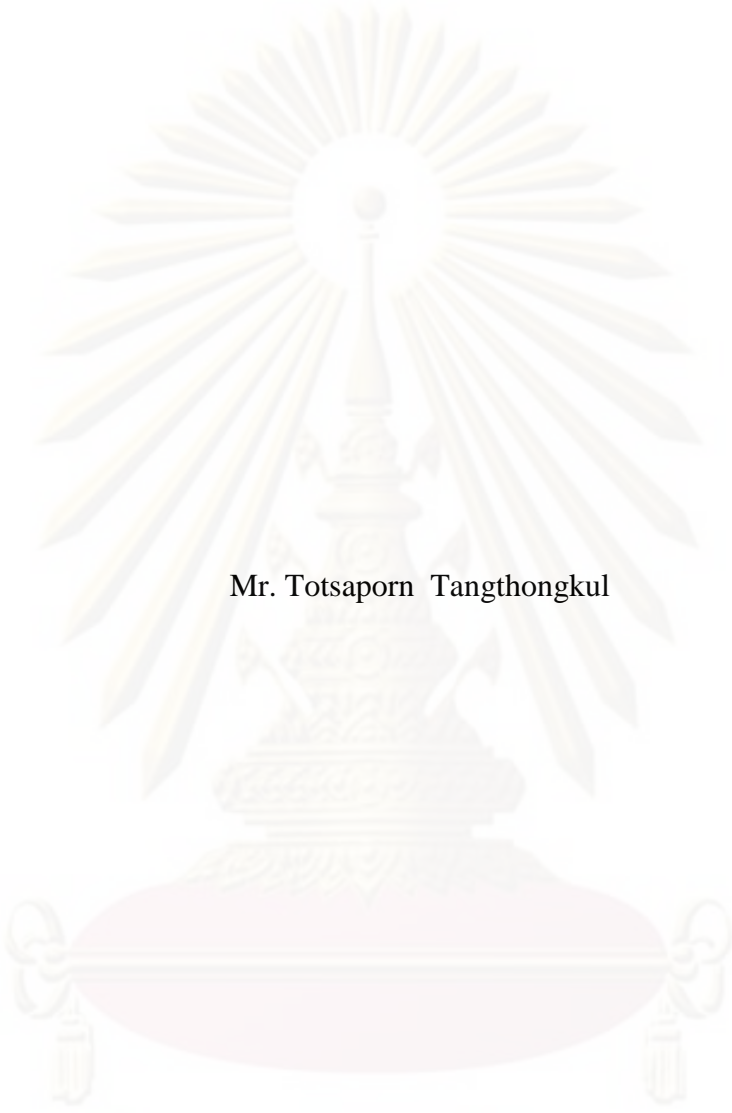
HYDROGENATION OF DIENE ELASTOMERS USING PALLADIUM CATALYST SUPPORTED ON CARBON FIBER

Mr. Totsaporn Tangthongkul

A Thesis Submitted in Partial Fulfillment of the Requirements

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                      FIBER
By   Mr. Totsaporn Tangthongkul
Field of Study   Petrochemistry and Polymer Science
Thesis Advisor   Assistant Professor Napida Hinchiranan, Ph.D.
Thesis Co-Advisor   Assistant Professor Prasert Reubroychareon, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Master's Degree

.... Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

.... Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)

.... Thesis Advisor
(Assistant Professor Napida Hinchiranan, Ph.D.)

.... Thesis Co-Advisor
(Assistant Professor Prasert Reubroychareon, Ph.D.)

.... Examiner
(Assistant Professor Voravee P. Hoven, Ph.D.)

.... External Examiner
(Assistant Professor Sommai Pivsa-Art, Ph.D.)

ทศพร ตั้งทองกูล : ไฮโดรจิเนชันของไดอีนอิลาสโทเมอร์โดยใช้ตัวเร่งปฏิกิริยา แพลเลเดียมบนตัวรองรับเส้นใยคาร์บอน. (HYDROGENATION OF DIENE ELASTOMERS USING PALLADIUM CATALYST SUPPORTED ON CARBON FIBER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร.นพิดา หิญชีระนันทน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ.ดร.ประเสริฐ เรียบร้อยเจริญ, 84 หน้า.

ไฮโดรจิเนชันเป็นวิธีการหนึ่งในการปรับปรุงโครงสร้างทางเคมีเพื่อเพิ่มความต้าน ทานต่อการสลายตัวแบบออกซิเดทีฟและทางความร้อนของอิลาสโทเมอร์ที่มีพันธะคู่โดยลด จำนวนโครงสร้างที่ไม่อิ่มตัว วัตถุประสงค์ของงานวิจัยนี้ คือ ศึกษาความเป็นไปได้ในการใช้ แพลเลเดียมบนตัวรองรับเส้นใยคาร์บอนเป็นตัวเร่งปฏิกิริยาไฮโดรจิเนชันของไดอีนอิลาสโทเมอร์ ได้แก่ ยางบิวทาไดอีน ยางในไทรล์ และยางธรรมชาติ โดยศึกษาผลของปัจจัยต่าง ๆ ต่อระดับ ไฮโดรจิเนชัน ได้แก่ อุณหภูมิ ความดันของแก๊สไฮโดรเจน ความเข้มข้นของยาง และความเข้มข้น ของตัวเร่งปฏิกิริยา วิเคราะห์ลักษณะของตัวเร่งปฏิกิริยาแพลเลเดียมด้วยเครื่องเอกซ์เรย์ดิฟแฟรก โทมิเตอร์ กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด และเทคนิคเทอร์โมกราวิเมตริก ระดับการ เกิดปฏิกิริยาไฮโดรจิเนชันสามารถคำนวณจากโปรตอนนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโตร สโกปี จากผลการทดลองทางจลนพลศาสตร์แสดงให้เห็นว่าไฮโดรจิเนชันของยางบิวทาไดอีนซึ่ง ถูกเร่งด้วยตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับเส้นใยคาร์บอนเป็นปฏิกิริยาอันดับหนึ่ง ค่า พลังงานกระตุ้นของปฏิกิริยาไฮโดรจิเนชันของยางบิวทาไดอีนที่เร่งปฏิกิริยาด้วยตัวเร่งปฏิกิริยา แพลเลเดียมบนตัวรองรับเส้นใยคาร์บอนมีค่าเท่ากับ 4.83 กิโลจูลต่อโมล จากผลการทดลองพบว่า ตัวเร่งปฏิกิริยาแพลเลเดียม (ร้อยละ 5.3 โดยน้ำหนัก) บนตัวรองรับเส้นใยคาร์บอนสามารถทำให้ เกิดปฏิกิริยาไฮโดรจิเนชันของยางบิวทาไดอีน ยางในไทรล์ และยางธรรมชาติ ได้ถึงร้อยละ 70.4, 46.4 และ 35.3 ตามลำดับ สำหรับยางธรรมชาติจะพบว่าโครงสร้างของผลิตภัณฑ์ที่ได้มี 2 ลักษณะ เนื่องจากมีการแข่งขันกันระหว่าง 2 ปฏิกิริยาคือปฏิกิริยาไฮโดรจิเนชันและปฏิกิริยา ซิส-ทรานส์ ไอโซเมอไรเซชัน

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ปีการศึกษา   2552   ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก
ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม

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Hydrogenation is one chemical modification methods to enhance the resistance of oxidative and thermal degradation of diene elastomers by reducing the amount of unsaturation in their structures. The purpose of this present work was to investigate the possibility to use palladium supported on carbon fiber (Pd/CF) as a catalyst for hydrogenation of diene elastomers such as butadiene rubber (BR), nitrile butadiene rubber (NBR) and natural rubber (NR). The effect of reaction parameters such as temperature, hydrogen pressure, rubber concentration and catalyst concentration on the level of hydrogenation of diene elastomers were studied. The palladium catalysts were characterized using X-ray diffractometer (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Degree of hydrogenation was calculated using proton nuclear magnetic resonance spectroscopy (^{1}H-NMR). The kinetic results indicated that the hydrogenation of BR catalyzed by Pd/CF exhibited a first-order behavior. The apparent activation energy for BR hydrogenation catalyzed by Pd/CF was 4.83 kJ/mol. The experimental results indicated that the palladium (5.3% wt) supported onto the carbon fiber could promote the hydrogenation of BR, NBR and NR to achieve 70.4, 46.4 and 35.3% hydrogenation, respectively. For NR hydrogenation, it was found that two structures of rubber product were formed as the result of competitive reactions: hydrogenation and *cis-trans* isomerization.

Field of Study:__Petrochemistry and Polymer Science Student's Signature _Totsaporn Tangthongkul_

Academic Year:_2009_   Advisor's Signature __Napida Hinchiranan__

                                                    Co-Advisor's Signature__PC__

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NOMENCLATURES

ACN	:	Acrylonitrile
BR	:	Butadiene Rubber
CF	:	Carbon Fiber
EDS	:	Energy Dispersive X-ray Spectroscopy
FTIR	:	Fourier Transform Infrared Spectroscopy
HBR	:	Hydrogenated Butadiene Rubber
HNBR	:	Hydrogenated Nitrile Butadiene Rubber
HNR	:	Hydrogenated Natural Rubber
NBR	:	Nitrile Butadiene Rubber
NMR	:	Nuclear Magnetic Resonance Spectroscopy
NR	:	Natural Rubber
PBD	:	Polybutadiene
Pd	:	Palladium
$Pd(OAc)_2$	:	Palladium(II) Acetate
SEM	:	Scanning Electron Microscopy
TGA	:	Thermogravimetric Analysis
XRD	:	X-ray Diffraction

CHAPTER I

INTRODUCTION

1.1 The Statement of Problem

Diene elastomers are produced by polymerization of a diene monomers or a diene monomer with a functional olefins such as butadiene rubber (BR), nitrile butadiene rubber (NBR), styrene butadiene rubber (SBR) including natural rubber (NR). Diene elastomers contain a large amount of carbon-carbon double bonds (C=C) in the polymer backbone resulting to degradation or oxidation when they are exposed to sunlight, oxygen and ozone, especially in severe operating conditions.

Hydrogenation, the addition of hydrogen (H_2) to an unsaturated moiety of unsaturated structure, is one of chemical modification methods to reduce the degree of unsaturation in the diene polymers. This technique can improve physical properties of the unsaturated polymers such as thermal resistance, light stability and solvent resistance (Rungnapa Tangthongkul, 2003). Diene elastomers can be hydrogenated by both non-catalytic and catalytic methods. For non-catalytic hydrogenation, it is normally carried out via diimide reduction process. At high reaction temperature (110-160°C), p-toluenesulfonyl hydrazide (TSH) is decomposed to form as reactive diimide (N_2H_2), which subsequently reduces carbon-carbon double bonds (Nang et al., 1976). The advantage of this method over others is not to require specialized hydrogenation reactor and high hydrogen pressure (McManus and Rempel, 1995). However, diimide hydrogenation is stoichiometric, and so far it is regarded as being unsuitable for large-scale processes. Since the reaction is carried out at high temperature, it also causes degradation and cyclization of polymer leading to inferior physical and mechanical properties (Harwood et al., 1973). To avoid these side reaction problems, catalytic hydrogenation has been more widely studied for diene elastomers.

Catalytic hydrogenations are classified as two types: homogeneous and heterogeneous catalytic systems depending on the state of the catalyst and the substrate. For homogeneous catalytic hydrogenation, the catalytically active species are molecularly dispersed within the resulting product. Homogeneous complexes normally contain only one type of active site resulting to the high selectivity (Rungnapa Tangthongkul, 2003). Since all these active sites are available, homogeneous catalysts are potentially more efficient than heterogeneous ones. However, homogeneous catalysts are difficultly separated from the hydrogenated product and the residual catalyst may lead the degradation of the final products. Therefore, many new developments for the catalytic reduction involving the use of heterogeneous catalyst, which the catalytically active species and the substrate are in different phases have been investigated. The main advantage of this catalyst is the ease of separation from the hydrogenated polymer. However, the efficiency of the heterogeneous catalyst depends on its surface area and the nature of support. At this point, the main problem for this catalyst system is normally related to the mass-transfer limitation effect that can inhibit the diffusion of polymer molecule through the pore of the catalyst during hydrogenation (Masayuki et al., 1999).

To minimize the effect of the mass transfer limitation of polymer molecules through the catalyst pore, carbon fiber (CF) seemed to be promising candidates for using as a catalyst support for heterogeneous catalytic reaction (Chambers et al., 1998; Park and Baker, 1999; Salman et al., 1999). It is expected to be efficient in liquid phase media due to its high external surfaces which can allow a significant decrease in critical mass transfer limitation (Planeix et al., 1994; Geus et al., 1995). This leads to increase the rate and the selectivity of the reaction (Sato et al., 2000).

1.2 Objective of Research Work

The objectives of this research were as follows:

1. To prepare palladium catalyst supported on carbon fiber for hydrogenation of diene elastomers.
2. To study the effect of reaction parameters such as temperature, H_2 pressure, concentration of reactant and catalyst including kinetics of the hydrogenation.

1.3 Scope of the Research Work

The preparation of palladium (Pd) catalyst for hydrogenation of diene elastomers and the effect of reaction parameters on the reduction of unsaturation level of diene elastomers were reported.

The experimental procedures were carried out as follows:

1. Studied previous research works.
2. Modified reactor for heterogeneous catalytic hydrogenation.
3. Prepared 5 wt% of Pd/CF catalyst via impregnation method.
4. Analyzed morphology, content of Pd and charge of Pd of Pd/CF catalyst using Scanning Electron Microscope (SEM), Thermogravimetric Analysis (TGA) and X-ray Diffraction (XRD), respectively.
5. Studied the activity and selectivity of Pd/CF catalyst for hydrogenation of small double bond molecules: 1-hexene, benzene and acrylonitrile.
6. Studied the activity of Pd/CF catalyst for hydrogenation of diene elastomers: BR, NBR and NR.
7. Studied the effect of temperature, H_2 pressure, concentration of reactant and catalyst on degree of hydrogenation of diene elastomers.
8. Studied the kinetics of hydrogenation system catalyzed by Pd/CF catalyst using BR as a reactant.

9. Analyzed the structure of reactants before and after hydrogenation using Fourier Transform Infrared spectroscopy (FTIR) and Proton Nuclear Magnetic Resonance spectroscopy (^{1}H–NMR), which also used to calculate the exact degree of hydrogenation.

10. Summarized and discussed the results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Diene Elastomers

Diene elastomers are polymers produced by polymerization of a diene monomer or a diene monomer with a functional olefin such as butadiene rubber (BR), nitrile butadiene rubber (NBR) including natural rubber (NR). Diene elastomers have become an important industrial material for a variety of applications, especially in the tire manufacturing industry. They are also used in the manufacture of various products including household, engineering, medical, and commercial goods.

2.1.1 Butadiene Rubber

Butadiene rubber (BR) or polybutadiene (PBD) is one of the most important commercial polymers after styrene butadiene rubber (SBR) and natural rubber (NR) in terms of tonnage consumed. It is produced from the 1,3-butadiene monomer. BR is made primarily by solution polymerization or emulsion polymerization. Considering polymerization of butadiene, there are three basically stereoregular forms of BR: *cis*-1,4-, *trans*-1,4- and 1,2-polybutadiene (Barlow, 1993) as shown in Figure 2.1.

cis-1,4   *trans*-1,4   1,2-*vinyl*
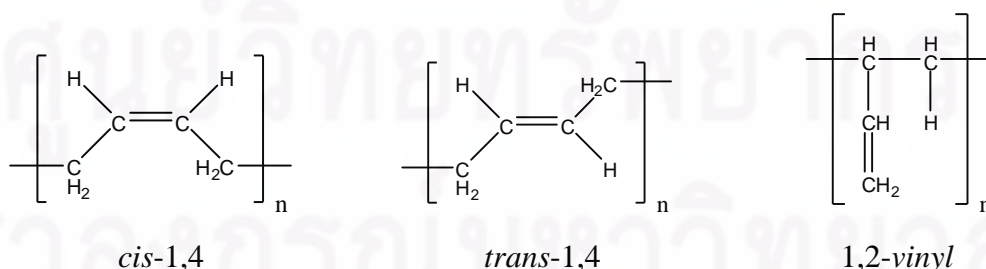
Figure 2.1 Various chemical structures of BR.

By using different catalysts and/or solvents for polymerization, BR can be produced and contain various proportions of the above forms. *Cis* and *trans* forms are predominantly used in a number of applications. The *trans* form emerges as a fibrous material, while the *cis* form is a rubber. The 1,2-content of BR also significantly influences its properties. It has been found that the 1,2-*vinyl* content of BR directly affects abrasion properties. The properties of BR show some superiority to both NR and SBR vulcanizates such as abrasion resistance and groove cracking resistance of tyres, low-temperature flexibility, heat aging resistance, high resilience at low deformations, ozone resistance in static and dynamic deformation, and ability to accept higher levels of filler and oil with less deterioration in properties (Sasisom Imerbsin, 2003).

It has been indicated that *cis* form of BR is a useful for blending process in the tyre industry due to its abrasion properties, low heat build-up and its cost. More than a half of BR produced is used for blending with SBR in passenger-car tyres and with NR in truck tyres. It is also used as the toughening rubber in high-impact polystyrene. Furthermore, it is used for producing playballs, children's toys, etc (Morton, 1973).

2.1.2 Nitrile Butadiene Rubber (Nagdi, 1993)

Nitrile butadiene rubber (NBR) or nitrile rubber is unsaturated copolymers of acrylonitrile and various butadiene monomers (1,2-butadiene and 1,3-butadiene). Its chemical structure of NBR is presented in Figure 2.2. They are available in five grades based on the acrylonitrile (ACN) content as shown in Table 2.1.

Table 2.1 Grade of NBR.

Grade of NBR	ACN content (%)
very low nitriles	18-20
low nitriles	28-29
medium nitriles	33-34
high nitriles	38-39
very high nitriles	45-48
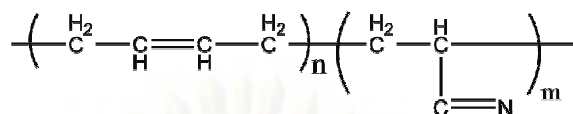
Figure 2.2 Chemical structure of NBR.

Many of the vulcanizate properties of NBR are directly related to the proportion of ACN content in the rubber. As the ACN content is increased, the change in the vulcanizate properties is shown in Table 2.2.

In general, NBR with high and very high ACN content is used in applications requiring good resistance to hydrocarbons of high aromatic contents (e.g., aromatic oils and gasolines). The medium grades of NBR are used for the products which contact to containing oil lower aromatic content or used in case where higher swelling of the elastomer is tolerable. The NBR with low and very low ACN content is applied for rubber parts contacting to liquid with low swelling effect (e.g., paraffinic oils and polyalphaolefins) or in cases that the importance of low-temperature flexibility is greater than oil resistance properties.

Table 2.2 Properties change of NBR vulcanizates when ACN content increase.

	Properties of
Increase	– Resistance to petroleum-based fluids and hydrocarbon fuels
	– Heat resistance
	– Ozone resistance
	– Abrasion resistance
	– Tensile strength
	– Hardness
	– Density
Decrease	– Low-temperature flexibility
	– Rebound resilience
	– Compressing set
	– Gas permeability

2.1.3 Natural Rubber

Natural rubber (NR) is also important industrial material for the tire industry. The most common source of NR is obtained by tapping the *Hevea brasiliensis* or Para rubber tree, which is indigenous to forests in the Amazon valley. Although NR can be obtained from more than 200 different species of plants, none could compete with Hevea rubber in yield, frequency of tapping, or longevity (Morton, ed., 1987). NR is a unique elastomeric polymer produced from natural rubber latex (NRL) defining as a milky fluid that consists of extremely small particles of rubber obtained from plants dispersed in aqueous medium. The structure of NR mainly composed with linear *cis*-1,4-polyisoprene almost 100% (Hofmann, 1989), (Figure 2.3).

Nowadays, the demand for NR in the commercial market receives competition from synthetic rubbers such as SBR and synthetic polyisoprene since it is not possible to control the quality of NR during its polymerization process unlike those of synthetic rubbers which have the specific pendent groups to improve some physical and chemical properties of rubbers. However, NR is still used in many applications due to the following reasons: superior building tack, green stock strength, superior processing, high strength in nonblack formulations, hot tear resistance, retention of strength at elevated temperature, high resilience, low hysteresis, excellent dynamic properties and general fatique resistance (Morton, ed., 1987).
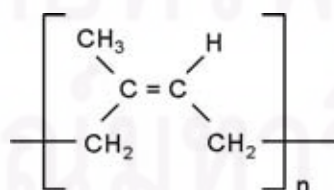
Figure 2.3 Chemical structure of NR or *cis*-1,4-polyisoprene.

Although, the carbon-carbon double bonds in the diene elastomers give advantage in terms of vulcanization and some chemical modifications, the presence of unsaturated carbon-carbon double bonds might cause degradation or oxidation when they are exposed to sunlight, oxygen and ozone, especially in severe operating conditions. Moreover, the non-polar hydrocarbon structure of NR also limited to be used in various applications. Thus, it is necessary to improve diene elastomers to have better chemical and weathering resistance properties. Double bonds are crucial for postpolymerization processes such as vulcanization (Rungnapa Tangthongkul, 2003).

2.2 Chemical Modification of Diene Elastomers

The chemical modification of diene polymers is a useful process for synthesizing polymers, which are inaccessible or difficult to prepare by conventional polymerization techniques. Chemical modifications such as crosslinking, grafting, degradation, oxidation, isomerization and cyclization have been studied for altering and optimizing the physical and mechanical properties of polymers (Bhowmick and Stephens, eds., 1988; McManus and Rempel, 1995; Singha et al., 1997). In other words, the chemical modification of polymer is a postpolymerization which is used to improve and optimize the chemical and mechanical properties of existing polymers or synthetic novel polymers having desirable functional groups. It has been shown that the hydrogenation of 1,4-polybutadiene produces a thermoplastic material with a structure identical to a linear polyethylene. The perfect alternating copolymer of ethylene with propylene can be achieved by hydrogenating 1,4-polyisoprene (Rungnapa Tangthongkul, 2003).

In the broadest sense, crosslinking, grafting, degradation, oxidation, isomerization, vulcanization, cyclization, hydrogenation, hydrocarboxylation, and hydroesterification are one of chemical modification reactions. Of these, most catalytic polymer chemical modifications studies have been devoted to hydrogenation. The catalytic hydrogenation of NBR is a significant commercial example due to its excellent properties in terms of superior ozone, peroxide, oil and solvent resistance at

elevated temperatures when it is compared to the unmodified NBR (Oppelt et al., 1976; Rempel and Azizian, 1984).

The important aspects to be considered with respect to the possibility of catalytic chemical reaction on polymers are: (i) the reactivity of the parent polymer (ii) the type and nature of catalyst i.e., its activity and selectivity (iii) the reaction conditions applied and (iv) the functionalities such as nitrile, carbonyl, halogen, etc. contained in the parent polymer (Rungnapa Tangthongkul, 2003).

2.3 Hydrogenation

Hydrogenation, one type of chemical modification of unsaturated polymers, is the addition of hydrogen (H_2) to reduce the amount of unsaturation in diene polymers. This modification process may lead to superior properties of the polymers such as thermal stability, light stability and resistance to oxygen, ozone, and solvent. Diene elastomers can be hydrogenated by both non-catalytic and catalytic methods. For the catalytic hydrogenation, it can be classified as homogeneous and heterogeneous catalyst systems (Napida Hinchiranan, 2004).

2.3.1 Non-Catalytic Hydrogenation

The main method of non-catalytic hydrogenation is carried out using diimide reduction, which is generated from *p*-toluenesulfonylhydrazide (TSH). At high temperature (110-160°C), TSH decomposes to form the reactive diimide (N_2H_2), which subsequently reduces carbon-carbon unsaturation (Nang et al., 1976). The advantage of this method over others is not to require specialized hydrogenation reactor and high pressure of hydrogen gas (McManus and Rempel, 1995). The diimide hydrogenation is stoichiometric and it may be unsuitable for large-scale processes. Since the reaction is carried out at high temperature, it causes degradation and cyclization of polymer leading to inferior physical and mechanical properties (Harwood et al., 1973). To avoid these side reaction problems, the catalytic

hydrogenation via homogeneous and heterogeneous catalysts has been more widely studied for improving the thermal and oxidative stability of diene polymers.

2.3.2 Catalytic Hydrogenation

Catalytic hydrogenation is divided into two types: homogeneous and heterogeneous catalytic hydrogenation depending on the state of the catalyst and the substrate.

2.3.2.1 Homogeneous Catalytic Hydrogenation

For homogeneous catalytic hydrogenation, the catalytically active species is molecularly dispersed within the polymer chain. Homogeneous complexes normally contain only one type of active site resulting to the high selectivity. Since all these active sites are available, homogeneous catalysts are potentially more efficient than heterogeneous catalysts. Mohammadi and Rempel (1989) used $RuCl(CH_3COO)(CO)(P(C_6H_5)_3)_2$ as a catalyst for hydrogenation of polybutadiene (PBD) in toluene solution to obtain 97% hydrogenation at 150°C under 4.1 MPa of hydrogen pressure. The detailed kinetics of the PBD hydrogenation was also examined. The rate of hydrogenation increased with increasing initial C=C concentration and hydrogen pressure. A first order dependence on the reaction rate with respect to the total ruthenium concentration in the presence of excess triphenylphophine was obtained. The reaction rate showed an inverse dependence on the increase in the triphenylphophine concentration.

Guo and Rempel (1992) explored the hydrogenation of polybutadiene (PBD) and nitrile butadiene rubber (NBR) in the presence of $RuCl(CO)(OCOPh)(PPh_3)_2$. About 97% hydrogenation of 1,2–PBD was achieved by using $RuCl(CO)(OCOPh)(PPh_3)_2$ as the catalyst in toluene under 4 MPa of hydrogen pressure at 150°C. The increase in the hydrogen pressure increased the hydrogenation rate and decreased the possibility of isomerization. The *cis*-PBD was hydrogenated in *o*-chlorobenzene at 85°C under less than 101 kPa of hydrogen pressure to give ca. 70% hydrogenation. The isomerization competed with hydrogenation to obstruct the

complete hydrogenation reaction. The investigated kinetic studies were shown to be first order dependence of the hydrogenation rate on carbon-carbon double bond concentration and hydrogen pressure. The reaction rate also followed the first order with respect to Ru concentration at low concentration. At high concentration of Ru, the rate of hydrogenation became insensitive to further increase in catalyst concentration. This result may be explained by the formation of a dimeric Ru complex at high concentration of catalyst. The presence of triphenylphosphine on the hydrogenation rate retarded the formation of the active species and led to a decrease in the hydrogenation rate. Only 40% completion of NBR hydrogenation was achieved at 105°C under 87 kPa of hydrogen pressure. A first order dependence of hydrogenation rate on the olefin substrate and the total catalyst concentration was observed. The hydrogenation rate shows a first order towards zero order dependence with respect to hydrogen pressure. The rate of hydrogenation decreased with increasing the nitrile content in the polymer.

Singha et al. (1994) reported hydrogenation of nitrile butadiene rubber (NBR) latex in the presence of water soluble analog of Wilkinson catalyst, $RhCl(DPM)_3$ (DPM = diphenyl phosphinobenzene m-sulfonate). The reaction was carried out at 75°C and atmospheric hydrogen pressure yielding more than 60% mole hydrogenation. The degree of hydrogenation increased with increasing temperature, pressure, and catalyst concentration. However, the hydrogenation was accompanied by a partial loss in rubber solubility. Hydrogenation occurred with no significant change in the average particle size of latex as well as particle size distribution.

Kitikorn Charmondusit et al. (2003) reported that $OsHCl(CO)(O_2)(PCy_3)_2$ has been found to be an excellent homogeneous catalyst for hydrogenation of cis-1,4-polyisoprene (CPIP), which more than 97% hydrogenation was observed at 130°C in 15 min. The kinetic studies were carried out in the range of 115-140°C with 35-69 bar of hydrogen pressure. The results of investigation showed that the reaction exhibited a first order dependence on catalyst concentration and carbon-carbon double bond concentration and a second order with respect to hydrogen pressure. The apparent activation energy was found to be 109.3 kJ/mol. The relative viscosity of

hydrogenated polymer indicated that no side reaction such as degradation or crosslinking occurred over the range of conditions studied. Natural rubber can be quantitatively hydrogenated using $OsHCl(CO)(O_2)(PCy_3)_2$ in combination with added acid (Kitikorn Charmondusit, 2002). The presence of a strong acid and the high coordinating power of the reaction solvent enhanced the rate of hydrogenation.

Rungnapa Tangthongkul (2003) studied the kinetics of the hydrogenation of synthetic *cis*-1,4-polyisoprene, natural rubber and natural rubber latex in the presence of $Ru(CH=CH(Ph))Cl(CO)(PCy_3)_2$. It was observed that the hydrogenation rate of these rubbers followed pseudo first order kinetics in carbon-carbon double bond concentration under all sets of reaction conditions studied. The kinetic results suggested that the hydrogenation reaction of isoprene rubbers showed a first-order behavior with respect to total catalyst concentration and hydrogen pressure. An inverse first-order dependence on added PCy_3 was also observed. The apparent activation energy of *cis*-1,4-polyisoprene hydrogenation was estimated as 51.1 kJ/mol over the temperature range of 130 to 180°C, whereas it was 25.3 kJ/mol for natural rubber hydrogenation and 29.2 kJ/mol for natural rubber latex hydrogenation (over the temperature range of 140 to 160°C). The addition of a small amount of *p*-toluenesulfonic acid to the system could substantially increase the rate of reaction. The impurities in the natural rubber showed the severely reduced the catalytic activity. The main polymer chain length and molecular weight was decreased during the hydrogenation due to the reaction conditions employed.

However, homogeneous catalysts are difficultly separated from the hydrogenated product and the residual catalyst may lead the degradation of the final products. Therefore, many new developments for the catalytic reduction involved the use of heterogeneous catalyst which the catalytically active species and the substrate are in different phases have been investigated.

2.3.2.2 Heterogeneous Catalytic Hydrogenation

For heterogeneous catalytic hydrogenation, the catalytically active species and the substrate are in different phases. The main advantage of this catalyst is to be

easily separated from the hydrogenated polymer. However, the efficiency of the heterogeneous catalyst depends on its surface area and the nature of support. At this point, the main problem for this catalyst system is normally related to the mass-transfer limitation effect due to pore size of the catalyst. This can inhibit the diffusion of polymer molecule during hydrogenation process (Masayuki et al., 1999).

Chang and Huang (1998) studied the hydrogenation of polystyrene-*block*-polybutadiene-*block*-polystyrene thermoplastic elastomers (SBS rubbers) using palladium catalyst supported on alumina (Al_2O_3). The palladium particles were prepared by impregnating palladium (II) acetate ($Pd(CH_3COO)_2$) in Al_2O_3 supports. The reactions were carried out at 3.4 MPa and temperature ranging from 80 to 180°C. The results of catalytic performance on hydrogenation showed the reactivity of SBS microstructures in the order vinyl-1,2 > *trans*-1,4 > aromatic. Although the increase in the reaction temperature promotes the reaction rate, it decreased the selectivity to the hydrogenation of olefinic microstructures. Since the reaction was controlled by both chemical reaction and internal diffusion, the reactivity of SBS rubbers was greatly influenced by the metal dispersion and pore diameter of the catalysts. About 15% of aromatic microstructures of the SBS rubbers were hydrogenated at 98% conversion of olefinic microstructures.

Masayuki et al. (1999) studied the hydrogenation of nitrile butadiene rubber (NBR) catalyzed by pore-size controlled smectites (SM) load with palladium (Pd) catalyst. At atmospheric pressure and at 5.1 MPa of hydrogen, the hydrogenation of C=C bonds of NBR polymers proceeded by the Pd/SM catalysts with mesopores larger than 60 Å. When the mesopores of catalysts were smaller than 40 Å; in contrast, the reaction very slightly proceeded at atmospheric pressure and very slowly proceeds at 5.1 MPa of hydrogen, respectively. The reaction was controlled by the pore sizes of catalysts, which determine the diffusion of the polymer molecules onto the dispersed palladium particles within the pores.

Napida Hinchiranan et al. (2008) studied the hydrogenation of natural rubber (NR) in the presence of palladium deposited on barium sulfate ($Pd/BaSO_4$). It

was found that the structure of rubber product was formed as the result of competitive reactions: hydrogenation and *cis-trans* isomerization. The level of *cis-trans* isomerization increased with increasing hydrogen pressure up to 55 bar. The *trans-1,4* configuration of NR was more difficult to hydrogenate on the catalyst surface than the *cis* structure because of the higher steric hindrance and structure stability. A maximum hydrogenation level of ca. 9% was achieved at a temperature of 130°C. The degree of hydrogenation tended to decrease when the reaction temperature was higher than 130°C due to the predominance of the isomerization reaction which led to a higher degree of the *trans* structure which was difficult to hydrogenate. The increase in the rubber concentration reduced the catalytic activity for both reactions due to the entanglement of rubber molecules. The conversion of both reactions also depended on the solvent type used in the reaction. It was found that hexane was the most appropriate solvent for the selective hydrogenation of NR catalyzed by Pd/BaSO$_4$.

2.4 Palladium Catalyst for Hydrogenation

Generally, group VIII transition metals are widely used for decades as hydrogenation catalysts. The hydrogenation efficiency of each metal is varied with each substrate and supports. From the previous literatures, palladium is the extremely active catalyst for carbon-carbon double bond saturation, particularly in the presence of multiple unsaturation because it is much more labile than other metals (Ramesh et al., 2000). Palladium metal has unique catalytic properties in both homogeneous and heterogeneous reactions. For heterogeneous catalysis, palladium is used as a catalyst for oxidation and hydrogenation reactions. One of the most remarkable properties of palladium is the ability to dissociate and dissolve hydrogen. Atomic hydrogen occupies the octahedral interstices between the palladium atoms of the cubic-closed packed metal. Palladium can absorb up to 935 times of its own volume of hydrogen. Depending on hydrogen partial pressure and temperature, a so-called α- and β-hydride is formed (Nitikon Wongwaranon, 2006).

Like other group VIII metals, palladium can be used for hydrogenation of unsaturated hydrocarbons. Palladium shows the highest selectivity of these metals in heterogeneously catalyzed semi-hydrogenation of alkynes and dienes to the corresponding alkenes (Arnold et al., 1997). Activity of palladium for hydrocarbon hydrogenation is based on the ability for the dissociative adsorption of hydrogen and chemisorption of unsaturated hydrocarbons. The chemisorption of alkenes and alkynes is based on the interaction of the d-band of the palladium metal with the π-bonding system of the unsaturated hydrocarbons (Pallassana et al., 2000; Mittendorfer et al., 2003). Industrially used catalysts for acetylene hydrogenation contain relatively low palladium content (<0.1% wt) and are supported on metal oxides like alumina. Palladium shows high activity but only limited selectivity and long-term stability for hydrogenation of acetylene. The limited selectivity is mainly due to enhanced ethane formation and the formation of by-products like C4 and higher hydrocarbons. Palladium shows a strong deactivation behavior because of hydrocarbon and carbon deposits resulting to the requirement of a frequent exchange or regeneration of the catalyst in the hydrogenation reactor. Moreover, fresh or regenerated catalysts show high activity and consequently increase ethylene consumption and reduce selectivity. Furthermore, high activity of fresh or regenerated catalysts causes the overheating of the reactor because of the exothermic hydrogenation reaction (Nitikon Wongwaranon, 2006).

Sárkany et al. (1984) studied the hydrogenation of a mixture of 0.29% mole acetylene (C_2H_2), 0.44% mole hydrogen gas (H_2) and ethylene (C_2H_4) up to 100%, a so-call tail-end mixture, on palladium black and several Pd/Al_2O_3 catalysts. Hydrogenation of C_2H_4 increased with time on stream for all the Al_2O_3-supported catalysts. However, the opposite behavior was noted with palladium black.

Susmita et al. (1992) studied the effect of reaction parameters on the conversion of nitrile rubber hydrogenation catalyzed by palladium acetate. They reported that the level of hydrogenation increased with increasing reaction time, reaction temperature, hydrogen pressure and catalyst concentration. It was also found that this catalyst was not selective to $-C\equiv N$ group, but it was very effective to

hydrogenate the $-C=C-$ group located on the backbone of polymer. The maximum conversion at 96% could be achieved when the hydrogenation was carried out at 333 K under 2.7 MPa of H_2 pressure and 0.54 mmol of catalyst concentration for 1 h in acetone.

Jackson and Shaw (1996) studied the competitive hydrogenation of phenyl acetylene and styrene over Pd/C catalyst. They found that the order in hydrogenation of phenyl acetylene changed from zero-order to first-order at approximately 60% conversion. This behavior was ascribed to catalyst surface being unable to saturate with the hydrocarbon due to low concentration in solution.

Aramendia et al. (1997) studied the hydrogenation of citral with palladium catalyst supported on mixed 80:20 $SiO_2/AlPO_4$ and sepiolite from Vallecas (Madrid, Spain). They investigated the influence of reaction variables such as temperature, hydrogen pressure and the type of solvent in order to optimize the reduction process. The solvent has a marked effect on the reduction rate. They found that the presence of additives of Lewis acid type such as $FeCl_2$ increases the selectivity towards geraniol and nerol.

Joongjai Panpranot et al. (2004) investigated and compared the characteristics and catalytic properties of Pd/MCM−41 and Pd/SiO$_2$ catalysts in terms of palladium dispersion, catalytic activities for liquid-phase hydrogenation of 1-hexene and deactivation of the catalysts. High Pd dispersion was observed on Pd/MCM−41 with large pore catalyst, while the other catalysts showed relatively low Pd dispersion due to significant amount of Pd being located out of the pores of the supports. Based on CO chemisorption results, the catalyst activities seemed to be primarily related to the Pd dispersion and not to diffusion limitation since turnover frequencies (TOFs) were nearly identical for all the catalysts used in this study. In all cases, leaching and sintering of Pd caused catalyst deactivation after 5 h batch reaction. However, compared to Pd/SiO$_2$ with a similar pore size, Pd/MCM−41 exhibited higher hydrogenation activity and lower amount of metal loss.

2.5 Fiber–Supported Catalyst

High-strength fibers used in advanced composites are produced from the same material or hybrid combination. The available fibers are not only carbon, glass, and aramid, but high-modulus polyethylene (PE), boron, quartz, ceramic and newer fiber such as poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) are also counted as industrial used fiber. These fibers can be grouped into three broad categories: carbon, organic resin and inorganic compound. Within each group, several classes of high performance fiber materials have been developed to satisfy the basic desired criteria of low density, high strength and high stiffness (Passarin Jongvisuttisun, 2004).

2.5.1 Boron Fiber

Boron fibers (Figure 2.4a) are proved to be good reinforcement for light metal alloys, particularly when the fiber is protected by a coating of silicon carbide (SiC) or boron carbide (B_4C). The American space shuttle is composed of a skeleton made up of more than 200 tubes in boron fiber-reinforced aluminum, but the very high cost of the fiber has restricted much wider use. Most of the applications originally foreseen for boron fibers have been taken over by carbon fibers; although, they are used in some sports goods. These fibers are limited in their possible temperature range, as reactions occur at the interface around 1,000°C (Bunsell and Berger, 2001).

2.5.2 Silicon Carbide Fiber

Silicon carbide fibers (Figure 2.4b) are produced by a technique similar to process of boron fibers. They contain a possible reinforcement for metal-matrix composites such as titanium- and intermetallic-matrix composites. These fibers are based on materials which are readily available and the substrates can either be tungsten wire or a carbon filament, which is less expensive. Fibers of large diameters, 140 μm, are made using various chlorosilanes such as CH_3SiCl_3, which gives SiC and 3HCl. The fiber produced has a mantle of silicon carbide, which, in the case of a tungsten core, is a pure SiC, whereas carbon can be included in the mantle if a carbon core is used. Carbon can migrate to the fiber surface which, in any case, is further

modified to prevent loss of fiber properties during composite manufacture. The fibers produced by Textron are known as SCS-*n* (Wawner, 1988), where *n* is the number of microns of surface coating added onto the diameter. The variations of the silicon/carbon content of this layer are closely controlled to permit optimum fiber protection for different matrices so that the SCS−6 fiber is seen as being particularly attractive for titanium-matrix composites. These SiC fibers have very good mechanical properties with a Young's modulus greater than 400 GPa, and can be used at high temperatures around 1,000°C. Similar SiC fibers, a tungsten core is made by DERA in the United Kingdom. These fibers have a diameter of 100 μm (Bunsell and Berger, 2001).

2.5.3 Carbon Fiber

Carbon is an important support material in heterogeneous catalysis, in particular for liquid-phase catalysis. Activated carbon made from natural materials is used widely in this aspect. The reproducibility as well as the microporosity of activated carbon has often hampered the catalyst development. Carbon fibers (Figure 2.4c) can be produced on a large scale in a reproducible manner with unique options to steer the metal-support interactions, lyophilicity and texture (Geus and de Jong, 2000).

Carbon fibers (CF) made by carbonization of bamboo fibers were the first filaments used in Edison's incandescent electric lamps, but they were extremely brittle and rapidly replaced by tungsten wire (Sitting, 1980). The route adopted in the United States in the 1950s and early 1960s for producing fibers from the next lightest element after boron was to use fibers regenerated from cellulose. This was proved that a slow process gave the carbon yield is only 24%. However, such fibers are interesting for their thermal conduction properties and are still used in carbon-carbon heat shields and brake pads (Kaverov et al., 1995). The approach taken in Great Britain and Japan used polyacrylonitrile (PAN) fibers as precursors for making carbon fibers. An alternative route for making carbon fibers is from pitch obtained either from the residue of oil refining or the coking of coal process.

Figure 2.4 Various types of fibers; (a) boron fiber (b) silicon carbide (SiC) fiber and (c) carbon fiber (CF).

CF, alternatively graphite fiber or carbon graphite, is a material consisting of extremely thin fibers about 0.005–0.010 mm in diameter and mostly composed of carbon atoms. The carbon atoms are bonded together in microscopic crystals that are more or less parallely aligned to the long axis of the fiber. The crystal alignment makes the fiber very strong for its size. Several thousand carbon fibers are twisted together to form a yarn, which may be used by itself or woven into a fabric (Serp et al., 2003). The density of carbon fiber is also considerably lower than that of steel. Thus, it is ideal to use it for applications requiring low weight. The properties of CF such as high tensile strength, low weight, and low thermal expansion are attractive for aerospace, civil engineering, military, and motorsports, along with other competition sports. Moreover, it is very strong under stretching or bending. However, it is relatively expensive when it is compared to similar materials such as fiberglass or plastic. It is also weak when it is compressed or exposed to high shock.

Rodriguez et al. (1994) published an article in which they used fibers grown from synthesis gas and iron as the catalyst at temperatures of 873 K. Introduction of an active phase (Fe or FeCu) onto the CF was done via an incipient-wetness technique, followed by calcination and reduction. In comparison with alternative supports (γ-alumina and activated carbon), the FeCu/CF catalyst displayed an order of magnitude higher activity for ethylene hydrogenation. The authors ascribed that this activity increased a unique metal-support interaction between the Fe−Cu particles and the basal-plane regions of the CF.

Park and Baker (1999) focuses on the use of platelet type fibers exposing exclusive graphite edge sites. Using a phosphorus-based treatment, preferential blocking of so-called armchair faces occurred. Deposition of nickel onto the modified CF was enabled to promote the active of the nickel particles for hydrogenation of light alkenes reside on the zigzag faces.

2.6 Literature Reviews

Some previous works used CF as the support for hydrogenation to reduce the effect of mass-transfer limitation of the porous heterogeneous catalyst. CF is the innovative material that has potential to be used as the catalyst support (Serp et al., 2003). To compare with activated carbon, carbon fiber presents a high specific surface area without microporosity, preventing mass transfer limitations.

Pham-Huu et al. (2001) studied the hydrogenation of the carbon-carbon double bond in cinnamaldehyde using palladium catalyst (5% wt) supported on carbon nanofiber. Palladium particles were homogeneously deposited on the outer surface of the carbon nanofibers by the classical incipient wetness impregnation method. About 91% conversion of cinnamaldehyde to hydrocinnamaldehyde was achieved at a reaction temperature of around 80°C, under continuous hydrogen flowing at atmospheric pressure. For comparison, the catalytic test was also performed over the commercially available activated charcoal supported palladium catalyst (5% wt) under the same reaction conditions. About 60% conversion of cinnamaldehyde to 3-phenyl propanol was achieved (corresponding to the hydrogenation of both C=C and C=O bonds). It showed that the absence of microporosity in the carbon nanofibers favours both the high activity and selectivity which is confirmed by comparison with the commercially available activated charcoal supported palladium catalyst.

Joannet et al. (2002) studied the use of palladium supported on filamentous active carbon as effective catalyst for liquid-phase hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol. They have reported that activated carbon fibres (ACF) in the

form of woven fabrics were suitable supports for the preparation of structured palladium-based catalysts. Dispersion of metallic Pd up to 43% was obtained after Pd deposition via ion exchange from aqueous solutions. The activity of Pd/ACF catalysts were tested in the 2-butyne-1,4-diol hydrogenation towards 2-butene-1,4-diol in aqueous solutions at 0.6 MPa of H_2 pressure at 30°C for 1 h. It was found that the hydrogenation conversion was achieved to 80% with 97% selectivity.

Semagina et al. (2007) studied the hydrogenation of 1-hexyne using palladium catalyst (0.45% wt) supported on active carbon fiber. Monodispersed palladium nanoparticles were prepared via modified microemulsion method and deposited on active carbon fibers by impregnation method. The selectivity of catalyst for changing 1-hexyne to be 1-hexene was higher than 96% with 90% conversion when the reaction was carried out under 1.3 MPa of hydrogen pressure at 30°C, in the presence of n-heptane.

CHAPTER III

EXPERIMENTAL AND CHARACTERIZATION

3.1 Materials

Butadiene rubber (BR, 97.5% *cis*-configuration) was received from BST Elastomers Co., Ltd. (Bangkok, Thailand). Nitrile butadiene rubber (NBR) of Krynac® 3345F grade (33±1% ACN) obtained from Bayer Elastomers S.A. (France). Natural rubber (NR, STR−5L) was provided from Thai Hua Chumpon rubber Co., Ltd. (Samutsakorn, Thailand). The compositions of BR, NBR and NR were summarized in Appendix A. Carbon fiber (CF) was purchased from Future Fiber Limited Partnership (Bangkok, Thailand). The characteristic of CF was summarized in Appendix B. Palladium acetate was obtained from Sigma-Aldrich (Steinheim, Germany). The 99.99% hydrogen gas (H_2) for hydrogenation experiments was supplied from Praxair Inc. (Samutprakarn, Thailand). Hexane from SK Chemicals (Ulsan, Korea), monochlorobenzene from RCI Labscan Limited (Thailand), 1-hexene from Fluka (Steinheim, Germany), benzene from Panreac (Barcelona, Spain), acrylonitrile from Aldrich (Steinheim, Germany), nitric acid from J.T.Baker (Thailand) and acetone from J.T.Baker (U.S.A.) were all reagent grade and used as received.

3.2 Catalyst Preparation (Bussard, 2008)

For impregnation of palladium (Pd), the surface of carbon fiber (CF) was firstly treated by boiling in deionized water ca. 30 min. Then, it was immersed in 5% aq. nitric acid (HNO_3) for 6 h at 80°C under reflux. The resulting fiber was rinsed again by deionized water and dried overnight at 80°C. Palladium (II) acetate ($Pd(OAc)_2$) dissolved in acetone was loaded onto the surface-treated CF by impregnation method and then also dried at 80°C for 2 h.

3.3 Hydrogenation Process

The desired amount of rubber was dissolved in 150 ml of organic solvents. The rubber solution was transferred into the saturation unit (Figure 3.1); while, Pd/CF catalyst (the length of each pieces of CF supporter was ca. 1 cm) was loaded into the high pressure reactor for hydrogenation unit. To ensure that oxygen inside the reactor and the reactant was removed, the rubber solution was bubbling by passing hydrogen gas at 21 bar followed by continuously purging for 30 min. The reactor containing catalyst was also purged with hydrogen gas at 7 bar for 30 min. To hydrogenate the rubber, the hydrogenation reactor containing catalyst was heated to the required reaction temperature. Subsequently, the H_2-saturated rubber solution was transferred from the saturation unit to the hydrogenation reactor and then pressurized to the target reaction pressure when the reaction temperature was constant. During hydrogenation, the solution was stirred at a constant agitation rate at 600 rpm for a given reaction time. When hydrogenation was ceased, the reactor was cooled down and catalyst was isolated from the resulting product by centrifugation. The hydrogenated product was precipitated in ethanol and then dried at 50°C.
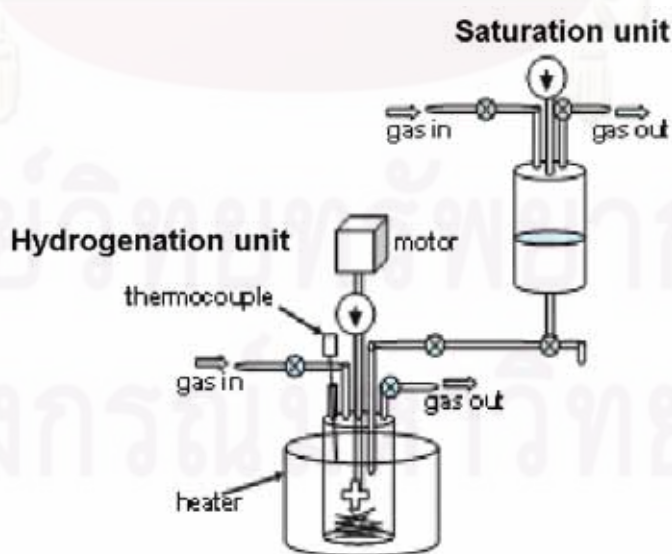
Figure 3.1 Experimental apparatus for hydrogenation.

3.4 Characterization Methods

3.4.1 Characterization of Catalyst

3.4.1.1 Scanning Electron Microscope (SEM)

The surface morphology of carbon fiber (supporter) and palladium particle-distribution morphology of catalysts (Pd/CF) were studied by scanning electron microscope (SEM). SEM images were obtained using a JEOL JSM-6400 SEM.

3.4.1.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine the content of palladium of catalysts (Pd/CF). TGA was performed on a Perkin Elmer TGA. The temperature increased under air atmosphere from 40 to 1,000°C at a constant heating rate of 10°C/min.

3.4.1.3 X-ray diffraction method (XRD)

The oxidation state and structure form of palladium deposited on carbon fiber was evaluated by X-ray diffraction method (XRD). XRD patterns were obtained using a D8−Discover, Bruker.

3.4.2 Characterization of Hydrogenated Products

3.4.2.1 Fourier Transform Infrared Spectroscopic Analysis (FTIR)

Infrared spectra were collected on a Thermo 470 FTIR spectrometer. The hydrogenated products were prepared by casting as films on potassium bromide plates.

3.4.2.2 ^{1}H−NMR Spectroscopic Analysis

The degree of hydrogenation was determined via ^{1}H−NMR spectroscopic analysis. ^{1}H−NMR spectra were recorded on the solutions of the rubber in CDCl$_3$ by using a Varian Mercury 400 MHz NMR spectrometer.

3.5 The Degree of Hydrogenation Determination

The degree of hydrogenation of each experiment was evaluated using ^{1}H–NMR spectroscopy. The peak area of saturated protons (−CH_2− at 1.5 (NBR only) and 1.2 ppm and −CH_3 at 0.8 ppm) was measured in order to calculate the %hydrogenation of butadiene rubber (BR) and nitrile butadiene rubber (NBR) using Eq. 3.1:

$$\%\text{Hydrogenation} = \frac{\text{Peak area of saturated} -CH_2- \text{ and } -CH_3}{\text{Total peak area}} \times 100 \qquad (3.1)$$

The peak area of unsaturated protons (=CH at 5.1 ppm, −CH_2− at 2.0 ppm and −CH_3 at 1.67 and 1.60 ppm) was measured in order to calculate the %hydrogenation of natural rubber (NR) using Eq. 3.2 and 3.3:

$$\%\text{Unsaturation} = \frac{\text{Peak area of unsaturated}}{\text{Total peak area}} \times 100 \qquad (3.2)$$

$$\%\text{Hydrogenation} = 100 - \%\text{Unsaturation} \qquad (3.3)$$

The example for %hydrogenation calculation is illustrated in Appendix D.

3.6 Determination of *cis-trans* Isomerization Level

The *cis-trans* isomerization was simultaneously occurred during natural rubber (NR) hydrogenation catalyzed by Pd/CF. The level of *cis-trans* isomerization of NR was evaluated using ^{1}H–NMR spectroscopy. The peak areas of methyl proton of *cis* (1.67 ppm) and *trans* (1.60 ppm) structure were measured in order to calculate the % *cis* structure and % *trans* structure of NR using Eq. 3.4 and 3.5:

$$\% \text{ cis structure} = \frac{\text{Peak area of cis structure}}{\text{Total peak area of cis and trans structure}} \times \%\text{Unsaturation} \qquad (3.4)$$

$$\% \text{ trans structure} = \%\text{Unsaturation} - \% \text{ cis structure} \qquad (3.5)$$

The example for the % *cis* and *trans* structure calculation is illustrated in Appendix D–3.
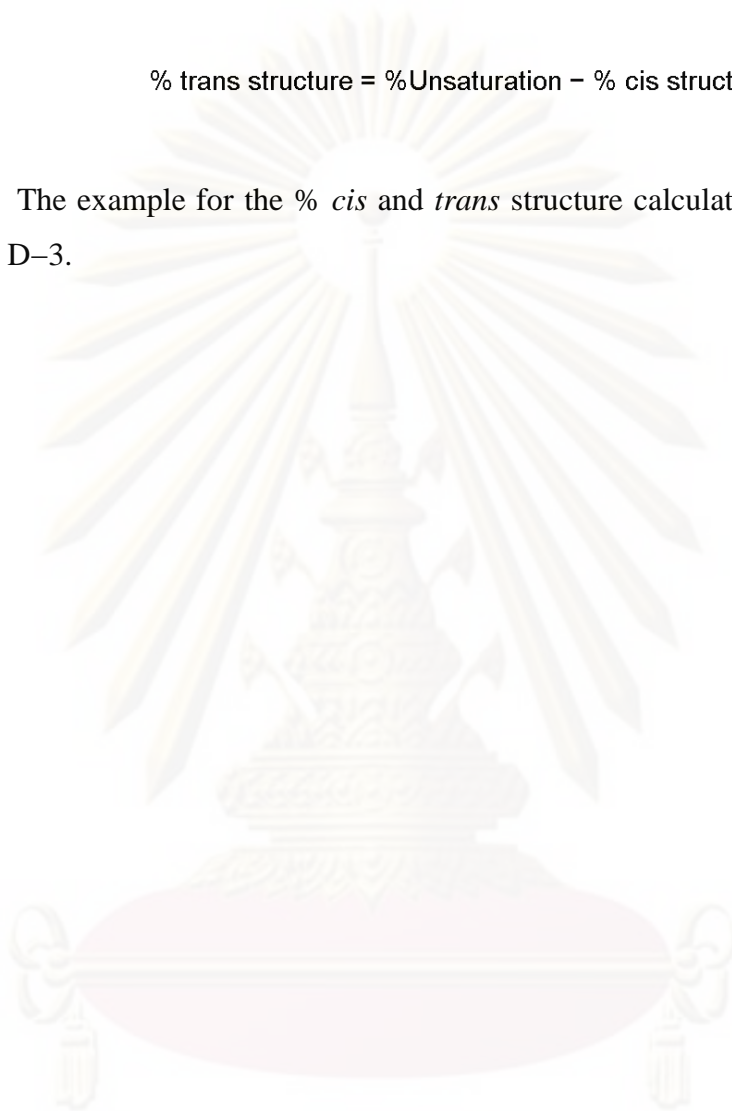
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Catalysts

The morphology of carbon fiber (CF) and palladium (Pd) deposited on CF was studied using a scanning electron microscope (SEM). Figure 4.1 shows SEM images of CF before (Figure 4.1a) and after surface treatment (Figure 4.1b). It showed that the surface of CF before and after surface treatment was smooth and there was no pore appeared on the surface of CF. After impregnation of Pd, Pd particles of various sizes were observed as shown in Figure 4.1c.

The oxidation state of Pd metal on CF catalyst was studied using X-ray diffraction method (XRD). Figure 4.2 shows XRD pattern of Pd/CF prepared via impregnation method. Pd/CF exhibited six peaks at 2θ of 11.0°, 12.5° and 13.6°, which ascribed as palladium (II) acetate and 15.0°, 22.7° and 25.8°, which were the peak characteristics of carbon fiber (Appendix C). Thus, the oxidation state of Pd catalyst was +2.

The content of Pd metal on CF was analyzed using thermogravimetric analysis (TGA). Figure 4.3 shows TGA curve of Pd/CF catalyst. It showed that the initial weight loss at the temperature range of ca. 130 to 240°C might be due to acetate content, whereas degradation of CF was occurred at the range of 400 to 720°C. Therefore, it was concluded that the residual weight of Pd metal was 5.3%.
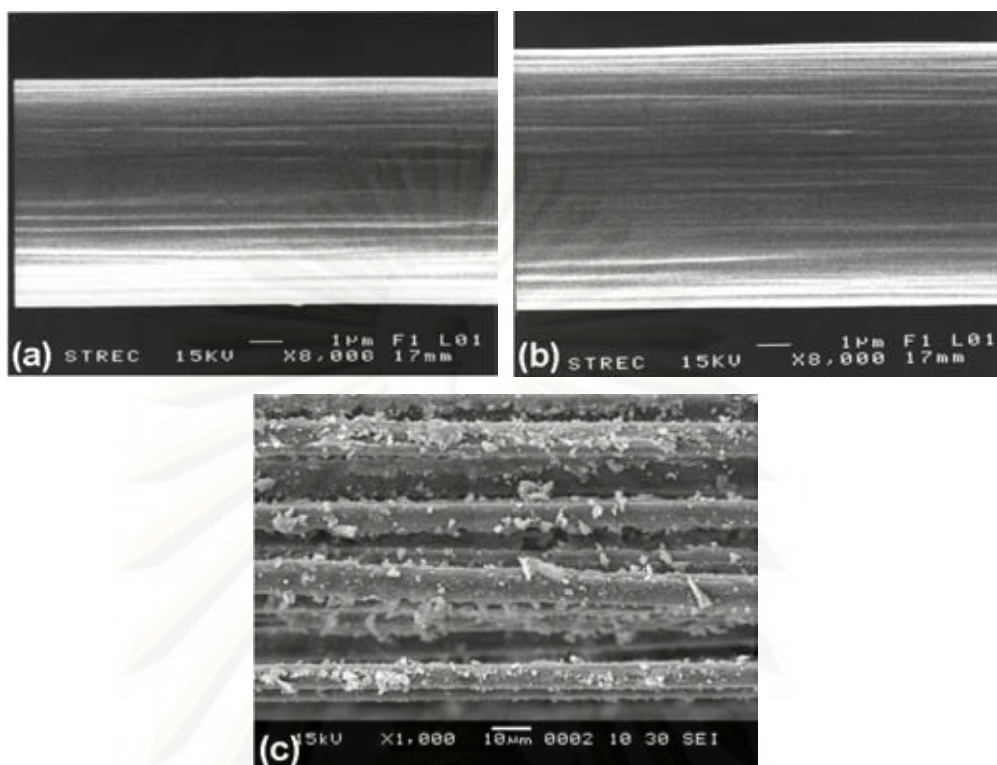
Figure 4.1   SEM images of CF (a) before and (b) after surface treatment and (c) Pd particles supported on CF prepared via impregnation method.
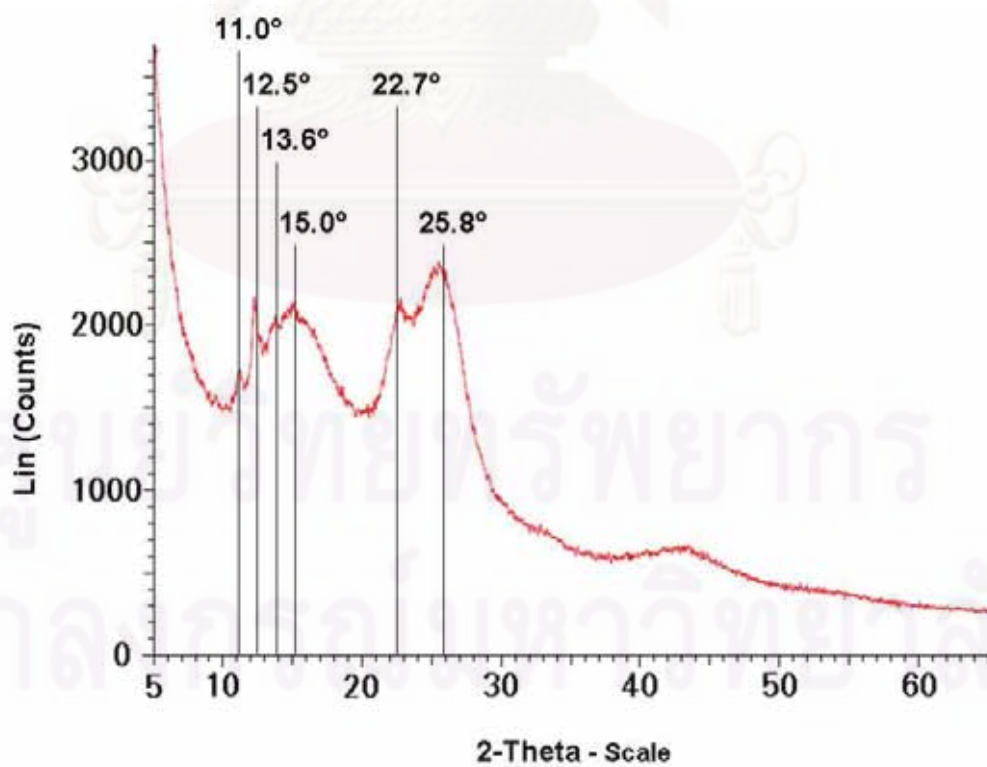
Figure 4.2   XRD pattern of Pd/CF prepared with impregnation method.
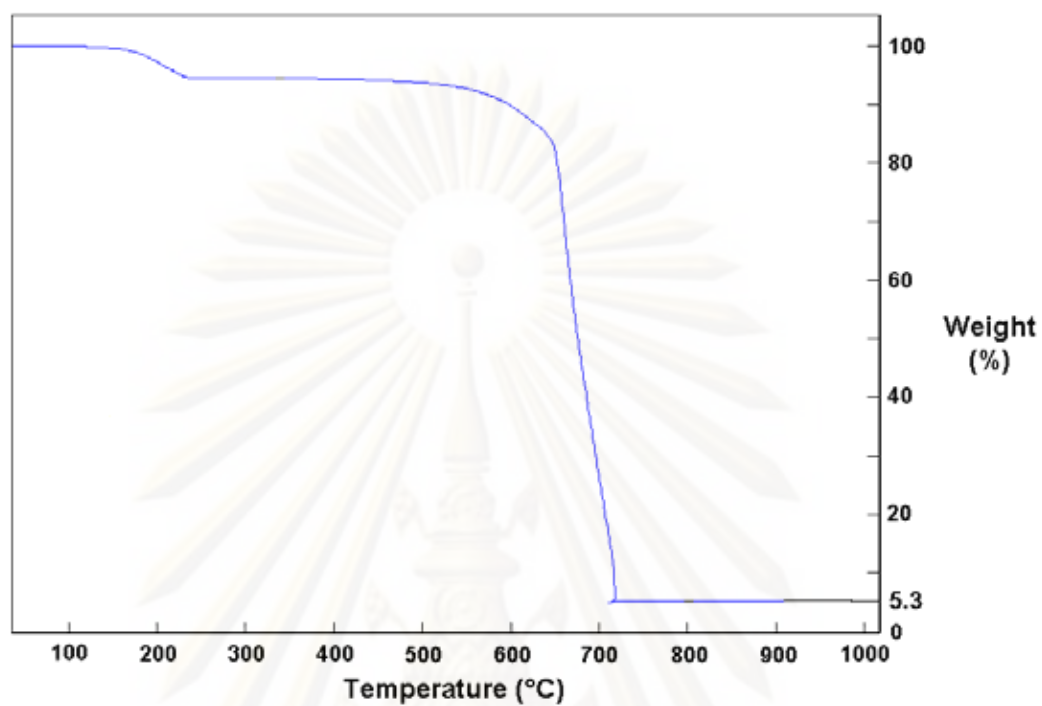
Figure 4.3   TGA pattern of Pd/CF prepared with impregnation method.

4.2 Hydrogenation of Small Molecules Catalyzed by Pd/CF Catalysts

4.2.1 Hydrogenation of 1–Hexene

The FTIR spectra of 1-hexene and its hydrogenated product are shown in Figure 4.4. The disappearance of the bands at 3,076 and 1,642 cm^{-1} due to the hydrogenation of =C–H stretching and C=C stretching. To confirm the FTIR results, a typical ^{1}H–NMR spectra of 1-hexene before and after hydrogenation are shown in Figure 4.5. The hydrogenation led to the reduction of the peaks at 5.8, 5.0 and 2.1 ppm, which were assigned to =CH–, H$_2$C= and =C–CH$_2$– groups, and the new peaks was appeared at 1.3 and 0.9 ppm which were the characteristic signals for hexane.

Figure 4.4 FTIR spectra of (a) 1-hexene and (b) hydrogenated product. Hydrogenation condition: Pd catalyst = 0.05 g of 5.3% wt Pd/CF (24.9 µmol of Pd); 1-hexene = 100 ml; H$_2$ pressure = 14 bar; Temperature = 50°C; Time = 4 h (89.2% hydrogenation).
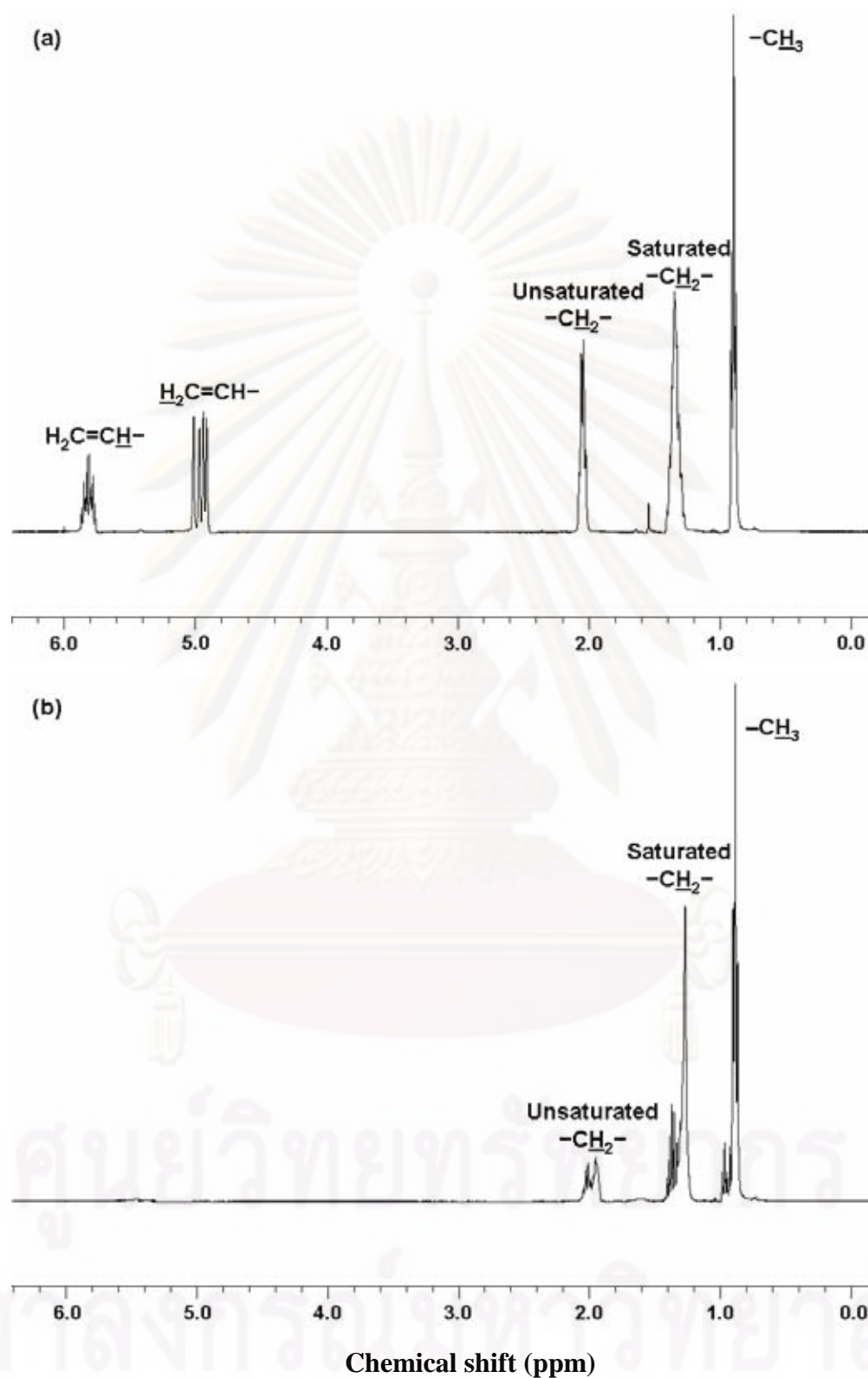
Figure 4.5 ^{1}H–NMR spectra of (a) 1-hexene and (b) hydrogenated product catalyzed by Pd/CF (89.2% hydrogenation).

4.2.2 Hydrogenation of Benzene

For benzene hydrogenation, the FTIR spectra of benzene before and after hydrogenation are shown in Figure 4.6. The peaks intensity at 3,034 cm^{-1} assigned to =C−H stretching and 1,478 cm^{-1} assigned to C=C ring stretching did not change after hydrogenation. ^{1}H−NMR spectra of benzene before hydrogenation compared to the one after hydrogenation was shown in Figure 4.7. The peak of benzene at 7.4 ppm assigned to −CH=CH− group did not change after hydrogenation. These showed that C=C bonds of benzene ring could not be hydrogenated by using this catalyst under studied reaction conditions.

Figure 4.6   FTIR spectra of benzene (a) before and (b) after hydrogenation. Hydrogenation condition: Pd catalyst = 0.05 g of 5.3% wt Pd/CF (24.9 μmol of Pd); benzene = 100 ml; H$_2$ pressure = 14 bar; Temperature = 50°C; Time = 4 h.
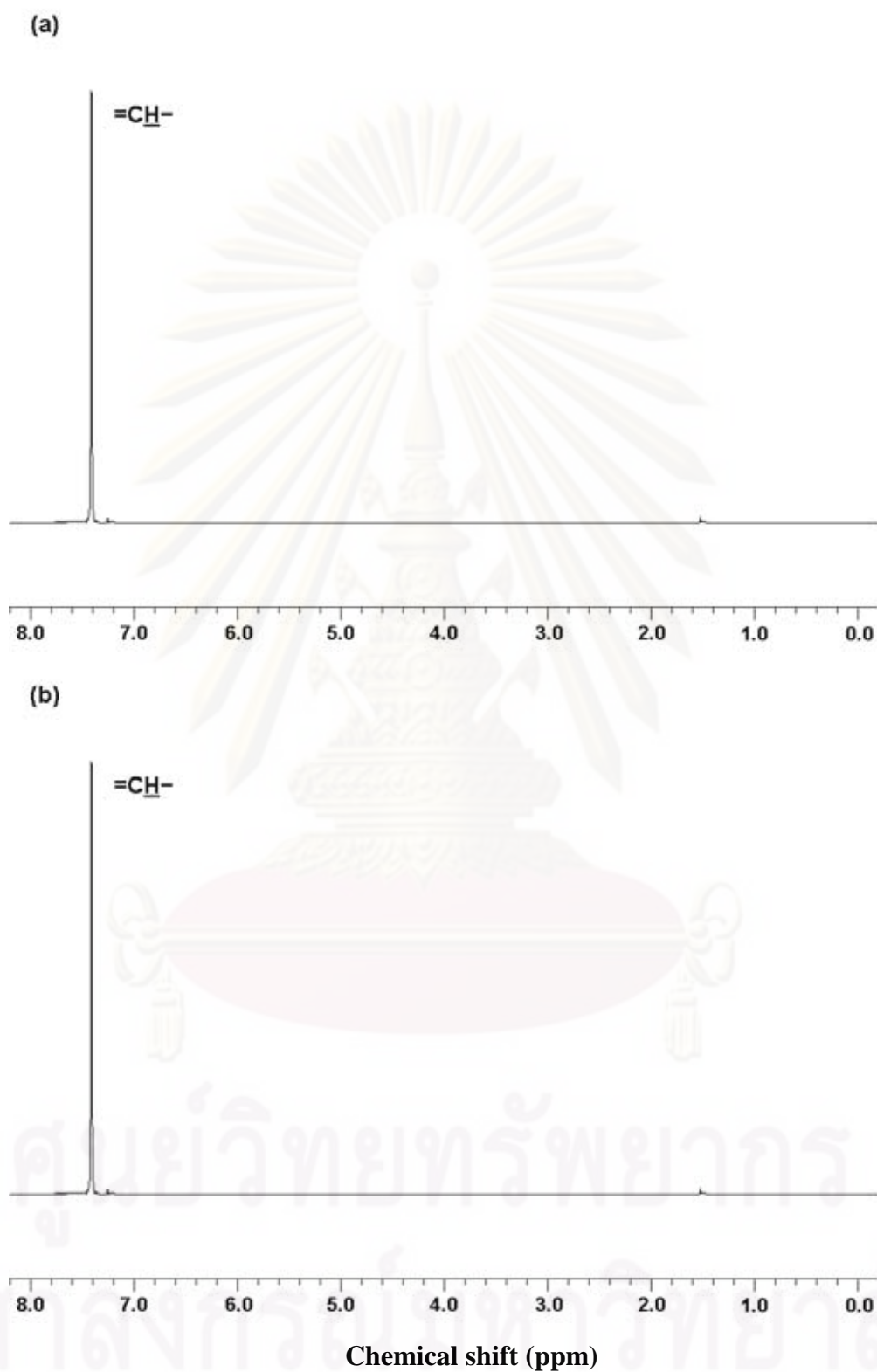
Figure 4.7 ^{1}H–NMR spectra of (a) benzene and (b) hydrogenated product catalyzed by Pd/CF.

4.2.3 Hydrogenation of Acrylonitrile

The FTIR spectra of acrylonitrile and its hydrogenated product are shown in Figure 4.8. The bands at 3,068 and 1,609 cm^{-1} assigned to =C–H stretching and C=C stretching of acrylonitrile were not appeared after hydrogenation. The peak intensity at 2,226 cm^{-1} assigned to C≡N stretching did not change during hydrogenation. No new peak assigned to N–H stretching also appeared after hydrogenation. This absence showed this catalyst had high selectivity to hydrogenate C=C bonds. A typical ^{1}H–NMR spectrum of acrylonitrile was compared to that of hydrogenated product as shown in Figure 4.9. The hydrogenation led the reduction in the peaks of acrylonitrile at 6.2–6.0 and 5.6 ppm, which were assigned to H$_2$C= and =CH– groups, respectively. The new peaks at 2.3 and 1.2 ppm attributed to propionitrile were also appeared in the hydrogenated product.
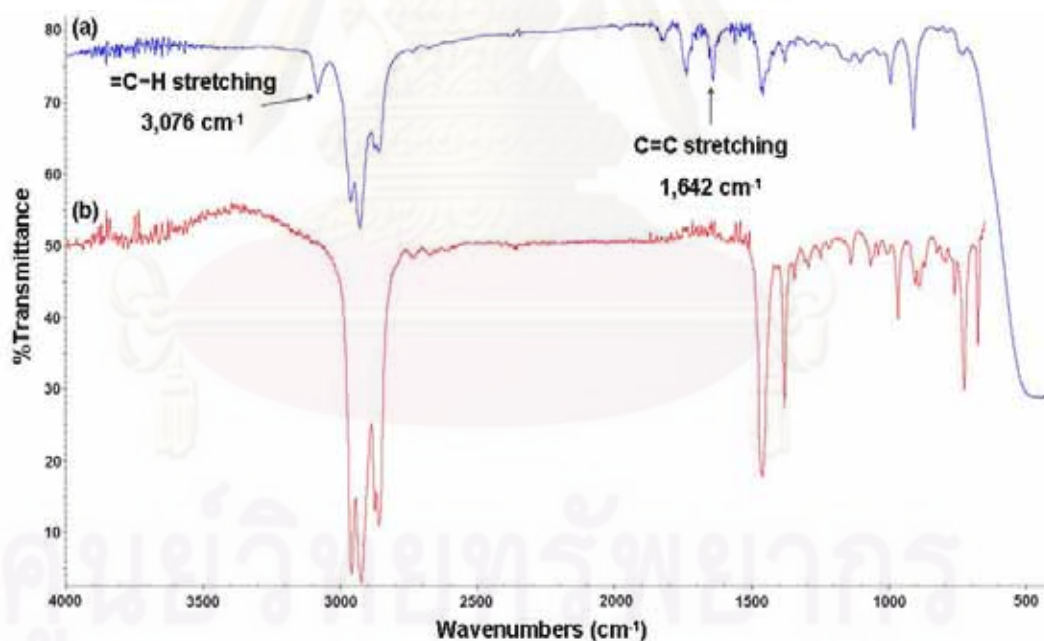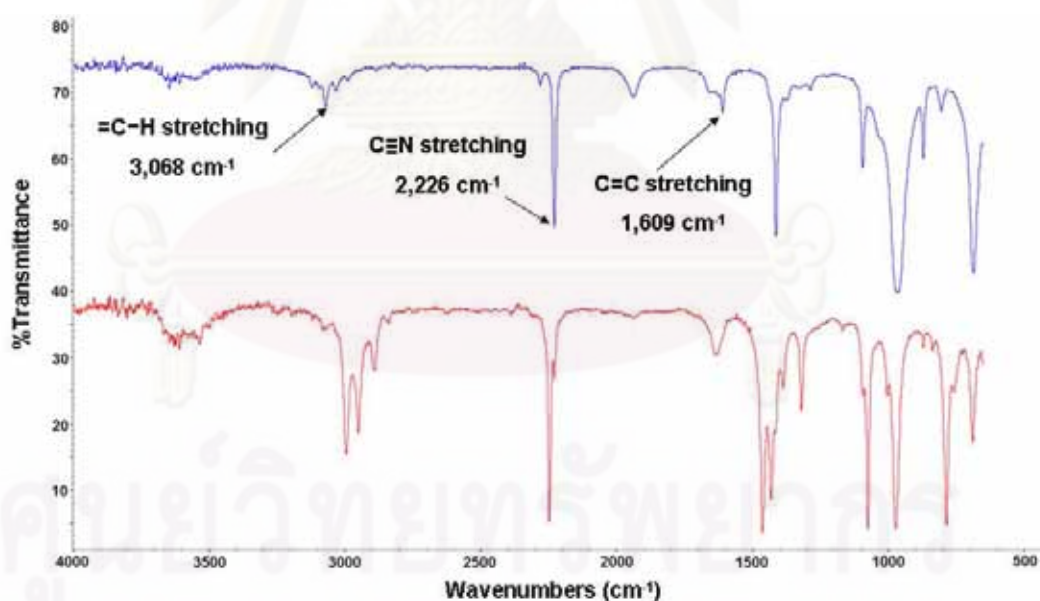

Figure 4.8   FTIR spectra of (a) acrylonitrile and (b) hydrogenated product. Hydrogenation condition: Pd catalyst = 0.05 g of 5.3% wt Pd/CF (24.9 μmol of Pd); acrylonitrile = 100 ml; H$_2$ pressure = 14 bar; Temperature = 50°C; Time = 4 h (46.9% hydrogenation).
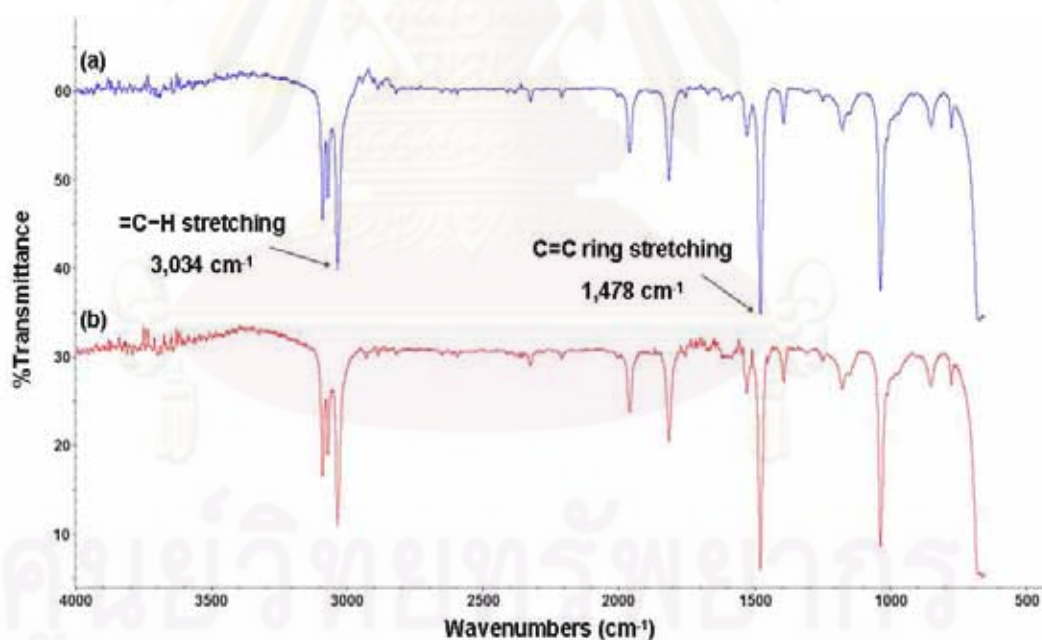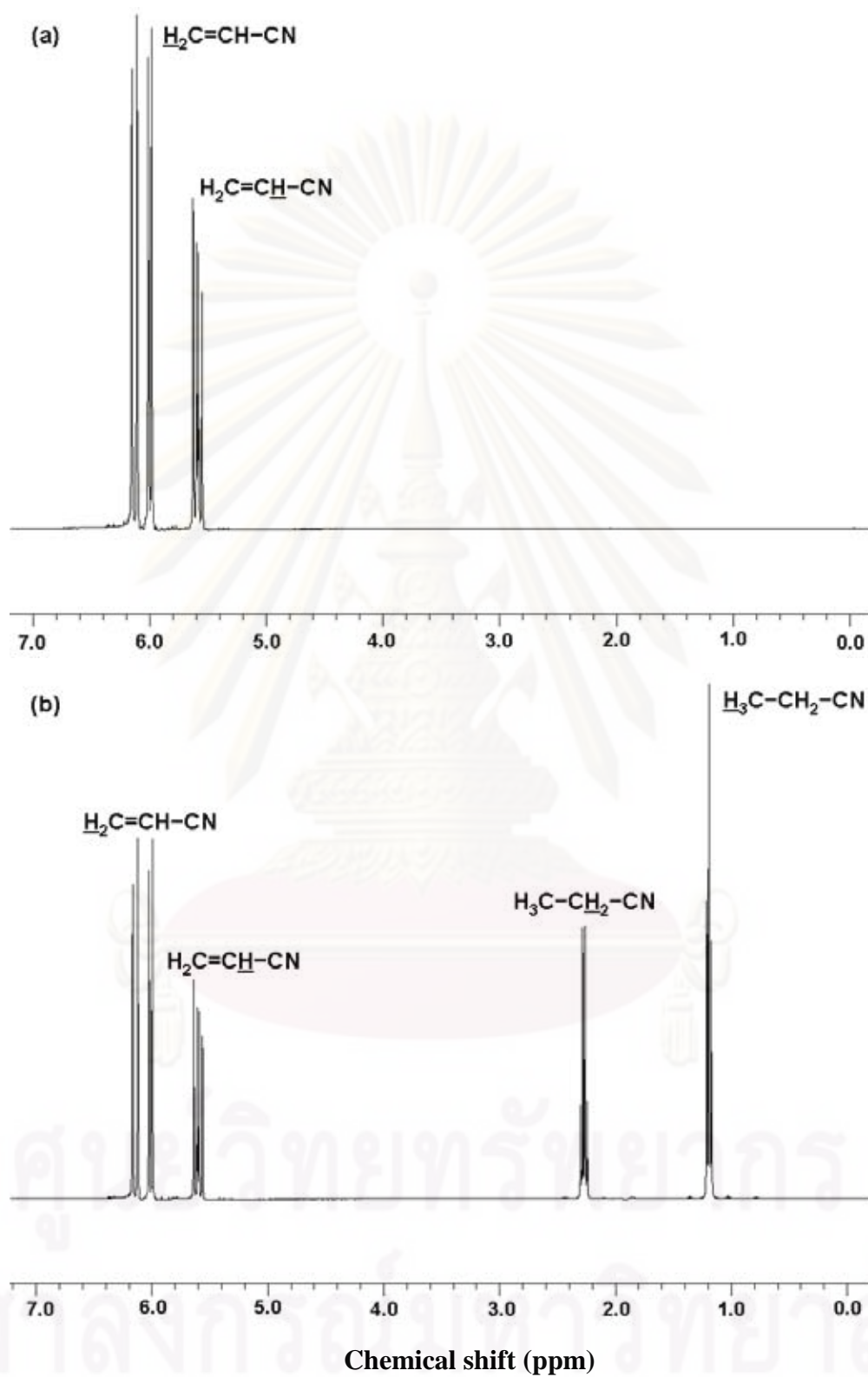
Figure 4.9   ¹H–NMR spectra of (a) acrylonitrile and (b) hydrogenated product
catalyzed by Pd/CF (46.9% hydrogenation).

4.3 Hydrogenation of Macromolecules Catalyzed by Pd/CF Catalysts

4.3.1 Hydrogenation of Butadiene Rubber

Butadiene rubber (BR) is a diene elastomer. It is synthesized from polymerization of butadiene monomer, which contains two carbon-carbon double bonds. Like most diene elastomers, BR has carbon-carbon double bonds in its backbone chain. Palladium catalyst has been reported to be an active catalyst for the selective hydrogenation of carbon-carbon double bonds (Ramesh et al., 2000). In order to investigate the hydrogenation of butadiene rubber in the presence of palladium catalyst in detail, comprehensive kinetic studies for this system were undertaken.

4.3.1.1 Structure Characterization Using FTIR and NMR Spectroscopy

The structure of hydrogenated butadiene rubber (HBR) is similar to the structure of a polyethylene (Guo and Rempel, 1990). FTIR spectra of butadiene rubber before and after hydrogenation are illustrated in Figure 4.10. The characteristic FTIR spectrum of HBR product indicated that the C=C stretching ($1,656$ cm^{-1}), C–H wagging of vinyl group (991 and 913 cm^{-1}) and C–H wagging in *cis*-alkene (739 cm^{-1}) disappeared while the intensity of the peak at 773 cm^{-1} attributed to –CH_2– increased.

Figure 4.11 shows a comparison of the ^{1}H–NMR spectra of BR and HBR. The characteristic ^{1}H–NMR signal attributed to olefinic protons (5.4 ppm) and unsaturated –CH_2– (2.1 ppm), tended to be decreased; while the new signals, saturated –CH_2– (1.2 ppm) and –CH_3 (0.8 ppm), were observed after the hydrogenation process. The actual degree of hydrogenation for each experiment could be calculated from the peak areas at 1.2 and 0.8 ppm and the summation of peak areas between 5.4 and 0.8 ppm as described in Appendix D.
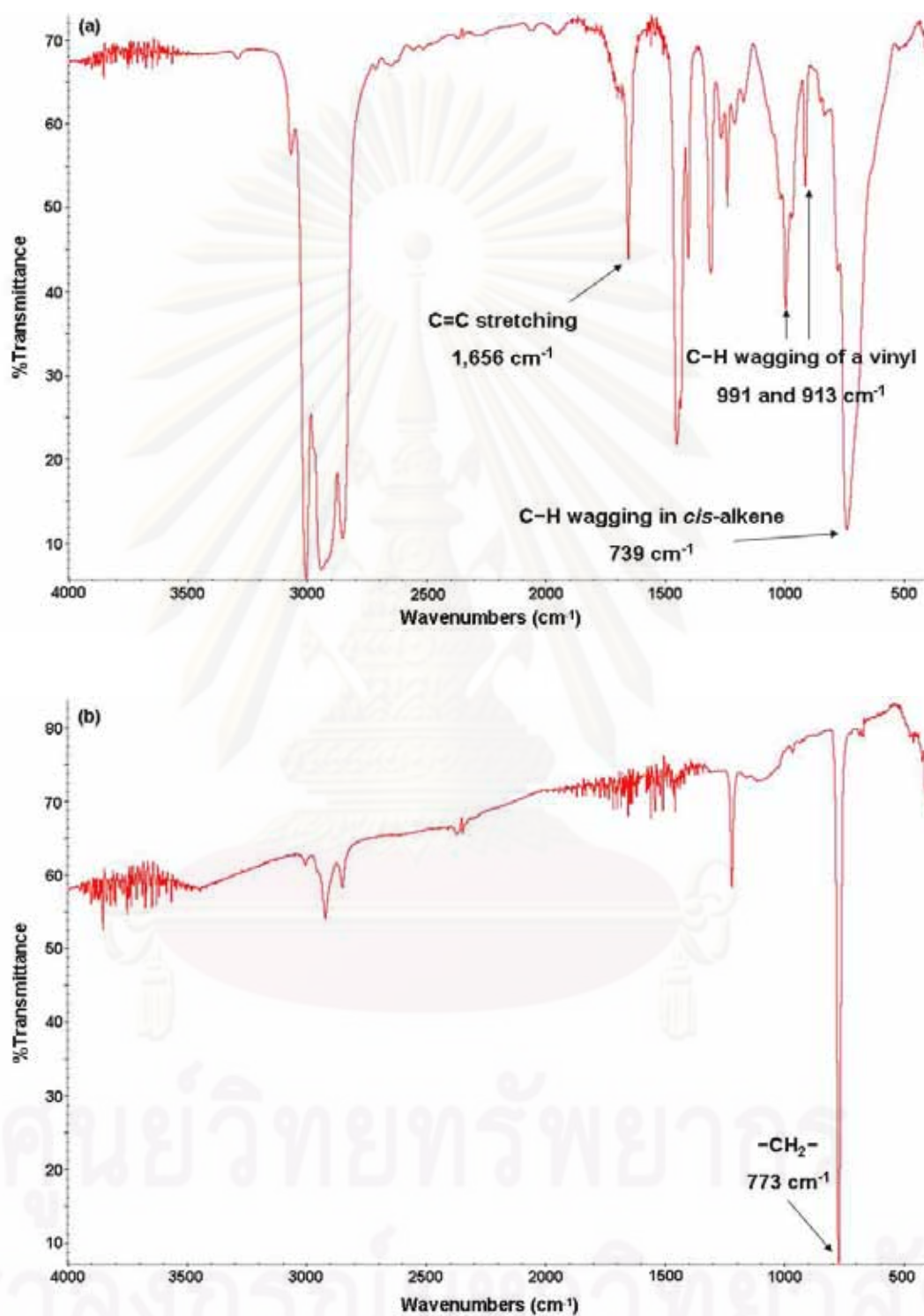
Figure 4.10 FTIR spectra of (a) BR and (b) HBR catalyzed by Pd/CF (70.4% hydrogenation).
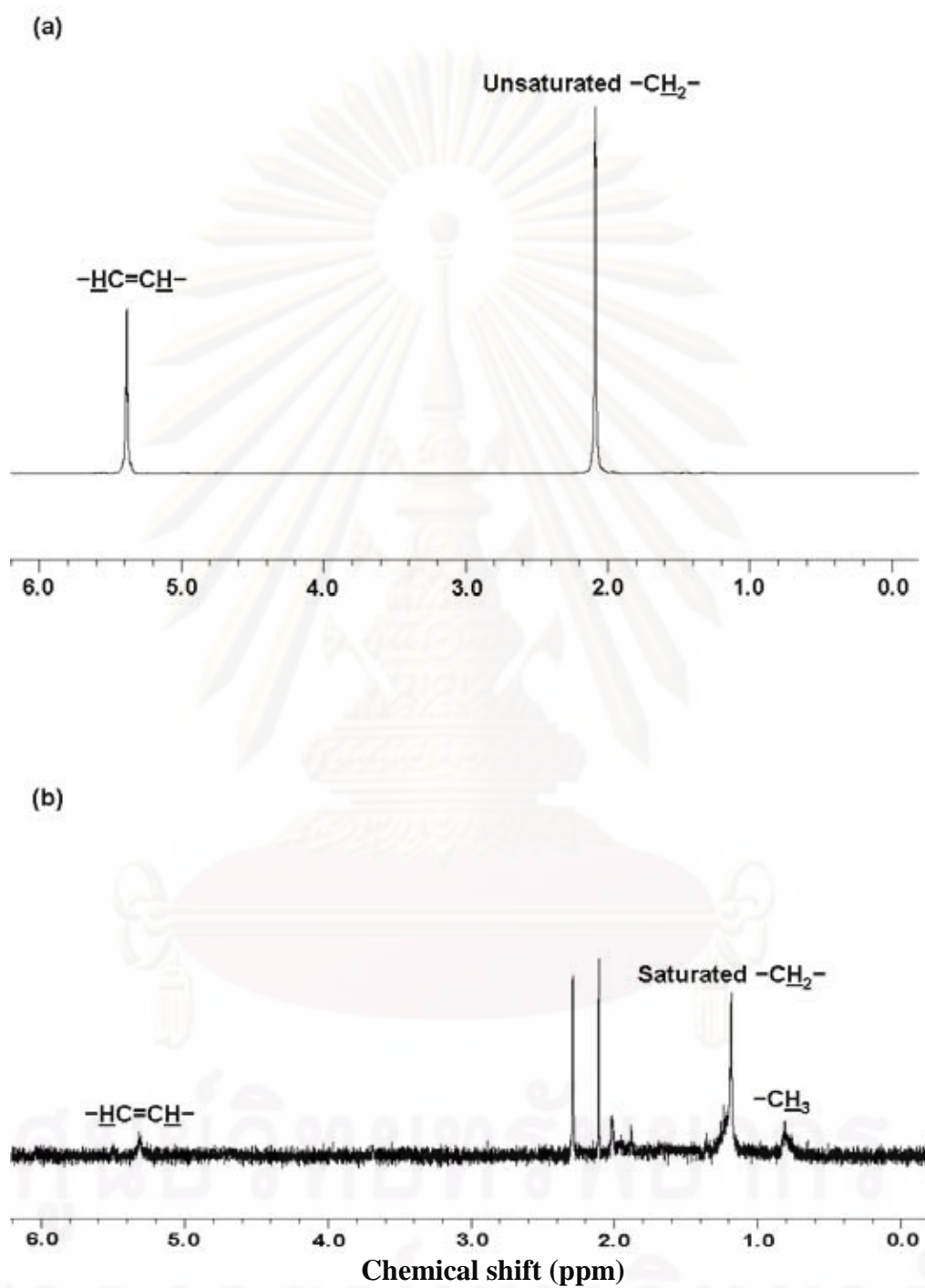
Figure 4.11 ^{1}H−NMR spectra of (a) BR and (b) HBR catalyzed by Pd/CF (70.4% hydrogenation).

4.3.1.2 Kinetic Experimental for Butadiene Rubber Hydrogenation

All kinetic data for the BR hydrogenation using palladium catalyst supported on carbon fiber (Pd/CF) was obtained using the high pressure reactor. Figure 4.12a shows the olefin conversion profiles and corresponding ln plots for the BR hydrogenation carried out in the high pressure reactor. The reaction rate equation corresponds to a pseudo first order reaction rate model with respect to double bond concentration, [C=C], as shown in Eq. 4.1:

$$-\frac{d[C=C]}{dt} = k'[C=C] \qquad (4.1)$$

where k´, the pseudo-first-order rate constant. The hydrogen consumption plot indicates that the reaction was apparently first-order in the olefinic substrate, which according to Eq. 4.2 can be expressed in terms of the conversion of unsaturated double bonds (extent of hydrogenation), x, as:

$$\ln(1-x) = -k't \qquad (4.2)$$

where t is the reaction time. Figure 4.12b shows a linear plot of ln(1-x) versus time (t) for the BR hydrogenation. The pseudo-first-order rate constant is then readily determined from the slope of the corresponding line. The kinetic data of experiments are provided in Table 4.1. From Figure 4.12a, above 60 min, the slope of % conversion to time tended to be non straight linear because the active sites of catalyst were covered with rubber molecules resulting in the deactivation of catalyst. Moreover, the active sites of catalyst were covered with rubber molecules cause a decrease in the dispersion of catalyst in system; therefore, the degree of conversion was incomplete (lower 100% conversion) because the reaction was difficult to happen.
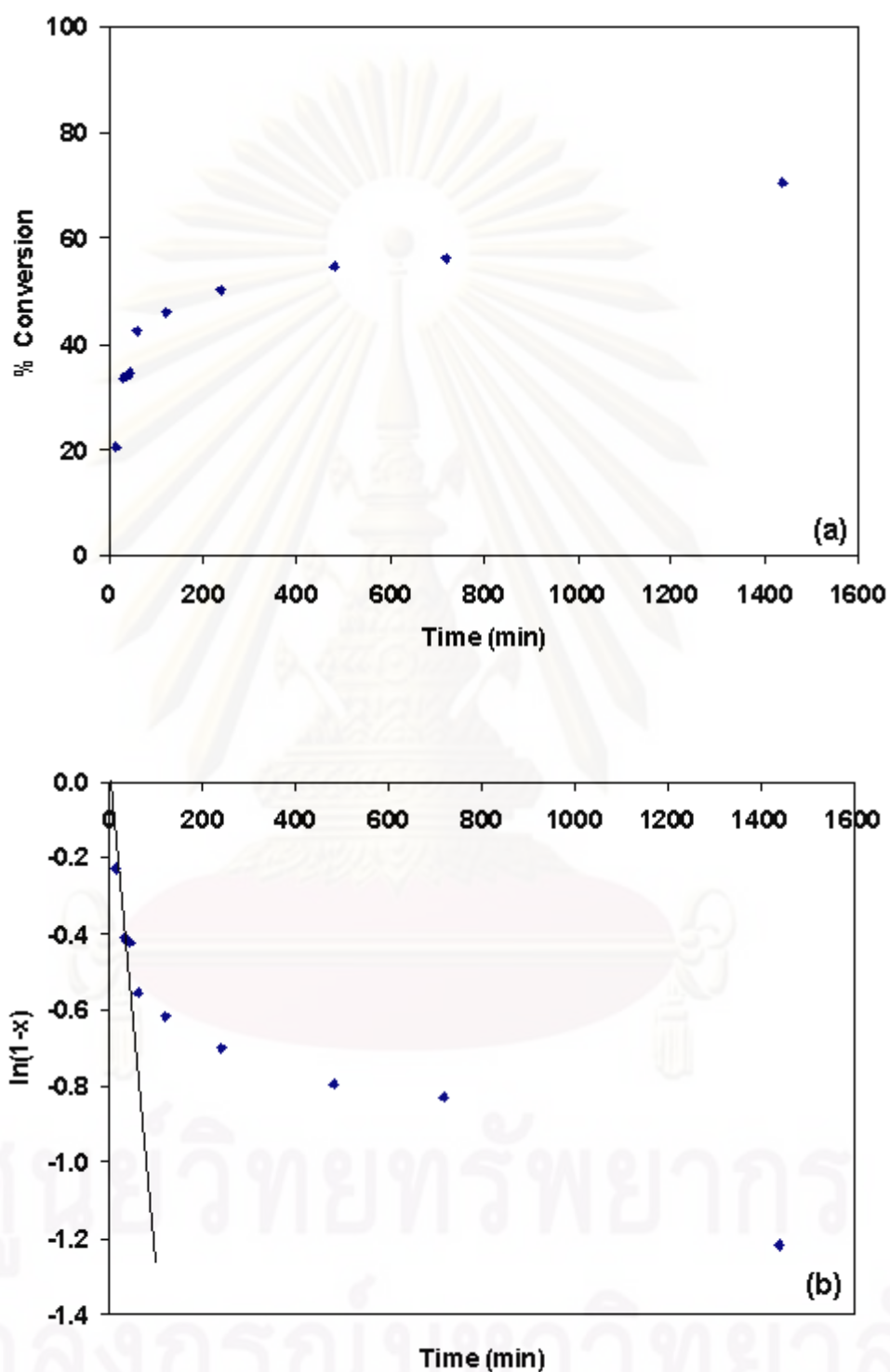
Figure 4.12 Hydrogenation profile of BR obtained from high pressure reactor: (a) olefin conversion profiles and (b) first-order ln plot. Pd catalyst = 29.9 μmol; [C=C] = 93 mM; H_2 pressure = 55 bar; T = 130°C in hexane.

Table 4.1   Kinetic data of BR hydrogenation catalyzed by Pd/CF

Exp.	[Pd] (µmol)	[BR] (mM)	P_{H2} (bar)	Temperature (°C)	Time (h)	Hydrogenation (%)	k´ x 10^4 (s^{-1})
1	29.9	93	55	120	0.25	28.0	-
2	29.9	93	55	120	0.50	33.9	-
3	29.9	93	55	120	0.75	42.3	-
4	29.9	93	55	120	1	43.9	-
5	29.9	93	55	120	2	46.7	-
6	29.9	93	55	120	4	47.9	-
7	29.9	93	55	120	8	49.7	-
8	29.9	93	55	120	12	51.0	-
9	29.9	93	55	120	24	54.7	1.90
10	29.9	93	55	130	0.25	20.5	-
11	29.9	93	55	130	0.50	33.7	-
12	29.9	93	55	130	0.75	34.5	-
13	29.9	93	55	130	1	42.7	-
14	29.9	93	55	130	2	46.1	-
15	29.9	93	55	130	4	50.4	-
16	29.9	93	55	130	8	54.8	-
17	29.9	93	55	130	12	56.3	-
18	29.9	93	55	130	24	70.4	1.68
19	29.9	93	55	140	0.25	13.5	-
20	29.9	93	55	140	0.50	37.8	-
21	29.9	93	55	140	0.75	39.5	-
22	29.9	93	55	140	1	40.2	-
23	29.9	93	55	140	2	44.2	-
24	29.9	93	55	140	4	51.1	-
25	29.9	93	55	140	8	53.3	-
26	29.9	93	55	140	12	56.0	-
27	29.9	93	55	140	24	57.1	1.72
28	29.9	93	55	150	0.25	33.6	-
29	29.9	93	55	150	0.50	43.7	-
30	29.9	93	55	150	0.75	44.6	-
31	29.9	93	55	150	1	45.3	-
32	29.9	93	55	150	2	46.7	-
33	29.9	93	55	150	4	48.2	-
34	29.9	93	55	150	8	50.2	-
35	29.9	93	55	150	12	50.9	-
36	29.9	93	55	150	24	53.7	2.13

Solvent = hexane.

4.3.1.3 Various Effect for Butadiene Rubber Hydrogenation

    4.3.1.3.1 Effect of Reaction Temperature

        A series of experiments were carried out over the temperature range of 120 to 150°C. The reaction conditions were maintained constant at 0.06 g of 5.3% wt Pd/CF (29.9 μmol of Pd), 93 mM of rubber concentration in hexane, and 55 bar of hydrogen pressure for 24 h. As illustrated in Figure 4.13, the degree of hydrogenation increased with increase in the temperature from 120 to 130°C. Above 130°C, the degree of hydrogenation tended to decrease because the hydrogenation is the exothermic reaction. However, the low reaction temperature might not be sufficient to overcome the activation energy and caused the very low conversion of hydrogenation (Napida Hinchiranan et al., 2008). The Arrhenius plot is shown in Figure 4.14. The apparent activation energy calculated from a least squares regression analysis of ln k′ versus 1/T was 4.83 kJ/mol. Nevertheless, the low apparent energy of activation may be due to an influence of mass transfer (Joannet et al., 2002).
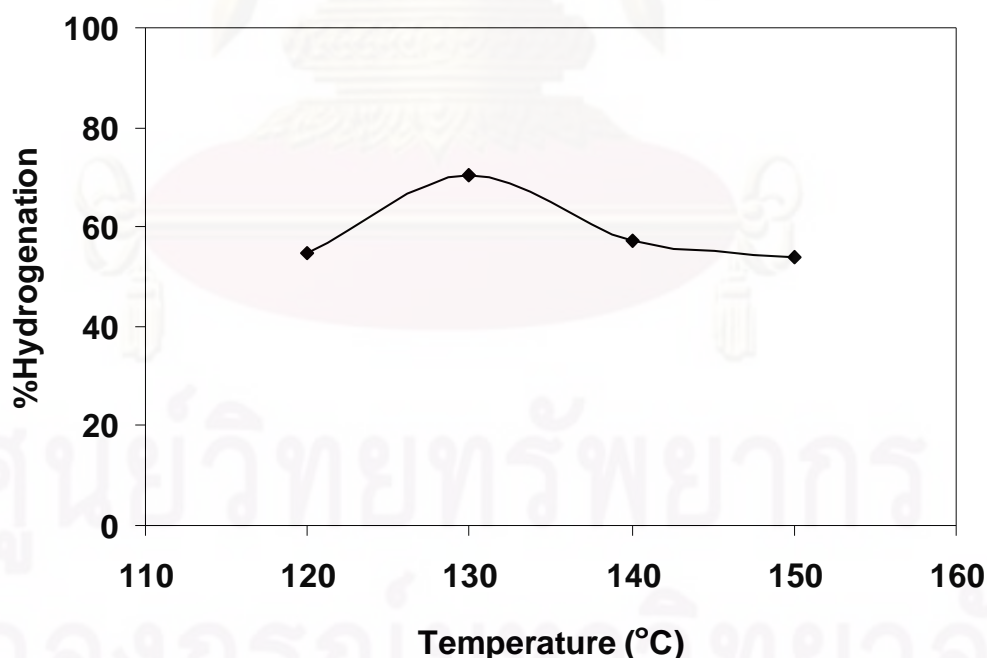
Figure 4.13   Effect of reaction temperature on the degree of hydrogenation of BR. Pd catalyst = 29.9 μmol; [BR] = 93 mM; H_2 pressure = 55 bar in hexane; time = 24 h.
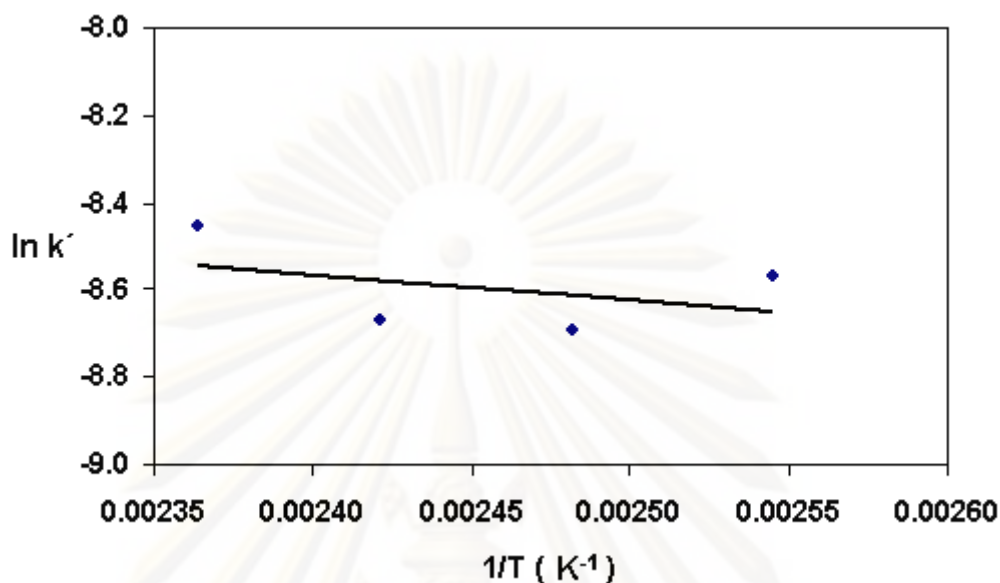
Figure 4.14 Arrhenius plot for the BR hydrogenation. Pd catalyst = 29.9 μmol; [C=C] = 93 mM; H_2 pressure = 55 bar in hexane.

4.3.1.3.2 Effect of Hydrogen Pressure

In order to investigate the effect of hydrogen pressure on the hydrogenation degree of BR, a series of experiments in which the hydrogen pressure was varied over the range of 28 to 69 bar was investigated. The effects of palladium catalyst loading (0.06 g of 5.3% wt Pd/CF = 29.9 μmol of Pd), reaction temperature (130°C), rubber concentration (93 mM) and reaction time (24 h) were kept constant. The results of these experiments (Figure 4.15) indicated that the degree of hydrogenation increased with increasing the hydrogen pressure from 28 to 55 bar. Above 55 bar, the hydrogenation level tended to decrease because the surface of palladium was saturated with hydrogen atom and there was no vacancy for the chemisorption of carbon double bonds in the rubber structure for hydrogenation (Napida Hinchiranan et al., 2008).
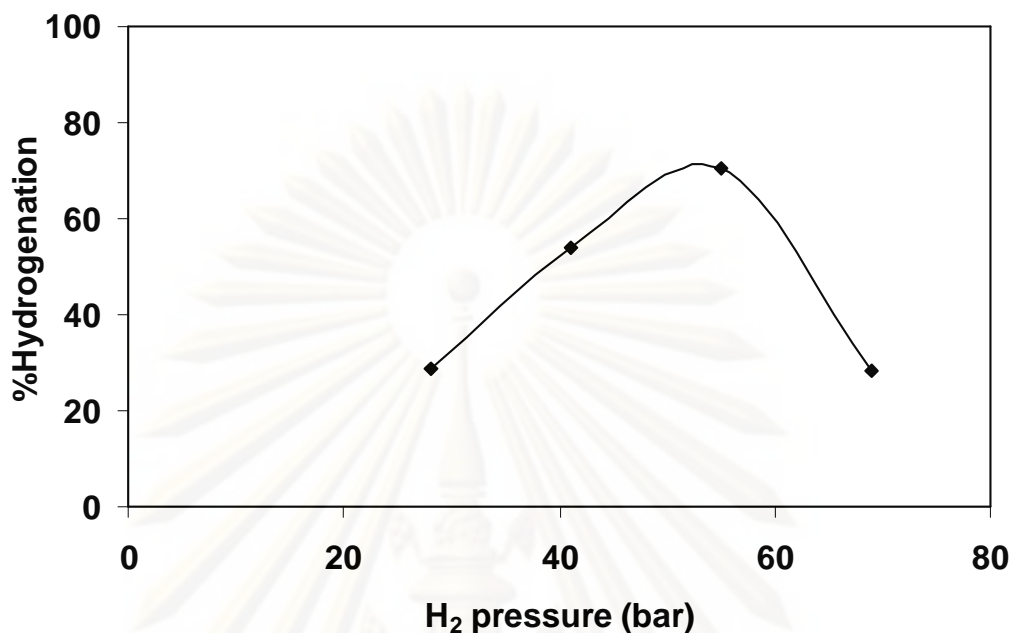
Figure 4.15   Effect of hydrogen pressure on the degree of hydrogenation of BR. Pd catalyst = 29.9 µmol; [BR] = 93 mM; T = 130°C in hexane; time = 24 h.

4.3.1.3.3 Effect of Rubber Concentration

The effect of rubber concentration on the degree of hydrogenation of BR was investigated by varying the rubber concentration as shown in Figure 4.16. The range of rubber concentration was 46 to 185 mM in hexane. The other reaction parameters were kept constant at 0.06 g of 5.3% wt Pd/CF (29.9 µmol of Pd) and 55 bar of hydrogen pressure at 130°C for 24 h. The result indicated that hydrogenation increased with increase in the concentration from 46 to 93 mM. Above 93 mM, the degree of hydrogenation tended to decrease because this reaction might be controlled by active site of catalysts. Moreover, an increase in the concentration of rubber causes a decrease in the mobility of catalyst due to the increase in the viscosity of solution, resulting in a decrease in the degree of hydrogenation.
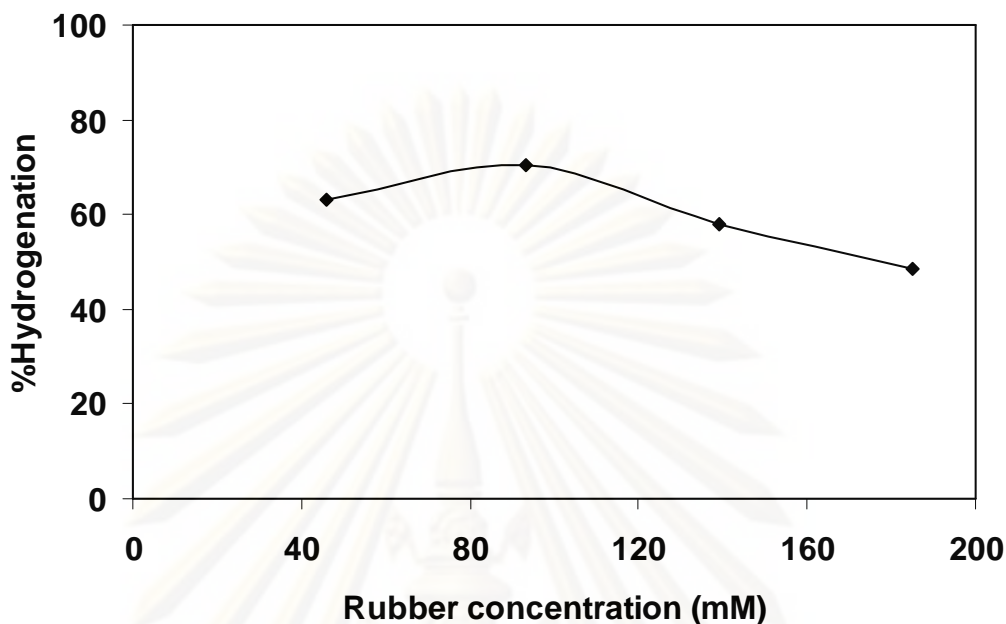
Figure 4.16   Effect of rubber concentration on the degree of hydrogenation of BR. Pd catalyst = 29.9 μmol; H_2 pressure = 55 bar; T = 130°C in hexane; time = 24 h.

4.3.1.3.4 Effect of Catalyst Concentration

In this series of experiments, the Pd catalyst concentration was varied over the range of 0.03 to 0.12 g of 5.3% wt Pd/CF (14.9 to 59.8 μmol of Pd) at 93 mM of BR and 55 bar of hydrogen pressure at 130°C in hexane for 24 h. As illustrated in Figure 4.17, the degree of hydrogenation increased with an increase in the catalyst concentration from 14.9 to 29.9 μmol. Above 29.9 μmol, the degree of hydrogenation tended to decrease. It might be explained that the increase in the CF content caused the obstruction of stirring resulting in poor dispersion of catalyst in the rubber solution.
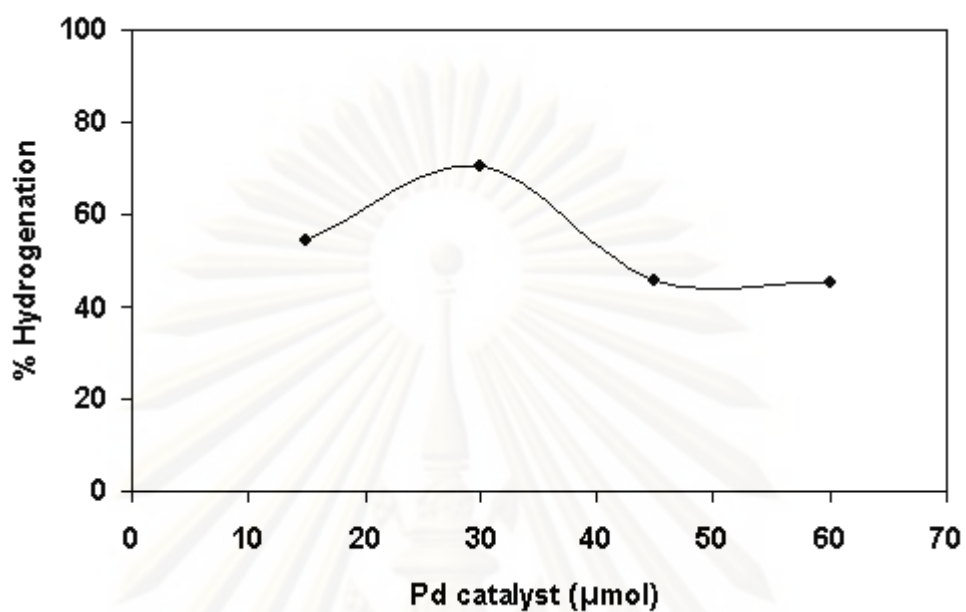
Figure 4.17   Effect of catalyst concentration on the degree of hydrogenation of BR.
[BR] = 93 mM; H_2 pressure = 55 bar; T = 130°C in hexane; time =
24 h.

4.3.2 Hydrogenation of Nitrile Butadiene Rubber

4.3.2.1 Structure Characterization Using FTIR and NMR Spectroscopy

The structure of nitrile butadiene rubber (NBR) before and after hydrogenation process was preliminarily characterized by infrared spectroscopy (FTIR) as shown in Figure 4.18. The FTIR spectra show characteristic peaks at 969, 922 and 752 cm^{-1} which are attributed to olefinic C–H bending of 1,4-trans, 1,2-vinylic and 1,4-cis units, respectively decrease with hydrogenation. The peak intensity at 2,230 cm^{-1} assigned to C≡N stretching did not change with hydrogenation. No new peak at around 3,500 cm^{-1} assigned to N–H stretching appeared after hydrogenation. This absence shows that C=C bonds were hydrogenated but C≡N bonds were not hydrogenated in NBR molecules.

Figure 4.19 shows the ^{1}H–NMR spectra of NBR and the polymeric product obtained from hydrogenation in the presence of Pd/CF. For the product of hydrogenation, the characteristic ^{1}H–NMR signal referred to olefinic proton (5.5, 5.3, 5.1 and 4.9 ppm) and –CH$_2$– unsaturated (2.3 and 2.1 ppm) tended to be slightly decreased; while the saturated peaks of –CH$_2$– (1.5 and 1.2 ppm) and –CH$_3$ (0.8 ppm) increased. The signal referred to –HCCN– (2.6 ppm) did not change with hydrogenation.
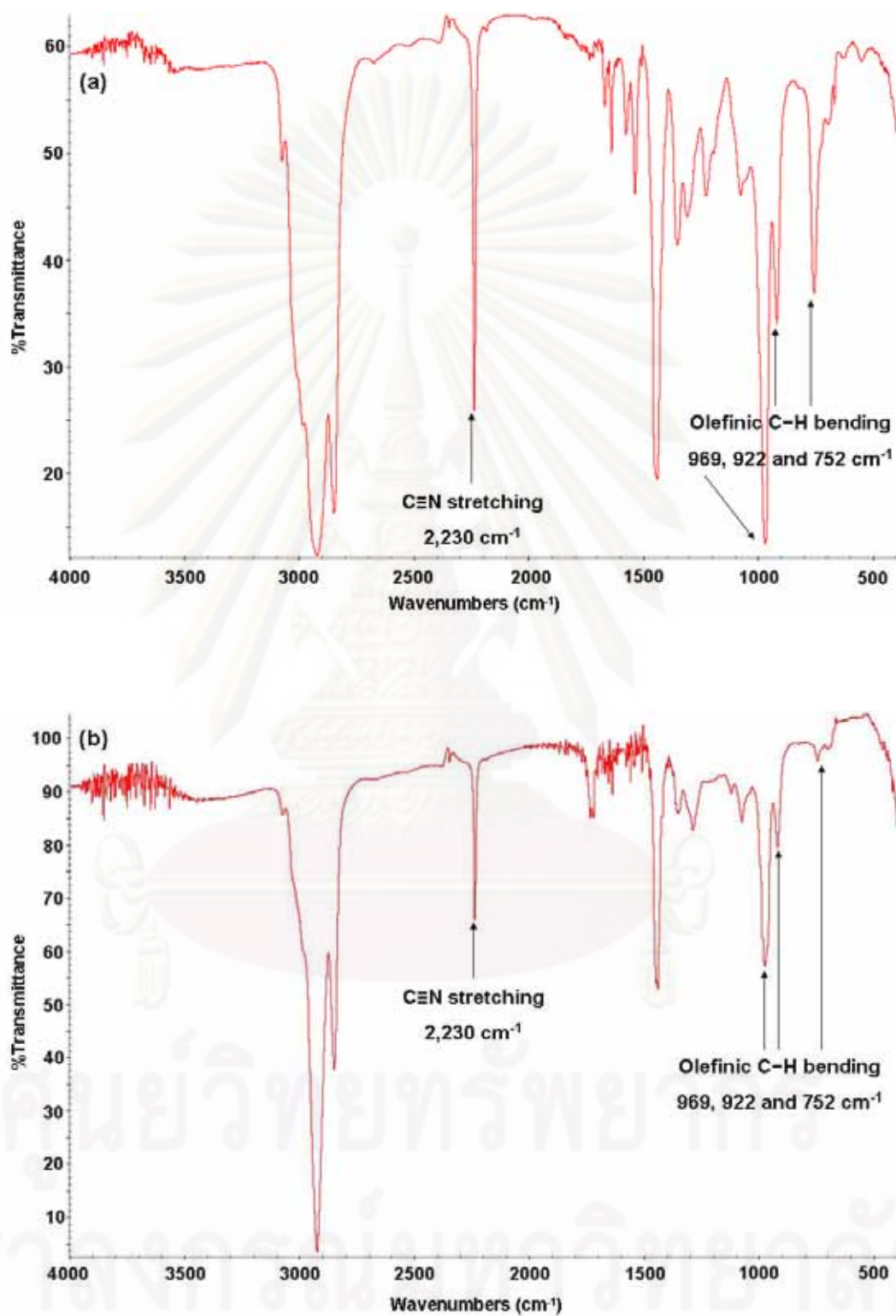
Figure 4.18   FTIR spectra of (a) NBR and (b) HNBR catalyzed by Pd/CF (46.4% hydrogenation).
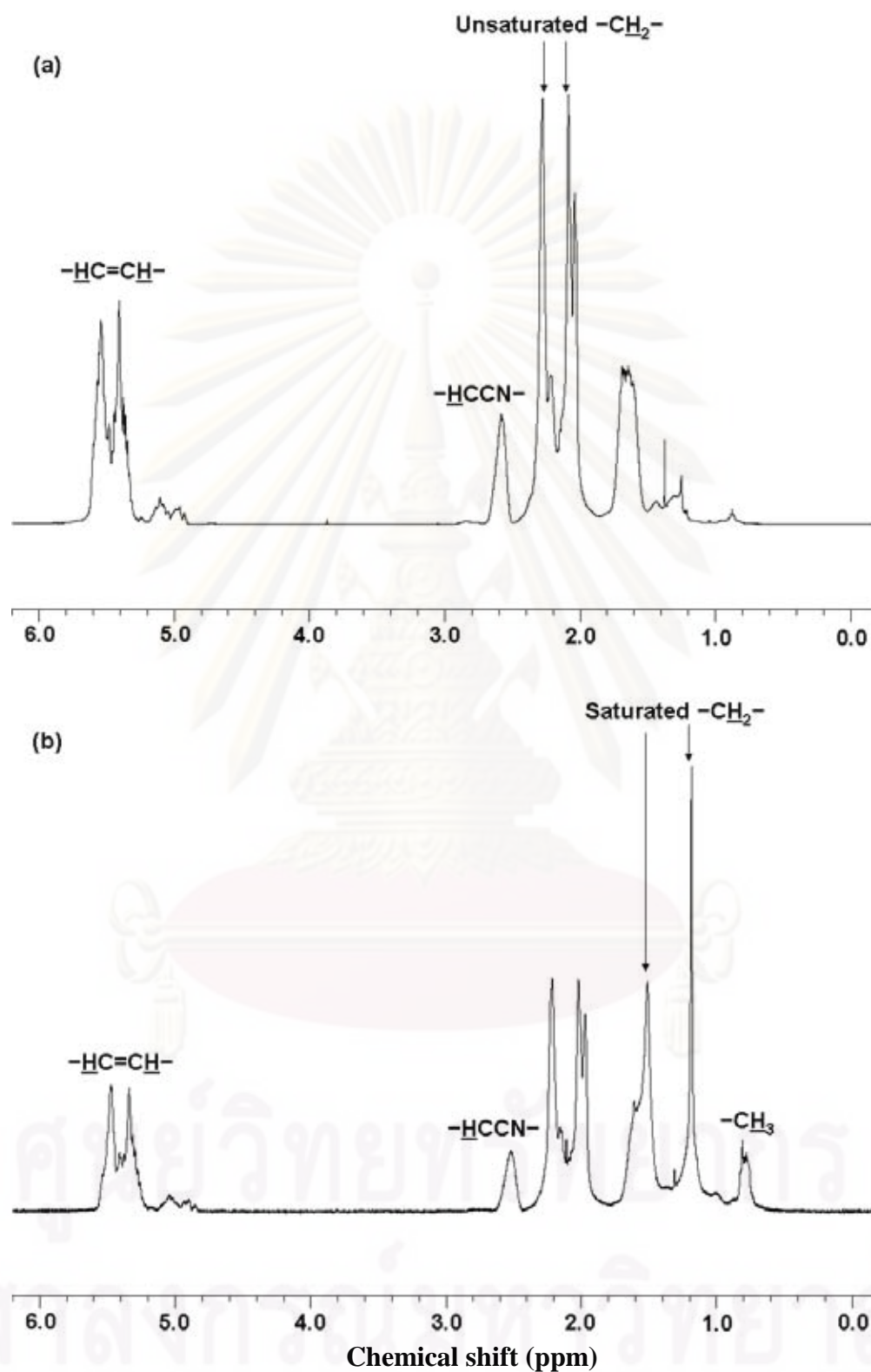
Figure 4.19 ^{1}H–NMR spectra of (a) NBR and (b) HNBR catalyzed by Pd/CF (46.4% hydrogenation).

4.3.2.2 Various Effect for Nitrile Butadiene Rubber Hydrogenation

4.3.2.2.1 Effect of Hydrogen Pressure

In order to investigate the effect of hydrogen pressure on the degree of hydrogenation of NBR, a series of experiments in which the hydrogen pressure were varied over the range of 28 to 55 bar were carried out in monochlorobenzene. The palladium catalyst loading (0.06 g of 5.3% wt Pd/CF = 29.9 μmol of Pd), reaction temperature (140°C), rubber concentration (47 mM) and reaction time (24 h) were kept constant. The results of these experiments displayed in Figure 4.20 indicated that the degree of hydrogenation increased with increasing the hydrogen pressure. Dong et al. (2002) studied the hydrogenation of NBR in xylene using Rh−Ru catalyst. They also found that the degree of hydrogenation increased with increase in the hydrogen pressure.
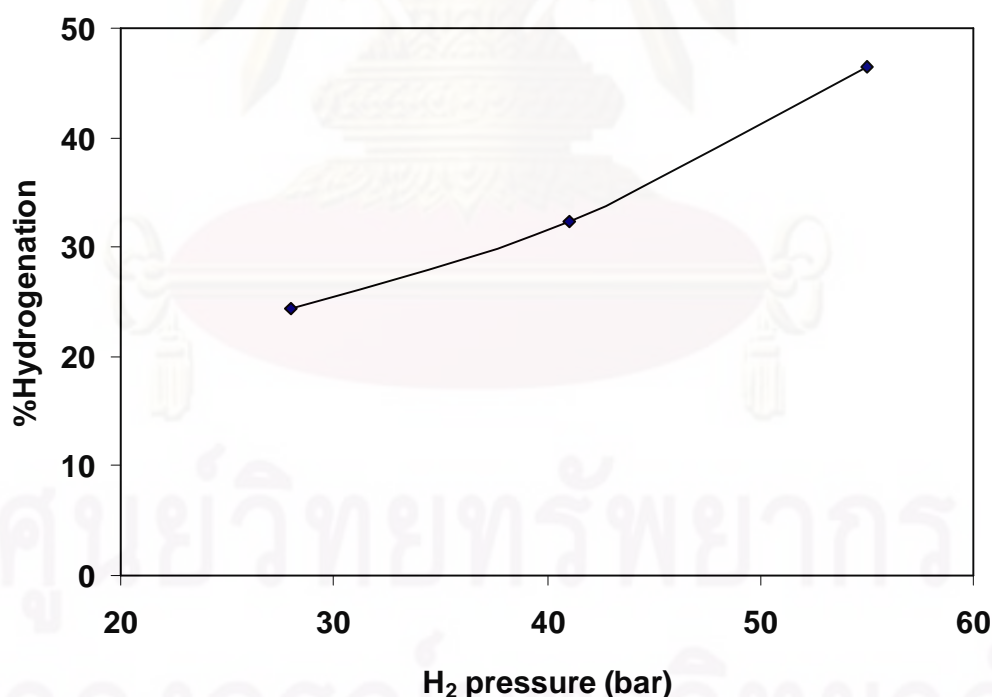
Figure 4.20   Effect of hydrogen pressure on the degree of hydrogenation of NBR. Pd catalyst = 29.9 μmol; [NBR] = 47 mM; T = 140°C in monochlorobenzene; time = 24 h.

4.3.2.2.2 Effect of Reaction Temperature

A series of experiments were carried out over the temperature range of 130 to 150°C. The reaction conditions were maintained constant at 0.06 g of 5.3% wt Pd/CF (29.9 µmol of Pd), 47 mM of rubber concentration in monochlorobenzene, and 55 bar of hydrogen pressure for 24 h. As illustrated in Figure 4.21, the degree of hydrogenation increased with increasing the temperature from 130 to 140°C. About 46% hydrogenation was achieved under the temperature of 140°C. However, the degree of hydrogenation decreased when reaction temperature was above 140°C. These results were similar to the observation reported by Dong et al. (2002) who studied the effect of bimetallic complex catalyst, Rh–Ru, for NBR hydrogenation. They found that the higher temperature (>140°C) could decrease the activity of catalyst for hydrogenation.

4.3.2.2.3 Effect of Catalyst Concentration

In this series of experiments in which the palladium catalyst concentration were varied over the range of 0.03 to 0.09 g of 5.3% wt Pd/CF (14.9 to 44.8 µmol of Pd) was carried out in monochlorobenzene at 47 mM of rubber concentration and 55 bar of hydrogen pressure; the temperature was 140°C for 24 h. As illustrated in Figure 4.22, the degree of hydrogenation increased with increase in the catalyst concentration from 14.9 to 29.9 µmol. Above 29.9 µmol, the degree of hydrogenation tended to decrease. It might explain that the increase in the CF content caused the obstruction of stirring resulting to poor dispersion of catalyst in the rubber solution.
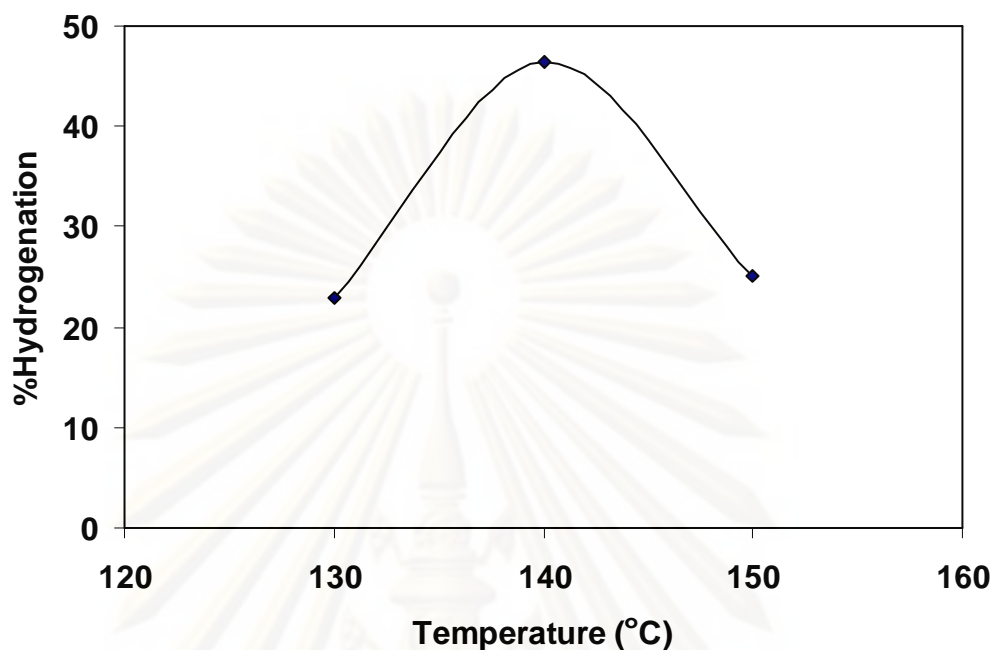
**Figure 4.21**   Effect of reaction temperature on the degree of hydrogenation of NBR. Pd catalyst = 29.9 μmol; [NBR] = 47 mM; H_2 pressure = 55 bar in monochlorobenzene; time = 24 h.
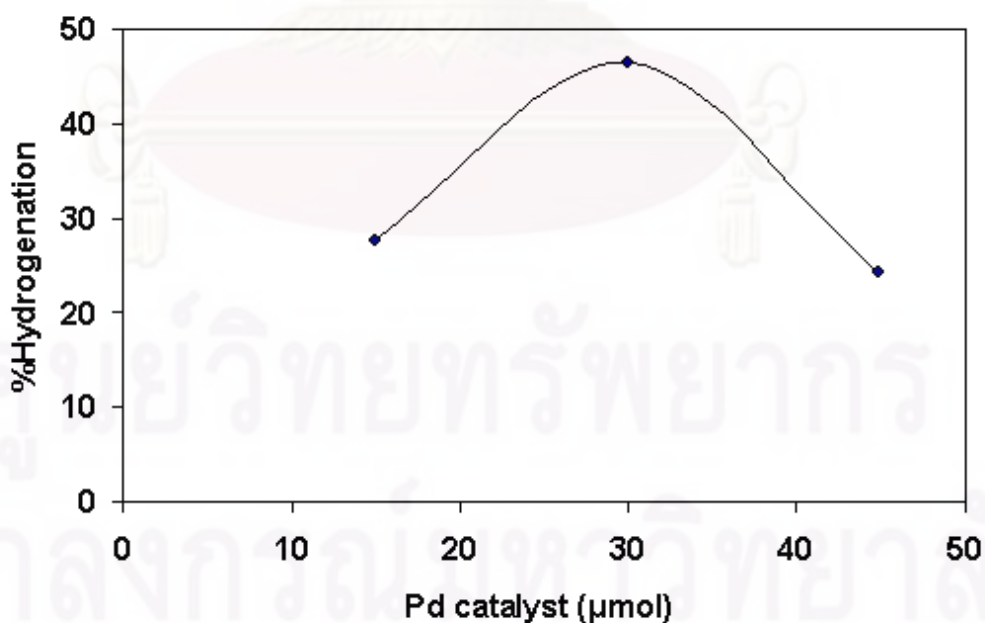
Figure 4.22   Effect of catalyst concentration on the degree of hydrogenation of NBR. [NBR] = 47 mM; H_2 pressure = 55 bar; T = 140°C in monochlorobenzene; time = 24 h.

4.3.3 Hydrogenation of Natural Rubber

4.3.3.1 Structure Characterization Using FTIR and NMR Spectroscopy

The structure of hydrogenated natural rubber (HNR) is similar to the structure of an alternating ethylene-propylene copolymer (Napida Hinchiranan, 2004). FTIR spectra of natural rubber (NR) before and after hydrogenation are illustrated in Figure 4.23. The characteristic FTIR spectrum of HNR product indicated that the C=C stretching (1,665 cm^{-1}) and olefinic C–H bending (839 cm^{-1}) tended to be decreased; while the intensity of the peak at 769 cm^{-1} attributed to $-CH_2-$ increased. For NR and HNR with impurities (proteins), the weak transmittance bands at 3,282 and 1,530 cm^{-1} which are characteristic vibrations of >N–H and >N–C=O (Aik-Hwee et al., 1992) remained after the hydrogenation process.

Figure 4.24 shows the ^{1}H–NMR spectra of NR and the polymeric product obtained from hydrogenation in the presence of Pd/CF. For the product of hydrogenation, the characteristic ^{1}H–NMR signal referred to olefinic proton (5.1 ppm) tended to be slightly decreased; while the saturated peaks of $-CH_2-$ (1.2 ppm) and $-CH_3$ (0.8 ppm) were observed. The ^{1}H–NMR spectrum also exhibited the simultaneous side reaction, *cis-trans* isomerization during hydrogenation. The ^{1}H–NMR signal at 1.60 ppm attributed to the methyl proton of *trans*-1,4-polyisoprene was adjacent to the signal at 1.67 ppm, referred to the methyl proton of *cis*-1,4 configuration (Samran et al., 2005).
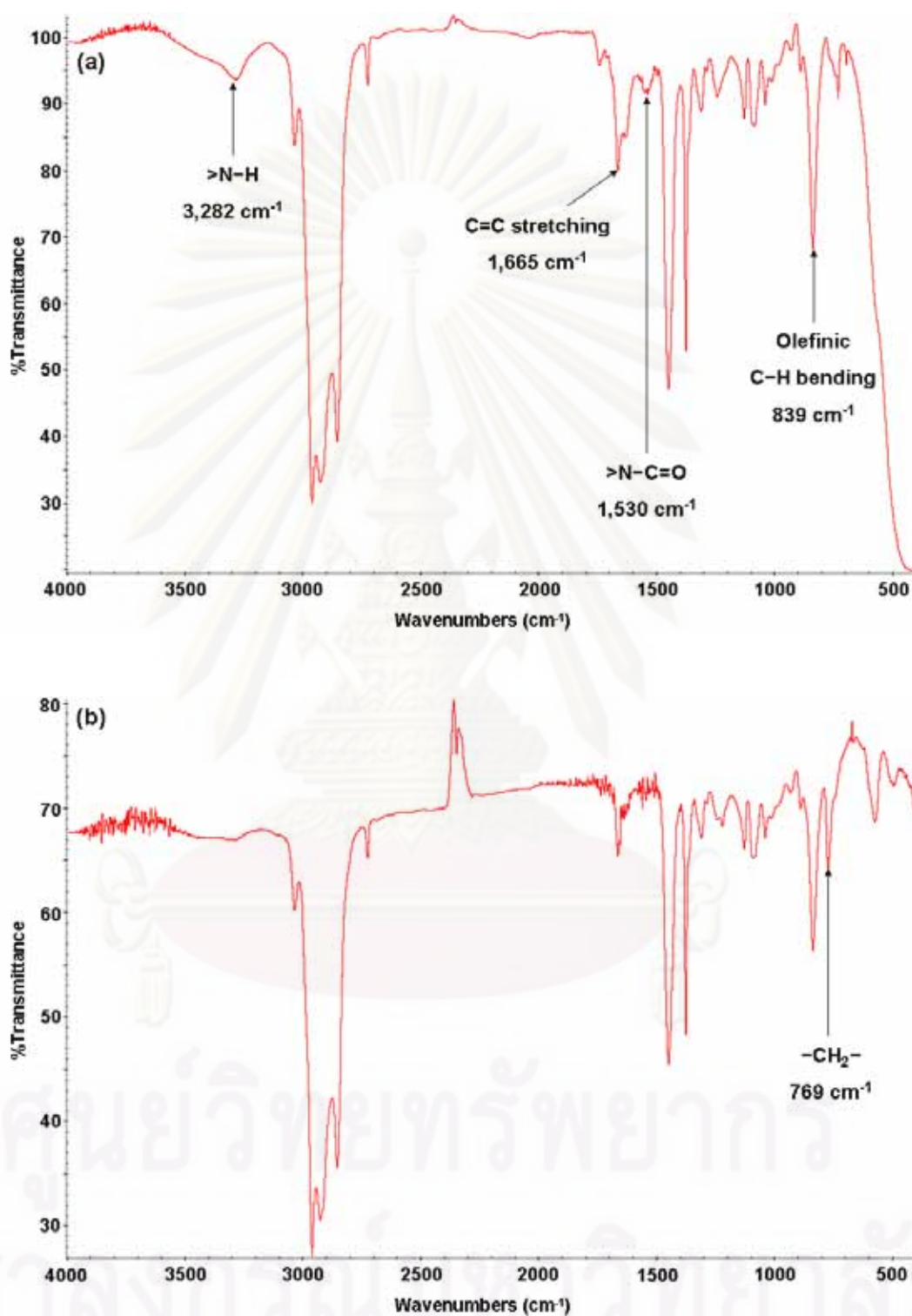
Figure 4.23 FTIR spectra of (a) NR and (b) HNR catalyzed by Pd/CF (35.3% hydrogenation).
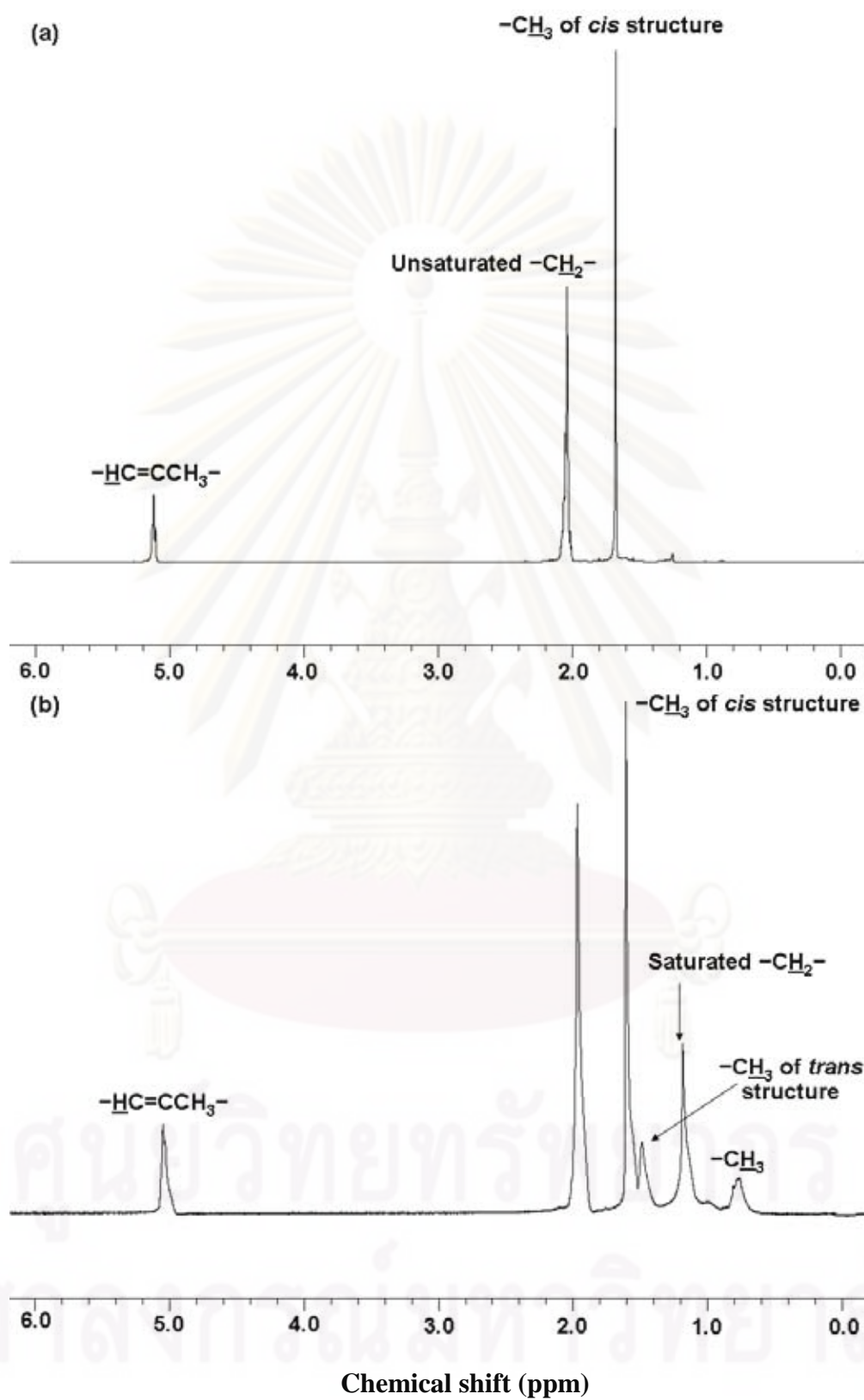
Figure 4.24 ¹H–NMR spectra of (a) NR and (b) HNR catalyzed by Pd/CF (35.3% hydrogenation).

4.3.3.2 Various Effect for Natural Rubber Hydrogenation

4.3.3.2.1 Effect of Hydrogen Pressure

The influence of hydrogen pressure on the degree of hydrogenation and *cis-trans* isomerization of NR was studied over the range of 28 to 55 bar of hydrogen pressure. The palladium catalyst loading (0.06 g of 5.3% wt Pd/CF = 29.9 μmol of Pd), reaction temperature (140°C), rubber concentration (74 mM) and reaction time (24 h) were kept constant. The results of these experiments displayed in Figure 4.25 indicated that the degree of hydrogenation and *cis-trans* isomerization increased with increasing the hydrogen pressure. The mechanism of *cis-trans* isomerization simultaneously occurred during hydrogenation has been reported (Zieverink et al., 2005). It was explained that either abstraction or insertion of hydrogen atom could accompany the chemisorption of an unsaturated carbon double bond on the active site of the catalyst to form the allylic π-complex or σ-complex. The allylic π-complexation requires abstracting the hydrogen atom; consequently, this is possibly occurred at low hydrogen pressure. In contrast, the use of high hydrogen pressure causes the abundance of hydrogen atoms on the catalytic surface to potentially form the σ-complex. The σ-complex may lead to the free rotation of the double bond, and then the hydrogen atom is removed to result in the *cis-trans* isomerization.
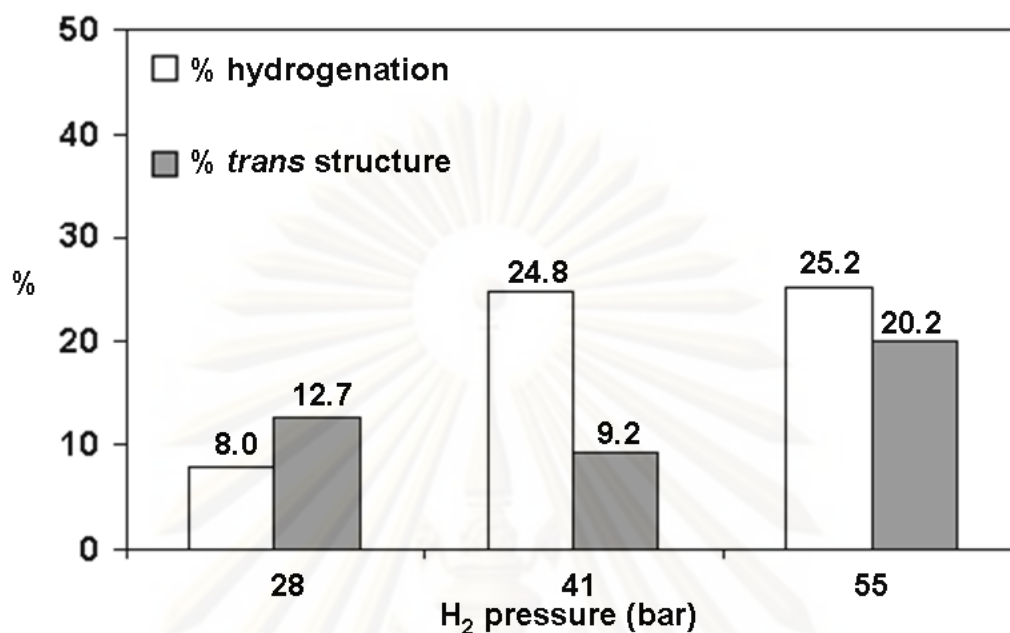
Figure 4.25   Effect of hydrogen pressure on the degree of hydrogenation and *cis-trans* isomerization of NR. Pd catalyst = 29.9 μmol; [NR] = 74 mM; T = 140°C in hexane; time = 24 h.

4.3.3.2.2 Effect of Reaction Temperature

A series of experiments were carried out over the temperature range of 130 to 150°C. The reaction conditions were maintained constant at 0.06 g of 5.3% wt Pd/CF (29.9 μmol of Pd), 74 mM of rubber concentration in hexane, and 55 bar of hydrogen pressure for 24 h. As illustrated in Figure 4.26, the degree of hydrogenation increased with increase in the temperature from 130 to 140°C. Above 140°C, the degree of hydrogenation tended to decrease because the impurities in NR might deactivate catalyst at higher temperature (Rungnapa Tangthongkul et al., 2004). However, the low reaction temperature might not be sufficient to overcome the activation energy and caused the very low conversion of hydrogenation. For *cis-trans* isomerization, it was found that the degree of *trans* structure increased with increase in the temperature from 130 to 140°C. Above 140°C, the degree of *trans* structure also tended to decrease due to the deactivation of catalyst at higher temperature.
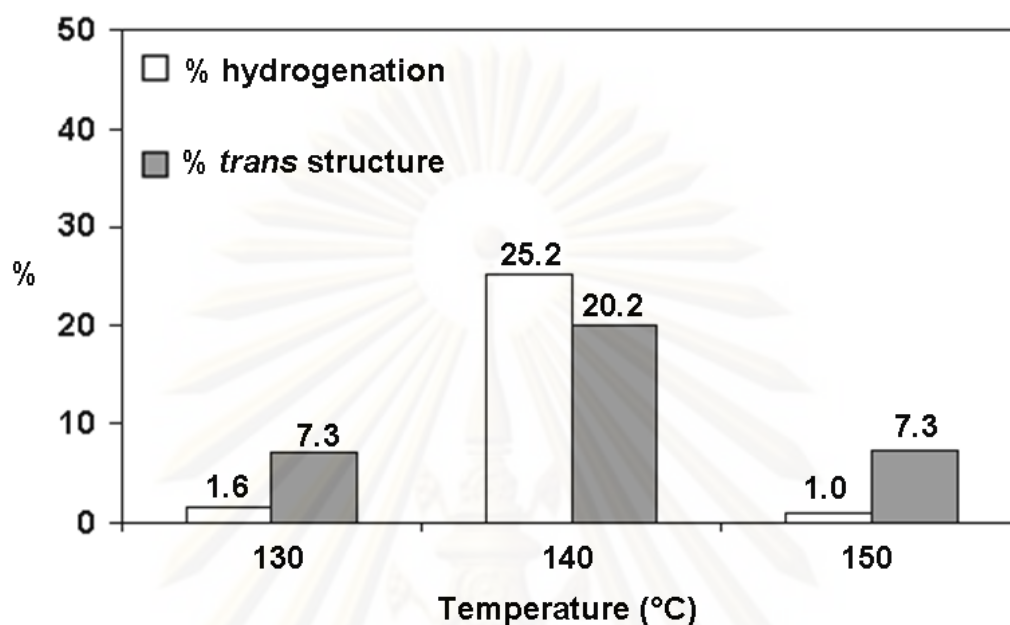
Figure 4.26 Effect of reaction temperature on the degree of hydrogenation and *cis-trans* isomerization of NR. Pd catalyst = 29.9 μmol; [NR] = 74 mM; H_2 pressure = 55 bar in hexane; time = 24 h.

4.3.3.2.3 Effect of Catalyst Concentration

In this series of experiments, the palladium catalyst concentration was varied over the range of 0.03 to 0.09 g of 5.3% wt Pd/CF (14.9 to 44.8 μmol of Pd) at 74 mM of rubber concentration and 55 bar of hydrogen pressure at 140°C in hexane for 24 h. As illustrated in Figure 4.27, the degree of hydrogenation increased with increase in the catalyst concentration. The observation indicated that the NR hydrogenation system required the higher loading of catalyst because impurities such as proteins in NR might reduce the catalytic activity (Napida Hinchiranan, 2004). For *cis-trans* isomerization, it was found that the increase in the catalyst concentration resulted to the lower degree of *trans* structure. It implied that this catalyst favor hydrogenation.
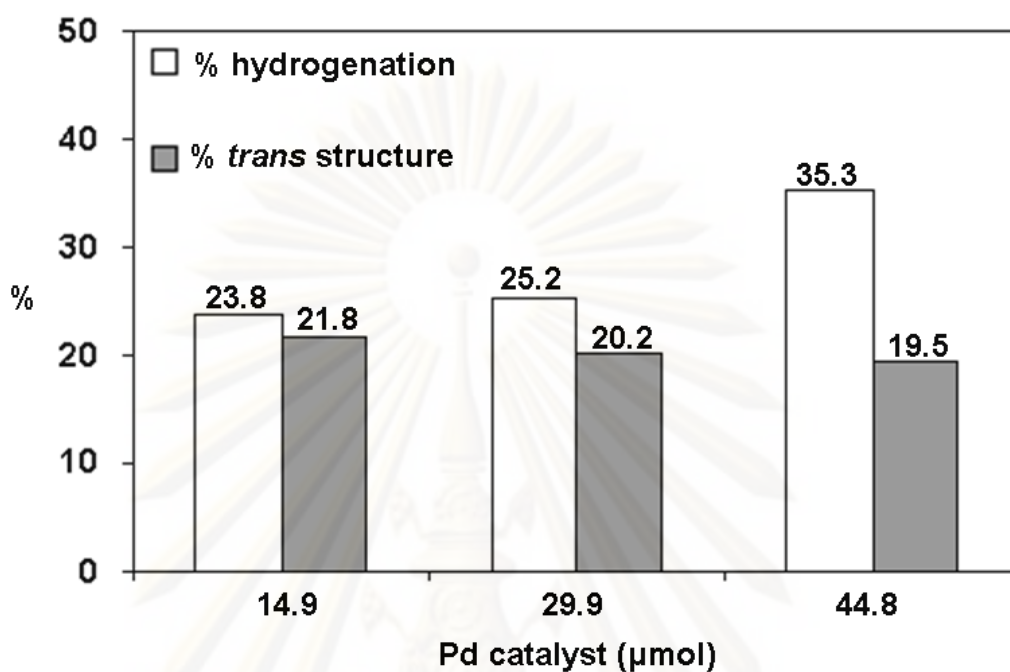
Figure 4.27 Effect of catalyst concentration on the degree of hydrogenation and *cis-trans* isomerization of NR. [NR] = 74 mM; H_2 pressure = 55 bar; T = 140°C in hexane; time = 24 h.

4.4 Stability of Catalysts

The stability of Pd/CF was also studied using thermogravimetric analysis (TGA). TGA curves of Pd/CF after hydrogenation reaction (Figure 4.28) was compared with that of one before hydrogenation which contained 5.3% wt of Pd (Figure 4.3). From Figure 4.28, the residual weight of Pd metal was 3.9%. It indicated that the 26.4% wt of Pd metal on CF was lost after hydrogenation.
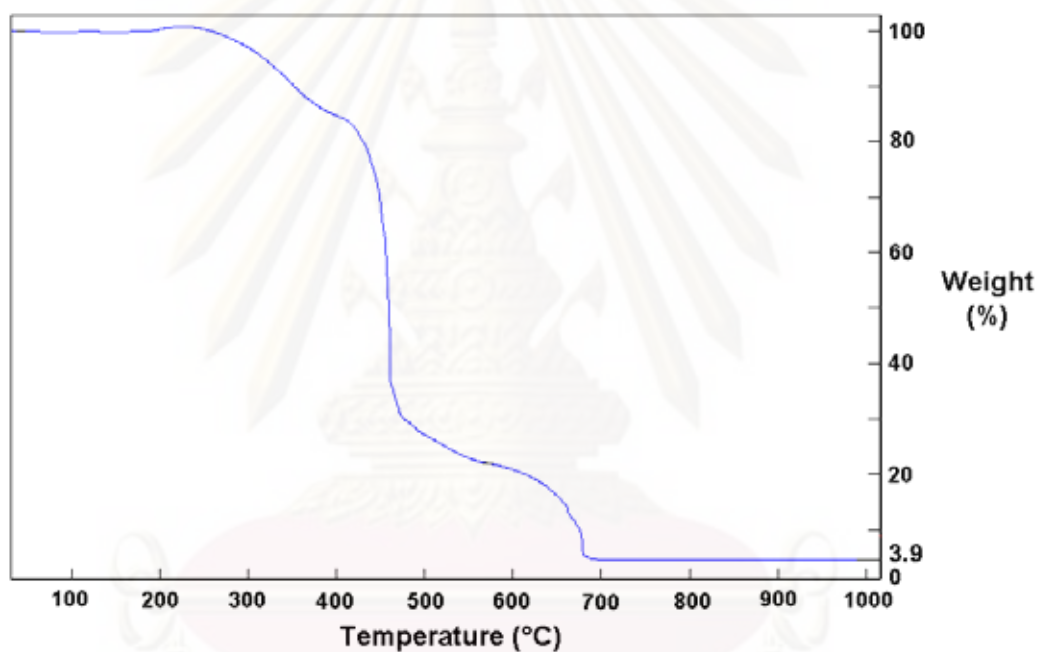
Figure 4.28   TGA pattern of Pd/CF after hydrogenation.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Characterization of Catalysts (Pd/CF)

The catalyst was prepared via impregnation method using palladium (II) acetate as precursor. The oxidation state of Pd catalyst was +2 due to XRD pattern exhibited peaks at 2θ of 11.0°, 12.5°, 13.6°, ascribed, to palladium (II) acetate. The content of Pd metal was 5.3% wt on the CF as verified using TGA.

5.1.2 Hydrogenation of Small Molecules Catalyzed by Pd/CF Catalysts

The hydrogenation of small molecules (1-hexene, benzene and acrylonitrile) catalyzed by Pd/CF. It indicated that the Pd/CF was an effective catalyst for 1-hexene hydrogenation towards hexane at high conversions. Whereas, the −C=C− group of benzene was not hydrogenated possibly due to the stability of aromatic structure. Moreover, this catalyst could not hydrogenated −C≡N group of acrylonitrile; while, it showed the high selectivity for hydrogenation of −C=C− group of acrylonitrile.

5.1.3 Hydrogenation of Macromolecules Catalyzed by Pd/CF Catalysts

5.1.3.1 Butadiene Rubber (BR)

Pd/CF has been used as the catalyst for the hydrogenation of BR. The NMR results of the hydrogenated BR products indicated that 70.4% hydrogenation was achieved in 24 h using 29.9 μmol of palladium catalyst at temperature of 130°C under 55 bar of hydrogen pressure. The kinetic results indicated that the hydrogenation followed the pseudo first-order. The apparent activation energy of BR hydrogenation was calculated as 4.83 kJ/mol.

5.1.3.2 Nitrile Butadiene Rubber (NBR)

A palladium catalyst (Pd/CF) prepared in this experiment offers catalytic activity and selectivity in the hydrogenation of NBR to produce a hydrogenated NBR. The FTIR results of the hydrogenated NBR confirmed that Pd/CF did not reduce the $-CN$ group. The degree of hydrogenation of NBR can be 46.4% at reaction temperature 140°C, 47 mM of rubber concentration and 29.9 µmol of Pd catalyst under 55 bar of hydrogen pressure.

5.1.3.3 Natural Rubber (NR)

The *cis-trans* isomerization was simultaneously occurred during NR hydrogenation catalyzed by Pd/CF. The degree of *cis-trans* isomerization increased with increasing hydrogen pressure up to 55 bar. The maximum hydrogenation level at ca. 35.3% was achieved at 140°C. The degree of hydrogenation tended to be decreased when reaction temperature was higher than 140°C possibly due to the exothermic heat of reaction. The increase in catalyst concentration added the catalytic activity of hydrogenation but reduced the catalytic activity of *cis-trans* isomerization.

5.1.4 Stability of Catalysts (Pd/CF)

The stability of Pd/CF was studied using TGA. It showed that the contents of palladium before and after hydrogenation were 5.3 and 3.9% wt, respectively. Thus, it indicated that the loss of Pd metal on CF after hydrogenation was verified.

5.2 Recommendations

A further study for the hydrogenation of diene elastomers should be concerned with the following aspects:

1. Effective Separation and Recovery for Palladium Catalyst after Hydrogenation Process of Diene Elastomers.

Studied the effective separation and recovery techniques to decrease the loss of palladium catalyst because palladium was very expensive.

2. Effect of Impurities in Diene Elastomers on Hydrogenation Process.

The presence of impurities such as proteins and lipids in diene elastomers results in a dramatic decrease in hydrogenation level. The investigation of impurity components in the diene elastomers should be carried out to understand their effect of impurities on the hydrogenation reaction.

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APPENDICES

Appendix A

Overall Compositions of Rubbers

Table A–1 Butadiene Rubber (BSTE BR 1220)

Properties	Test Results
Volatile matter (%)	0.06
Cis content (%)	97.5
Ash content (%)	0.01
Raw Mooney viscosity @ 100°C (ML1+4)	44.0
Compound Mooney viscosity (ML1+4)	65.0
Tensile strength, 35 min. (MPa)	16.4
Elongation, 35 min. (%)	410
300% modulus @ 145°C, 35 min. (MPa)	10.7

Table A–2 Nitrile Butadiene Rubber (Krynac[®] 3345F)

Properties	Test Results
Mooney viscosity ML (1+4) @ 100°C	45±5
ACN (%)	33±1
Ash content (max, %wt)	0.70
Volatile matter (max, %wt)	0.50
Density (g/cm^3)	0.97

Table A–3 Dry Natural Rubber (STR–5L)

Properties	Test Results
Dirt content (%wt)	0.04
Ash content (%wt)	0.40
Volatile matter (%wt)	0.80
Nitrogen (%wt)	0.60
Plasticity retention index (min)	60.0
Mooney viscosity	59.2

Appendix B

Characteristics of Carbon Fiber

Table B–1 Carbon Fiber (Future Fiber Limited Partnership, Thailand)**.**

Properties	Test Results
Tensile strength (GPa)	3.4
Tensile modulus (GPa)	235
Elongation (%)	1.3
Density (g/cm^3)	1.8
Filament count	12,000 or 6,000
Filament diameter (μm)	6.8
Specific heat (cal/g °C)	0.17
Thermal conductivity (W/m K)	17
Resistivity (Ωcm)	1.5×10^{-3}

All properties are measured at room temperature.

Appendix C

The Database of XRD Pattern

Table C–1 XRD pattern of palladium (II) acetate

Pattern : 00-018-1502		Radiation = 1.540598		Quality : Questionable

C₄H₆O₄Pd
/Pd(CH₃COO)₂

Palladium Acetate

2th	I	h	k	l
10.955	80			
12.457	100			
13.570	80			
15.107	80			
15.956	50			
17.869	50			
18.508	30			
19.713	30			
21.499	30			
23.901	50			
24.710	80			
26.426	80			
27.335	80			
27.507	80			
30.023	30			
30.928	30			
31.635	10			
32.461	50			
33.784	50			
34.827	50			
36.465	50			
37.621	50			
38.853	80			
40.875	10			

Lattice : Not assigned

S.G. : (0)

Mol. weight = 224.49

Melting point: 205°
Color: Orange-brown
Data collection flag: Ambient.

Stephenson et al., J. Chem. Soc., page 3632 (1965)

CAS Number: 19607-27-3

Radiation : CuKa

Lambda : 1.54180

Filter : Beta

d-sp : Not given

Table C–2 XRD pattern of carbon (Carbolite)

Pattern : 00-050-0926	Radiation = 1.540598		Quality : Indexed

C

Carbon
Also called: carbolite

2th	I	h	k	l
14.842	24	1	1	0
16.673	20	0	0	2
22.765	100	1	2	0
26.571	13	1	0	3
29.317	5	1	1	3
34.223	9	1	2	3

Lattice : Hexagonal

S.G. : (0)

$a = 11.92800$

$c = 10.62000$

Mol. weight = 12.01

Volume [CD] = 1308.55

$Dx = 0.015$

$Dm = 1.450$

Sample preparation: Prepared by quenching high-temperature carbon gas on a room temperature substrate in argon.
Color: Transparent
Data collection flag: Ambient.

Tanuma, S.-i., Palnichenko, A., J. Mater. Res., volume 10, page 1120 (1995)

Radiation : CuKa

Lambda : 1.54180

SS/FOM : F6= 13(0.0173,27)

Filter : Not specified

d-sp : Diffractometer

Table C–3 XRD pattern of carbon (Graphite)

Pattern : 01-089-8489	Radiation = 1.540598	Quality : Alternate

C

Carbon
Graphite - theoretical

Lattice : Base-centered orthorhombic		Mol. weight = 12.01
S.G. : Cmmm (65)		Volume [CD] = 143.01
a = 4.52500		Dx = 2.231
b = 5.33400		
c = 5.92500		
a/b = 0.84833	Z = 16	I/Icor = 2.04
c/b = 1.11080		

ICSD collection code: 088812
Hypothetical structure: Structure calculated theoretically.
Remarks from ICSD/CSD: REM   K Phase gra_crbl33_bo.
Test from ICSD: No R value given.
Test from ICSD: At least one TF missing.
Cancel:
Data collection flag: Ambient.

Fayos, J., J. Solid State Chem., volume 148, page 278 (1999)
Calculated from ICSD using POWD-12++

Radiation : CuKa1	Filter : Not specified
Lambda : 1.54060	d-sp : Calculated spacings
SS/FOM : F30=435(0.0020,35)	

2th	I	h	k	l
14.940	999	0	0	1
25.798	221	1	1	0
30.142	133	0	0	2
33.575	134	0	2	0
36.931	73	0	2	1
40.083	75	1	1	2
42.746	26	2	0	1
45.912	29	0	0	3
50.732	33	2	0	2
53.035	19	2	2	0
53.409	3	1	1	3
55.422	27	2	2	1
*55.422	27	1	3	0
57.802	1	1	3	1
58.068	10	0	2	3
62.218	1	2	2	2
62.359	2	2	0	3
62.669	1	0	0	4
64.108	5	3	1	0
64.441	16	1	3	2
66.242	1	3	1	1
68.933	5	1	1	4
70.571	1	0	4	0
72.455	6	3	1	2
72.717	7	2	2	3
73.005	6	0	2	4
74.787	1	1	3	3
76.862	19	2	0	4
78.614	4	0	4	2
81.089	1	0	0	5
82.390	1	3	1	3
84.214	15	2	4	0
85.832	7	4	0	0
86.159	7	2	4	1
86.534	10	2	2	4
86.835	5	1	1	5
87.772	2	4	0	1
88.522	4	1	3	4

Appendix D

Calculation by ^{1}H–NMR

D–1 Butadiene Rubber

The degree of hydrogenation was evaluated using ^{1}H–NMR spectra. The peak area of saturated protons ($-CH_2-$ at 1.2 ppm and $-CH_3$ at 0.8 ppm) was measured in order to calculate the %hydrogenation of butadiene rubber (BR) using the formula:

$$\%Hydrogenation = \frac{\text{Peak area of saturated } -CH_2- \text{ and } -CH_3}{\text{Total peak area}} \times 100$$

For example:

Chemical shift (ppm)

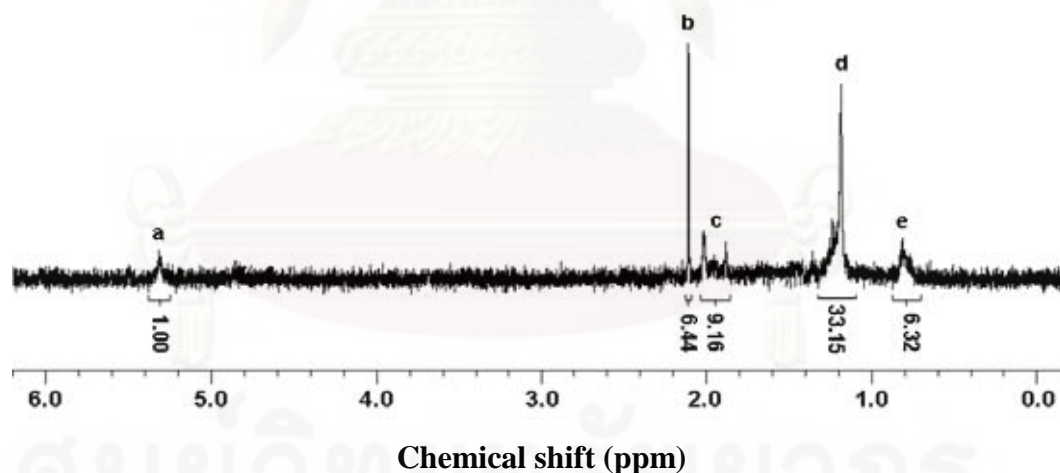**Figure D–1** ^{1}H–NMR spectra of HBR

a	= peak area of olefinic proton
b, c	= peak area of unsaturated $-CH_2-$
d	= peak area of saturated $-CH_2-$
e	= peak area of saturated $-CH_3$

%Hydrogenation = [(33.15+6.32)/(1+6.44+9.16+33.15+6.32)] x 100

= 70.4

D–2 Nitrile Butadiene Rubber

The degree of hydrogenation was evaluated using ^{1}H–NMR spectra. The peak area of saturated protons (–CH_2– at 1.5, and 1.2 ppm and –CH_3 at 0.8 ppm) was measured in order to calculate the %hydrogenation of nitrile butadiene rubber (NBR) using the formula:

$$\%Hydrogenation = \frac{Peak\ area\ of\ saturated\ -CH_2-\ and\ -CH_3}{Total\ peak\ area} \times 100$$

For example:

Chemical shift (ppm)

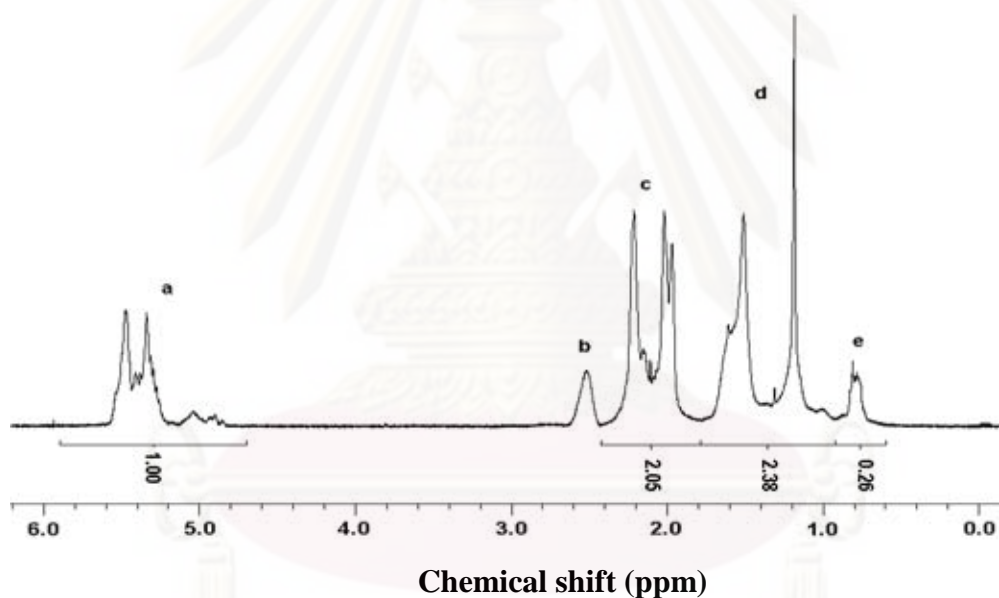**Figure D–2** ^{1}H–NMR spectra of HNBR

a = peak area of olefinic proton

b = peak area of saturated –HCCN–

c = peak area of unsaturated –CH_2–

d = peak area of saturated –CH_2–

e = peak area of saturated –CH_3

%Hydrogenation = [(2.38+0.26)/(1+2.05+2.38+0.26)] x 100

  = 46.4

D–3 Natural Rubber

The degree of hydrogenation was evaluated using ^{1}H–NMR spectra. The peak area of unsaturated protons (=C**H** at 5.1 ppm, –C**H**$_2$– at 2.0 ppm and –C**H**$_3$ at 1.67, and 1.60 ppm) was measured in order to calculate the %hydrogenation of natural rubber (NR) using the formula:

$$\%Unsaturation = \frac{Peak\ area\ of\ unsaturated}{Total\ peak\ area} \times 100$$

$$\%Hydrogenation = 100 - \%Unsaturation$$

The peak areas of methyl proton of *cis* (1.67 ppm) and *trans* (1.60 ppm) structure were measured in order to calculate the % *cis* structure and % *trans* structure of NR using the formula:

$$\%\ cis\ structure = \frac{Peak\ area\ of\ cis\ structure}{Total\ peak\ area\ of\ cis\ and\ trans\ structure} \times \%Unsaturation$$

$$\%\ trans\ structure = \%Unsaturation - \%\ cis\ structure$$

For example:

a   = peak area of olefinic proton

b   = peak area of unsaturated –CH_2–

c   = peak area of methyl proton

c_1 = peak area of methyl proton of *cis* structure

c_2 = peak area of methyl proton of *trans* structure

d   = peak area of saturated –CH_2–

e   = peak area of saturated –CH_3

%Unsaturation   = [(1+5.27+6.39)/(1+5.27+6.39+5.17+1.73)] x 100

                  = 64.7

%Hydrogenation   = 100 – 64.7

                  = 35.3

% cis structure   = [1.04/(1.04+0.45)] x 64.7

                  = 45.2

% trans structure   = 64.7 – 45.2
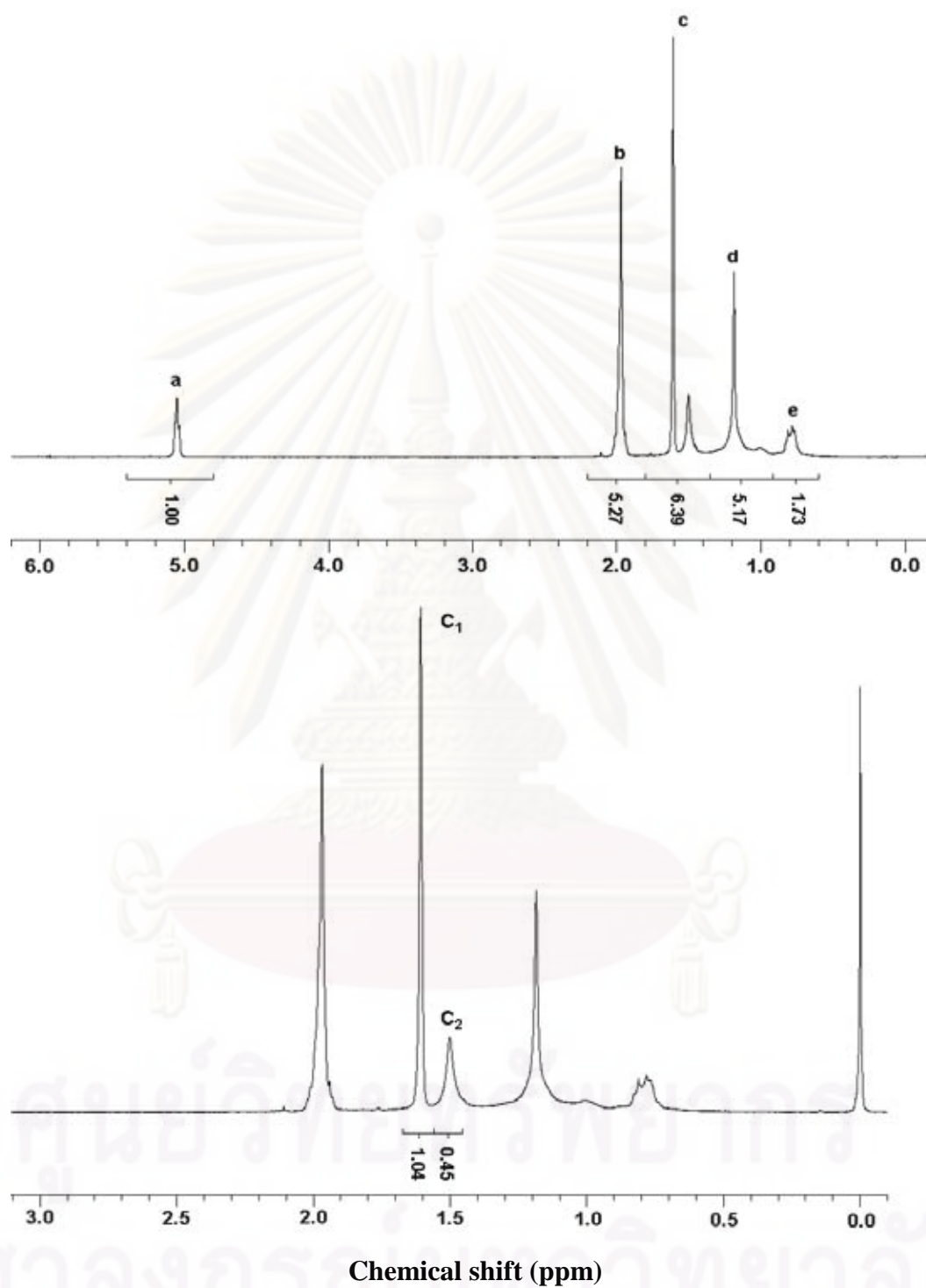
                  = 19.5

Figure D–3 ^{1}H–NMR spectra of HNR

Appendix E

The Data of Rubbers Hydrogenation Catalyzed by Pd/CF

Table E–1 Butadiene Rubber

Exp.	[Pd] (µmol)	[BR] (mM)	P_{H2} (bar)	Temperature (°C)	Time (h)	Hydrogenation (%)
1	29.9	93	55	120	24	54.7
2	29.9	93	55	130	24	70.4
3	29.9	93	55	140	24	57.1
4	29.9	93	55	150	24	53.7
5	29.9	93	28	130	24	28.7
6	29.9	93	41	130	24	53.7
7	29.9	93	69	130	24	28.4
8	29.9	46	55	130	24	63.2
9	29.9	139	55	130	24	57.8
10	29.9	185	55	130	24	48.6
11	14.9	93	55	130	24	54.8
12	44.8	93	55	130	24	46.1
13	59.8	93	55	130	24	45.7

Solvent = hexane.

Table E–2 Nitrile Butadiene Rubber

Exp.	[Pd] (µmol)	[NBR] (mM)	P_{H2} (bar)	Temperature (°C)	Time (h)	Hydrogenation (%)
1	29.9	47	28	140	24	24.4
2	29.9	47	41	140	24	32.3
3	29.9	47	55	140	24	46.4
4	29.9	47	55	130	24	23.0
5	29.9	47	55	150	24	25.1
6	14.9	47	55	140	24	27.8
7	44.8	47	55	140	24	24.4

Solvent = monochlorobenzene

Table E−3 Natural Rubber

Exp.	[Pd] (μmol)	[NR] (mM)	P_{H2} (bar)	Temperature (°C)	Time (h)	Hydrogenation (%)	Unsaturation (%)	
							Cis structure (%)	*Trans* structure (%)
1	29.9	74	28	140	24	8.0	79.3	12.7
2	29.9	74	41	140	24	24.8	66.0	9.2
3	29.9	74	55	140	24	25.2	54.6	20.2
4	29.9	74	55	130	24	1.6	91.1	7.3
5	29.9	74	55	150	24	1.0	91.7	7.3
6	14.9	74	55	140	24	23.8	54.4	21.8
7	44.8	74	55	140	24	35.3	45.2	19.5

Solvent = hexane

VITA

Mr. Totsaporn Tangthongkul was born on June 25, 1984 in Bangkok, Thailand. He graduated a Bachelor's degree of Science from Department of Chemistry, Faculty of Science, Chulalongkorn University in 2007. He has continued his study in Master's degree in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2007 and finished his study in 2009.

Oral presentation for the 35th Congress on Science and Technology of Thailand (STT 35) which organized by Burapha University in the topic of "HYDROGENATION OF BUTADIENE RUBBER USING PALLADIUM CATALYST SUPPORTED ON CARBON FIBER".