CHAPTER VI

HYDRODECHLORINATION OF CHLOROFORM

6.1 Introduction

Chlorine-containing compounds and chlorofluorocarbons (CFCs) are recognized as versatile chemicals generally used by a variety of manufacturers. Due to the fact that CFCs have many desirable properties, e.g., inertness, stability, and compressibility, which make them ideal choice as refrigerants, these same properties allow them to escape from the lower atmosphere without decomposition and contribute to stratospheric ozone depletion. According to the Montreal Protocol (1987), the goals for phasing out the use of a variety of ozone depleting chemicals, including most chlorofluorocarbons (CFCs) was established. One way to achieve this goal is the replacement of these CFCs with more environmental friendly chemicals. It was found that hydrochlorofluorocarbons (HCFCs) possess the useful properties as CFCs and at the same time they are much less harmful to the environment. Hydrodechlorination reaction is one of recommended process for transforming the large amount of CFCs existing today to more benign products via a catalytic reaction by a noble metal [Chen, 2002].

For instance, chloroform (CLF) is one of chlorine-containing reactant used in the manufacturing of the benign refrigerant, HCFC-22. Furthermore, it is also widely used as solvent, dry-cleaning reagents and degreasing agents. However, chloroform has been considered as a hazardous environmental pollutant and human carcinogen. The U.S. Environmental Protection Agency has identified chloroform as a hazardous waste. The release of chloroform to the environment contributes to air pollution and subsurface contamination, so the disposal of chloroform is regulated and currently subjected to more stringent regulations [ATSDR, 1997].

The ultimate disposal of chloroform has been accomplished through controlled incineration, preferably when mixed with another combustible fuel. High temperature combustion due to the presence of chlorine atom acting as a flame inhibitor, and

various toxic by-products such as phosgene, dibenzofurans and dibenzodioxins, generated from side reactions are great disadvantages of the incineration. The secondary treatments are required for the destruction of these toxic by-products, which results in an increase in operational costs. Other elimination methods of chloroform such as photochemical or biological degradation have been employed but limitations in their applications are the important disadvantages in use [Gregory and Reinhard, 2000; Schuth et al., 2000 and Schrick et al. 2002].

Since 1990, there has been a growing interest and a growing number of studies on the catalytic hydrodechlorination reaction of chlorine-containing compounds, especially CFCs. This is because catalytic hydrodechlorination has been advanced to be the most effective technique for the disposal of chlorinated compounds and preferred over the thermal incineration [Martino et al., 1999; Ordonez et al., 2000; Lopez et al., 2003]. This process consists of reacting the organochlorinated compounds with hydrogen, yielding hydrogen chloride and hydrocarbons. Hydrogen chloride can be easily separated by alkaline washing, and the harmless hydrocarbons can be burned or recovered. The benefits of catalytic hydrodechlorination over other methods are low temperature (< 300 °C) combustion and gaseous phase operation with short residence time; non-oxidative and non-destructive process, absence of highly toxic intermediates, possibility of useful products recovery and less toxic emissions.

In 1990s, the total consumption of the CFCs in Thailand had dramatically increased, particularly due to its uses as industrial solvents and refrigerants, with an average demand of 1,700 tons per year [Mission Thailand Weekly, 2002]. The increased use of CFCs led to an interest in the study on the hydrodechlorination reaction in the advantages of the treatment of CFCs and the transformation of CFCs to less toxic substances. In this work, chloroform, a small chlorinated compound, was used as a pollutant. By means of the catalytic hydrodechlorination reaction, a high porous support and a precious metal are needed. As described in Chapter III, the excellent properties of MCM-41 such as its one-dimensional, hexagonally ordered pore structure, large surface area, high thermal stability and some acidity make it attractive for catalyst support. The MCM-41 synthesized from rice husk silica in

Chapter IV was applied as a mesoporous silicate support for the hydrodechlorination of chloroform. The influences of reaction temperatures and metal loadings on the activity and selectivity of the catalytic hydrodechlorination in a comparison with a commercial catalyst are discussed in this chapter.

6.2 Objectives

1. To prepare and characterize the Pd/RH-MCM-41 supported catalyst.

2. To determine the activity and selectivity of the RH-MCM-41 supported catalyst over the hydrodechlorination of chloroform to hydrocarbons.

3. To investigate the influences of reaction temperature, metal loading and kinds of catalyst supports on the conversion of the hydrodechlorination reaction

4. To evaluate the comparative longevity of the RH-MCM-41 supported catalyst over the reaction.

6.3 Scope of the Study

1. The reaction of hydrodechlorination was carried out in a gaseous phase and controlled in a dry condition without moisture.

2. The catalyst preparation was conducted by means of an incipient wetness impregnation.

3. The effect of metal loading was studied by varying the loading from 0.5, 1.0 and finally 3.0 wt%.

4. The effect of the reaction temperature was examined at temperatures set to 100, 150, 175 and 200 °C.

5. The RH-MCM-41 synthesized from rice husk silica was utilized as a mesoporous support for palladium.

6.4 Literature Review

6.4.1 Chloroform

Chloroform has been used in the past as a solvent or an extraction solvent for fats, oils, greases, resins, lacquers, rubbers, gums, waxes, gutta-percha, penicillin, vitamins, flavors, floor polishes and adhesives in artificial silk manufacturing. It is also used as a dry cleaning reagent, fire extinguishers, an intermediate in the manufacturing of dyes and pesticides. In medical applications, it was previously used as an anesthetic and in dental surgery procedures, but now it has been replaced with other safer chemicals. The production of chloroform has gradually increased in demand since the 1980s due to the manufacturing of HCFC-22, the major chemical produced from chloroform which has been used as a refrigerant. The general properties and its effects related to the environment and human health are illustrated as follows.

6.4.4.1 General Properties

Chloroform ($CHCl_3$), also called trichloromethane, is a colorless liquid with a pleasant odor and a slight, sweet taste. The physical and chemical properties are presented in Table 6-1. Chloroform is both a synthetic and naturally occurring compound, although man-made source of it, such as septic systems and other water treatment processes involving chlorination, are responsible for most of the chloroform in the environment. Chloroform enters the air and water from some industrial processes, leaking containers, and waste disposal. It is also found in waste water from sewage treatment plants and drinking water to which chlorine has been added. Chlorine is added to most drinking water and many waste waters to destroy bacteria. Small amounts of chloroform are formed as an unwanted product during the process of adding chlorine to water. The amount of chloroform is normally expected to be in the air ranges from 0.02 to 0.05 parts of chloroform per billion parts (ppb) of air and from 2 to 44 ppb in treated drinking water [ATSDR, 1997]

Table 6-1 Physico-chemical properties of chloroform [ATSDR, 1997].

Properties		Characteristics
CAS number		67663
Synonyms		trichloromethane, methyl trichloride, formyl trichloride, methane trichloride, trichloroform, methenyl trichloride, trichlormethan
Molecular weight		119.39
Color		Clear, colorless liquid
Physical state		Liquid (at room temperature)
Melting point		-63 °C
Boiling point		61 °C
Density at 20 °C		1.48 g mL^{-1}
Odor		Chloroform-like, sweet
Odor threshold: Water		2.4 ppm (w/v)
Odor threshold: Air		85 ppm (v/v)
Water Solubility at 25 °C		$7.43 \times 10^3 \text{ mg mL}^{-1}$
Organic Solubility		Miscible with principle orgain solvents, alcohol, benzene, ether, oil
Partition coefficients:	Log K_{ow}	1.97
	Log K_{oc}	1.65
Vapor pressure at 20 °C		159 mm Hg
Henry's law constants:	at 20 °C	$3 \times 10^{-3} \text{ atm-m}^3 \text{ mol}^{-1}$
	at 25 °C	$4.06 \times 10^{-3} \text{ atm-m}^3 \text{ mol}^{-1}$
Autoignition temperature		> 1000 °C

6.4.4.2 Sources and Environment Fate

Chloroform is likely to enter the environment through its use as an industrial solvent, extractant and chemical intermediate as well as from its indirect production in the chlorination of drinking water, municipal sewage systema and cooling water. The majority of the environmental releases from industrial uses are into the atmosphere; releases to water and land will be primarily lost by evaporation and will end up in the atmosphere. Release into the atmosphere may be transported long distances and will photodegrade with a half-life of a few months. Spills and other releases on land will also leach into the groundwater where it will reside for long periods of time. Chloroform is not expected to bioconcentrate into the food chain but the contamination of food is likely due to its use as an extractant and its presence in drinking water. The majority of human exposure to it is from drinking water and ambient air, the latter particularly in the vicinity of industrial sources.

Terrestrial Fate: When spilled on land, chloroform would be expected to evaporate rapidly into the atmosphere due to its high vapor pressure. It is poorly adsorbed to soil, expecially soil with low organic carbon content such as subsoils and can leach into the groundwater.

Aquatic Fate: When released into water, most of chloroform will be primarily lost by evaporation into the atmosphere. Laboratory experiments have measured the half-life for evaporation to be several hours and modeling studies have suggested that the volatilization half-life is 36 hours in a river, 40 hours in a pond and 9-10 days in a lake. Field monitoring data suggested the half-life of chloroform to be 1.2 days in the Rhine River and 31 days in a lake in the Rhine basin. Chloroform from a municipal treatment plant injected into an estuarine arm of Chesapeake Bay entirely disappeared within 4 km in the spring and within 11 km in the winter under ice, and the decrease in concentration cannot be entirely due to dilution. Little chloroform will be adsorbed to sediment.

Atmospheric Fate: Chloroform released into the atmosphere will degrade by its reaction with hydroxyl radicals with a half-life of 80 days. It will be transported long distances and will partially return to the earth in precipitation. Most of chloroform in the air eventually breaks down, but this process is slow. The

breakdown products in air include phosgene, which is more toxic than chloroform, and hydrogen chloride, which is also toxic. Some chloroform may break down in soil. Chloroform does not appear to build up in great amounts in plants and animals, but we may find some small amounts of chloroform in foods.

6.4.4.3 Regulations, Analytical Methods and Treatment Technology

The Environmental Protection Agency (EPA) sets rules for the amount of chloroform allowed in water. The EPA limit for total trihalomethanes, a class of chemicals that includes chloroform, in drinking water is 100 micrograms per liter. Furthermore, EPA requires that spills of 10 pounds or more of chloroform into the environment must be reported to the National Response Center [ATSDR, 1997].

Table 6-2 lists the standards and regulations for chloroform. The American Conference of Governmental Industrial Hygienists (ACGIH) has set the threshold limit value (TLV) for chloroform in workplace air with an average concentration 10 ppm for a normal 8-hour workday or 40-hour workweek The Occupational Safety and Health Administration (OSHA) sets the levels of chloroform allowed in workplace air in the United States. The permissible occupational exposure limit is 50 ppm in air during an 8-hour workday, 40-hour workweek. The National Institute of Occupational Safety and Health (NIOSH) recommended that the worker exposure to chloroform in the workplace be controlled by the Chloroform Standard. The standard is 50 ppm designed to protect the health and provide for the safety of workers for up to a 10-hour workday, a 40-hour workweek over a working life time. The standard will be subject to further review and revision as necessary. Occupational exposure to chloroform is defined as the exposure to chloroform in any establishment where chloroform is used, manufactured or stored.

Table 6-2 Standards and Regulations for Chloroform [ATSDR, 1997].

Agency	Focus	Level	Comments
American Conference of Governmental Industrial Hygienists (ACGIH)	Air: workplace	10 ppm	Advisory; TLV/TWA*
National Institute for Occupational Safety and Health (NIOSH)	Air: workplace	50 ppm	Recommendation; 10-hour TWA; potential carcinogen
Occupational Safety and Health Administration (OSHA)	Air: workplace	2 ppm**	Regulation; PEL***over 8-hour workday

* TLV/TWA (threshold limit value/time-weighted average): time-weighted average concentration for a normal 8-hour workday or 40-hour workweek to which nearly all workers may be repeatedly exposed.

** The former OSHA PEL for chloroform was 50 ppm as a ceiling limit. OSHA proposed to revise this limit to 2 ppm, measured over a 60-minute period. This limit was based on the NIOSH (1977p, as cited in ACGIH 1986/Ex. 1-3, p. 130) REL, and NIOSH (Ex. 8-47, Table N6A) has indicated its concurrence with the proposed limit. In the final rule, OSHA is establishing a 2-ppm limit for chloroform, but is expressing this PEL as an 8-hour TWA limit.

*** PEL (permissible exposure limit): highest level averaged, over an 8-hour workday, to which a worker may be exposed. Note: A PEL of 50 ppm was enacted by the Occupational Safety and Health Administration in 1989, but that level, along with 375 others, was vacated for procedural reasons by the 11th Circuit Federal Court in 1993.

6.4.4.4 Health Effects

In humans, chloroform affects the central nervous system (brain), liver, and kidneys after a person breathes air or drinks liquids that contain large amounts of chloroform. Chloroform was used as an anesthetic during surgery for many years before its harmful effects on the liver and kidneys were recognized. Breathing about 900 parts of chloroform in a million parts of air (900 ppm or 900,000 ppb) for a short time causes fatigue, dizziness, and headache. Long period of chloroform exposure

may cause liver and kidney damages. Large amounts of chloroform can cause sores when the chloroform touches skin.

Results of studies of people who drank chlorinated water showed a possible link between the chloroform in chlorinated water and the occurrence of cancer of the colon and urinary bladder. Cancer of the liver and kidneys developed in rats and mice that ate food or drank water that had large amounts of chloroform in it for a long period of time. However, it has not been reported whether liver and kidney cancer would develop in people after long-term exposure to chloroform in drinking water. Based on animal studies, the Department of Health and Human Services (DHHS) has determined that chloroform may reasonably be anticipated to be a carcinogen (a substance that causes cancer). The International Agency for Research on Cancer (IARC) has determined that chloroform is possibly carcinogenic to humans. The EPA has determined that chloroform is a probable human carcinogen.

6.4.2   Background of Catalytic Reaction

6.4.2.1 Definition of Catalysis

A catalyst is a substance that increases the rate of a chemical reaction but does not change the position of the equilibrium. The principal function of a catalyst is to decrease the activation energy of the non-catalyzed reaction. Catalysis occurs when the presence of the catalyst provides an alternate path of lower activation energy by which the reactants can proceed to form the products. There is no change in the free energy of the reaction because the energies of the products and reactants are not affected by the catalyst.

Three terminologies for catalytic reaction should be concerned. *Conversion* is the fraction of reactants converted into either product. *Yield* is the conversion multiplied by its selectivity. *Deactivation* is a number of different processes that contribute to the loss of catalytic activity. The terminology of catalytic activity and selectivity are explained in the next following sections.

6.4.2.1.1 Catalytic Activity

Nature of chemisorption of a species on the surface contributes to the catalytic reactivity. The activity or conversion can be determined by the ratio of amount of reactant consumed and amount of reactant introduced in the reaction, mentioned in Equation (6-1).

$$\text{Activity} = \frac{\text{Reactant consumed}}{\text{Reactant introduced}} \quad \text{............................(6-1)}$$

If chemisorption is weak, low coverage of the adsorbate will be formed and surface reactivity (or catalytic activity) will be low. As the heat of adsorption increases, bonding to the surface becomes stronger, giving higher coverage and reducing of its activation energy. On the contrary, if the adsorbate interacts too strongly with the surface, it results in too stable to decompose or desorb the species and the products from the surface. In this case, the catalytic activity will be low. The relative catalytic activities for different metals can be characterized by the temperature at which a given rate of reaction is attained, lower reaction temperatures representing higher activities or by the rate coefficient (k) for the reaction at a given temperature, a high rate coefficient representing high activity [McCash, 2001].

6.4.2.1.2 Selectivity of Catalysts

A good catalyst must possess both high activity and long-term stability. But the most important attributed to a catalytic reaction is selectivity, which reflects its ability to direct the conversion of the reactant(s) along one specific pathway. High selectivity produces high yields of a desired product while suppressing undesirable competitive and consecutive reactions. *Selectivity* is the fraction that it constitutes of the total products as given in the below: [Thomas, 1997]

$$\text{Selectivity} = \frac{\text{mole of desired product}}{\text{mole of reactant consumed}} \quad \text{...............................(6-2)}$$

Catalysis is of crucial importance for the chemical industry, the number of catalysts applied in the industry is very large and catalysts come in many different forms; from heterogeneous catalysts in the form of porous solids over homogeneous catalysts dissolved in the liquid reaction mixture to biological catalysts in the form of enzymes. The general properties of desired catalysts are recognized in the performances of high and stable activity, high and stable selectivity, controlled surface area and porosity, good resistance to poisons, good resistance to high temperatures and temperature fluctuations, high mechanical strength and no uncontrollable hazards. The shape and size of catalysts are also important parameters affecting the diffusion phenomena of reactants toward the embedded metallic surface and their mechanical stability [Plembeck, 1995].

6.4.2.2 Classification of Catalytic Systems

The catalytic system can be divided into two distinct categories. When the catalyst is being the same phase as the reactants and no phase boundary exists, it is termed *homogeneous catalysis*. This may take place either in the gaseous phase or in the liquid phase. A catalyst, which operates on reactions taking place in different phases, is termed *heterogeneous catalysts*, which are great importance in chemical industry and in living organisms.

In heterogeneous catalysis, the reacting species are held on the surface of the catalyst by a physical adsorption while the reaction takes place. Figure 6-1 demonstrates the two mechanisms in the transformation of gas-phase species on the surface of support. Adsorption may be relatively weak (physical adsorption) or may have a strength comparable to the strengths of chemical bonds (chemisorption). In either case, adsorption is generally not uniform across a solid surface. Adsorption, and therefore catalysis, occurs primarily at certain favorable locations called *active sites*.
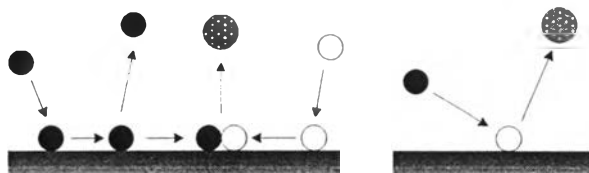
Figure 6-1 Two possible ways in which heterogeneous catalysis proceeds at the surface, (a) the Langmuir-Hinshelwood mechanism, (b) the Eley-Rideal mechanism [Thomas, 1997].

6.4.2.3 Preparation of Catalysts for Heterogeneous Catalysis

There is a wide variety of types of catalysts in commonly uses in heterogeneous catalytic reaction. Many of them are multicomponent with various kinds of metals, especially transition metals dispersed on oxide or carbonaceous support, e.g., crystalline porous solids which consist of well-defined Brønsted acid sites located at the inner walls of the particles. The main purposes of using a support are to achieve an optimal dispersion of the catalytically active components by means of an increase in contact surface area, and to stabilize it against sintering at high temperatures [Ertl, 1999].

A properly designed catalyst should have the attributes of activity, stability, selectivity and regenerability. There are two main steps in catalyst preparation. The first is the depositing of the active component precursor on the support, and the second is the transforming this precursor into the required active component, which can be found in oxide, sulfided or metallic state. The methods most frequently used to achieve deposition of the active precursors are impregnation, precipitation and ion exchange.

6.4.2.3.1 Impregnation and incipient wetness method

Impregnation is a common method applied to the preparation of catalysts. Depending on the interaction between the support and the precursors, the

impregnation can be distinguished into two types: dry impregnation and incipient wetness impregnation [Ertl, 1999].

Drying impregnation, sometimes called *capillary impregnation*, can be conducted by spraying a solution of a metal salt onto pellets of a pre-dried porous support without the amount of solution exceeding the pore volume of the support so that at the end of process no excess solution remains outside of the pore space. The pellets are then dried and calcined to transform the metal into an insoluble form. The metal salt can be deposited homogeneously through the pellet or most of the metal may be deposited near the outside of the pellet. The well distribution of the metal is controlled through the pH or through the addition of chelating agents to the impregnation liquid.

In contrast, incipient wetness impregnation is performed by impregnating a metal salt on a porous support in the presence of a liquid solvent. The metal loading in the finished catalyst is typically 1-5%. Figure 6-2 illustrates the preparation of the catalysts by using incipient wetness. The incipient wetness is performed when liquid containing metallic precursors, typically 1 cm^3 g^{-1} is slowly added to a dried porous solid powder and the liquid is first absorbed until it reaches the saturation state by the diffusion of the solvent. If the solvent-saturated support is further immersed in the impregnation solution to enhance metal diffusion phenomenon, this method is called *diffusion impregnation*. The precursor salt migrates from the solution into an inner surface by the driving force due to the gradient concentration. The migration time is obviously much longer than that of capillary impregnation [Bond, 1987]. In this work, the incipient wetness impregnation was employed for the preparation of Pd over the MCM-41 support because this technique is simple to apply and provides sufficient metal distribution for the hydrodechlorination reaction.
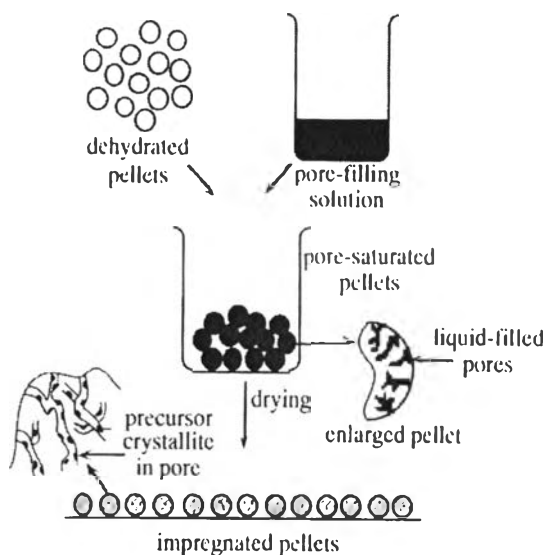
Figure 6-2 Schematic of the steps in the preparation of supported catalysts by impregnation to incipient wetness [Farrauto, 1997].

When high loading are required, incipient wetness impregnation is more difficult. This is because the solubility of the precursor is usually insufficient to achieve the required concentration in the volume of liquid equal to the pore volume of the support. Thus, multiple impregnations are needed to achieve the desired loading of the active component.

6.4.2.3.2 Precipitation Method

Precipitation of an active precursor onto a support suspended in a solution of the precursor can provide high loading, since the compounds dissolved in a large volume of liquid compared to the incipient wetness method are concentrated on the suspended support. The precipitation can be performed by changing the pH level, or the valence state of the active precursor, or the concentration of a complexing agent. To ensure a sufficient transport of the precipitating species into the porous media, a finely divided support is recommended. The overall process for the preparation of metal salt deposited on the pellet support by using the alkali precipitation method is demonstrated in Figure 6-3. The precipitation usually proceeds the location where the precipitating liquid is entering suspension. The rapid precipitation typically takes place outside the inner pores of the suspended solid and causes an increase in numbers

of nucleation and the growth of precipitates. The large crystallites of precursor obtained in the first stage of precipitation act as encounters to the migration of the soluble active precursor into the pores of the support. To prevent the formation of colloidal particles of the precursor outside the pore system, the optimum condition of the precipitating solution has to be adjusted [Ertl, 1999].
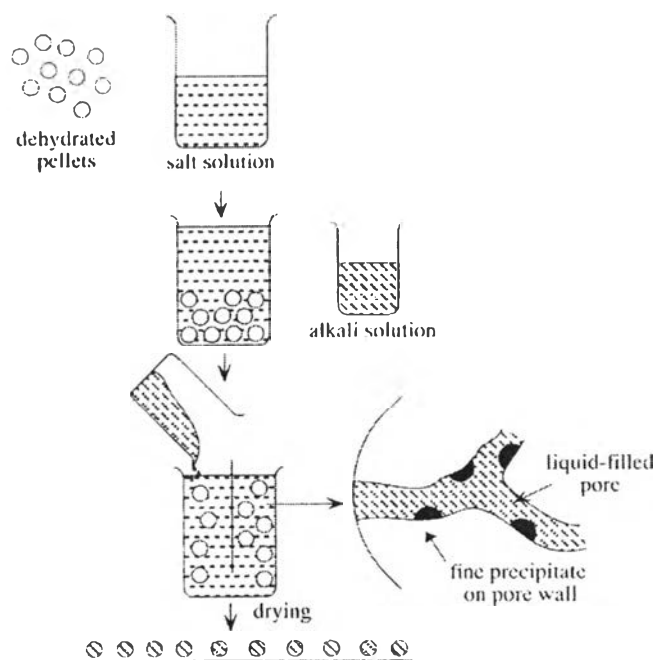

Figure 6-3 Schematic of steps in the preparation of supported catalysts by precipitation from the alkali solution [Farrauto, 1997].

6.4.2.3.3   Ion-exchange method

Ion exchange consists of replacing an ion in an electrostatic interaction with the surface of a support by another ion species. The support containing ion A is plunged into an excess volume of a solution containing ion B that is to be introduced. Ion B gradually penetrates into the pore space of the support and takes the place of ion A, which passes into the solution until an equilibrium is established. Almost solid supports are oxide which can behave like ion exchangers such as zeolites. The negative charges in zeolites are due to the presence of aluminum tetrahedron (AlO_4) and silicon tetrahedron (SiO_4), which provide four negative charges surrounding the center atom. These charges can be neutralized by the various cations such as Na^+ and

K^+, and be replaced by other cations during the ion-exchange operation. The number of ion-exchange sites depends upon the number of center atoms and is pH independent. The natural oxide surfaces, clay and silicates for examples are also cation exchangers. In the presence of water, metal oxide surfaces (Al, Si, Ti, Fe, etc.) are covered with hydroxyl groups which act as Brønsted bases, whereas the metals may behave as Brønsted acids. The exchanging reaction takes place as the given equations [Ertl, 1999]:

$$
\begin{aligned}
S - OH &= S - O^- + H^+ \\
S - OH + H^+ &= S - OH_2^+
\end{aligned}
\quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(6-3)}
$$

Where S is metal atom.

The last important step in the preparation of a supported metal catalyst is the reduction of the precursor to the metallic state. Catalysts based on oxides are usually activated by the reduction in H_2 in the reactor. The purpose of calcination is to convert the precursor to the oxide, which is usually the easiest compound to reduce. Some oxides such as palladium (II) oxide, are easily reducible and can be use without prior reduction. When reducing with hydrogen in the dry state, chlorides reduce at between 370 and 470 K. On the other hand, base metals are more difficult, they required higher temperatures for catalyst activation [Bond, 1987].

6.4.2.4 Catalyst Deactivation

Deactivation is a model for the changes in reactivity for a reaction on a catalytic surface in the presence of adsorbed inactive atoms. The deactivation of a catalytic reaction results from several different causes. The active sites of a catalyst may become poisoned by the adsorption of impurities. The growth and agglomeration of active species by the process of sintering may reduce the active surface area of catalysts. The fouling of the surface and blockages of pores by carbonaceous residues produced from the breakdown or cracking of some hydrocarbons can cause a loss of activity. The latter, termed *Coking*, contributes to the significant effect mostly found in many catalytic reactions of petroleum feedstock and are even common in reactions containing products in the form of carbon compounds [Thomas, 1997]. Therefore, it is

necessary to understand and be able to predict the loss of activity during the catalytic reaction. The useful model to predict the probability of carbon formation proposed by Anderson-Schulz-Flory [Anderson, 1984], can be utilized for the purpose of catalytic deactivation by means of coking.

6.4.2.5 Anderson-Schulz-Flory Product Distributions

The formation of carbon-containing compounds, which are typical by-products of catalytic reactions in the heterogeneous phase between a carbon-rich gas and the active surfaces of metal grains, has played an important role in relation to the activity and the coking phenomena of catalytic reactions. The convection and diffusion of small carbon molecules taken place over the catalyst reactive surface attribute to the retardation of the removal of reactive olefins, which brings about the probability of secondary readsorption. The propagation stage of the chain growth due to the stepwise extension of reactive C_1 intermediates occurs in a similar manner with the polymerization of olefins found in Fischer-Tropsch-type reactions. The growth probability and the chain length distribution can be estimated by using the Anderson-Schulz-Flory (ASF) distribution. By means of this model, longevity and selectivity of the hydrodechlorination of chloroform mentioned in this work can be determined as well as the tendency of coking caused by oligomers can be predicted.

The conversion of synthesis gas or syngas, a mixture of CO and H_2, into mainly hydrocarbons is known as the *Fischer-Tropsch* synthesis. Anderson was the first to introduce a kinetic model for the Fischer-Tropsch reaction. This model was deduced from a polymerization model proposed by Schulz and Flory [Schulz and Flory, 1936]. Nowadays, it is referred to as the Anderson-Schulz-Flory (ASF) mechanism [Anderson, 1984]. Initially, CO and H_2 are dissociatively adsorbed on the active surface to form CH_2-species. Starting from C_1, -CH_2 building blocks can be continuously inserted, eventually resulting in a C_n species at the surface. The hydrocarbon chain can be terminated by either hydrogenation leading to alkanes or hydrogen abstraction resulting in alkenes. The chain growth probability (α) for a CH_2 monomer insertion to a hydrocarbon chain is defined as the ratio of the propagation rate (k_p) and the sum of the propagation and termination (k_t) rates (Equation 6-4).

$$\alpha = \frac{k_p}{k_p + k_t} \qquad\qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6\text{-}4)$$

It is empirically established that α is generally independent of the chain size. However, for very small chains, *i.e.* C_1 and C_2, the independence is not obeyed. The Anderson-Schulz-Flory distribution is described by the following Equation:

$$\log\left(\frac{W_n}{n}\right) = 2\log\left(\ln\left(\alpha\right)\right) + n\log\alpha \dots\dots\dots\dots\dots\dots\dots\dots(6\text{-}5)$$

In this formula, W_n is the weight fraction of oligomers containing n carbons and n represents the carbon number. When the logarithm of the relative weight fraction $\log(W_n/n)$ is plotted against the carbon number (n), the chain growth probability ($\log(\alpha)$) can be determined from the slope of the straight line.

6.4.3 Catalytic Hydrodechlorination

Hydrodechlorination reaction, a heterogeneous catalytic reaction, has become the most preferable process from an environmental standpoint. It can be used in the area of pollution abatement such as in the destruction of undesired by-products containing C-Cl bonds and the reclamation of chlorine-containing waste into profitable commodities. Additionally, it is widely used in the way of transforming the large amounts of CFCs that exist today into the more environmentally benign HFCs. This method has advantages over the traditional incineration method where the reaction products of hydrodechlorination are less harmful, and generally for the catalytic reaction, the reaction can take place under lower required temperature.

The hydrodechlorination reaction is the reaction between H_2 and an organic compound that contains C-Cl bond(s). During the reaction, chlorine is removed from the compound as HCl product and the original C-Cl bond is replaced with a new C-H bond (Equation 6-1).
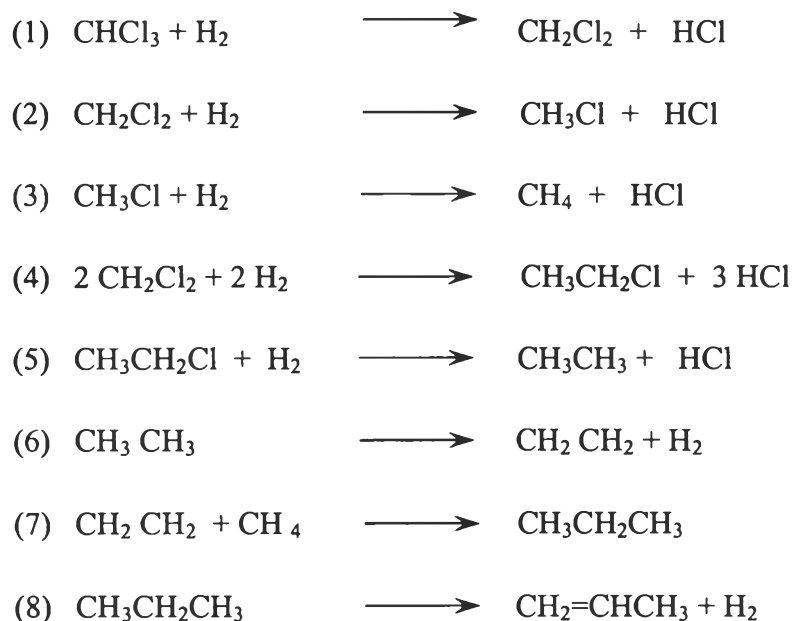
$$R\text{-}Cl + H_2 \rightleftharpoons R\text{-}H + HCl \qquad \dots\dots\dots\dots\dots \textbf{(6-6)}$$
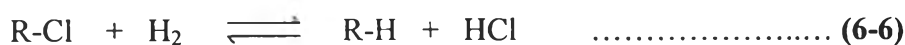
Chen (2002) studied the hydrodechlorination reaction kinetics on a group of $CH_{4-x}Cl_x$ (x=1-4) compounds measured on the Pd/carbon catalysts. It was found that the hydrodechlorination reaction rates correlated with the strength of the gaseous phase C-Cl bond energy and the first C-Cl bond scission on the surface is the rate determining step of the hydrodechlorination reaction, which is in an agreement with Thompson (2000). The observed hydrodechlorination reaction kinetics of $CH_{4-x}Cl_x$ (x=1-4) compounds supports a previously proposed Langmuir-Hinshelwood type of hydrodechlorination reaction mechanism. That is, (1) the gaseous phase of H_2 and HCl are in equilibrium with surface H and Cl; (2) adsorbed Cl is the most abundant surface intermediate; and (3) the irreversible scission of the first C-Cl bond is the rate-determining step. The overall hydrodechlorination reaction rate for these series of compounds can be written as Equation (6-7).

$$ r = \frac{K\,[RCl]}{\left(1 + \dfrac{k\,[HCl]}{[H_2]^{0.5}}\right)} \quad\dotfill(6\text{-}7) $$

Where K is the equilibrium constant and k is the rate-determining step.

6.4.3.1 Hydrodechlorination of Chloroform

The hydrodechlorination of CLF in the presence of excess hydrogen can yield several products of hydrocarbons and its derivatives. The main product of the reaction is methane. The formation of C-C bonds to produce the products of hydrocarbons containing C_2-C_7 was observed to be approximately 37% at 175 °C, whereas the chlorinated derivatives such CH_2Cl_2 was formed at the selectivity as low as 0.6%. The reactivity of CLF increases in the order of $CH_2Cl_2 < CHCl_3 < CCl_4$ [Mori, 2002]. The possible reactions taking place in the reactor could be written as follows:

(1) $CHCl_3 + H_2$ $\longrightarrow$ $CH_2Cl_2 + HCl$

(2) $CH_2Cl_2 + H_2$ $\longrightarrow$ $CH_3Cl + HCl$

(3) $CH_3Cl + H_2$ $\longrightarrow$ $CH_4 + HCl$

(4) $2\ CH_2Cl_2 + 2\ H_2$ $\longrightarrow$ $CH_3CH_2Cl + 3\ HCl$

(5) $CH_3CH_2Cl + H_2$ $\longrightarrow$ $CH_3CH_3 + HCl$

(6) $CH_3\ CH_3$ $\longrightarrow$ $CH_2\ CH_2 + H_2$

(7) $CH_2\ CH_2 + CH_4$ $\longrightarrow$ $CH_3CH_2CH_3$

(8) $CH_3CH_2CH_3$ $\longrightarrow$ $CH_2{=}CHCH_3 + H_2$

6.4.3.2 Catalyst Supports and Metal Catalysts for Hydrodechlorination

The hydrodechlorination reaction is quite exothermic and thus with the presence of a catalyst it can be driven to completion at the lower operation temperature. There are many studies related to the number of novel metals used in hydrodechlorination catalysts [Chen, 2002; Schuth, 2000]. It is also reported that the catalyst supports, where the metal catalysts impregnate and perform well dispersion, have played a role in the enhancement of catalytic reactivity. With the excellent properties of high porosity and a large surface area, microporous and mesoporous solids are commonly utilized as a support for the hydrodechlorination reaction [Ordonez, 2000; Lopez, 2003].

Hydrodechlorination reaction is usually performed over noble metals. Different metals will lead to different hydrodechlorination reaction activity and selectivity. Hydrodechlorination reaction has been studied on a number of metals, including Pd, Pt, and Rh. It is found that Pd usually has the highest hydrodechlorination reaction activity and is the most selective metal catalyst for this reaction, thus it is applied as catalyst in a large number of papers on the hydrodechlorination reaction.

The hydrodechlorination process requires a catalyst in order to operate at mild temperatures. Precious metals such as Pd, Pt and Rh [Martino et al., 1999; Ordonez et al., 2000; Gregory and Reinhard, 2000; Schuth et al., 2000 and Centi, 2001] and hydro-treatment catalysts such as Ni-Mo (Martino et al., 1999 and Ordonez et al., 2000) have shown activity for hydrodechlorination reactions. The most active hydrodechlorination catalysts are supported precious metals, which are active at the moderate pressure and temperature (1–0.5 Mpa, 250 °C); whereas hydrotreatment catalysts operate at more severe conditions (10 MPa, T >350 °C) [Lopez et al., 2003].

In 1998, Malinowski and his coworkers found that the Pd catalysts are superior in the hydrodechlorination of CFC-12 and CH_2Cl_2. It was also established that the high conversion of halogen removal was achieved and nonselective production of methane, a major product of the hydrodechlorination reaction, was due to hydrogenation of the bare C_1 surface species. In a comparison of Pd-based catalyst, the other kinds of precious metals and their supports for hydrodechlorination have been undertaken toward the reactions, developed for improving their catalytic behavior and their applied usage with to various halogenated pollutants.

There is a large quantity of accumulated knowledge on the supporting metals on carriers such as Al_2O_3, SiO_2, carbon, and zeolites and on achieving high metal dispersions. The large surfaces of ordered micro and mesoporous materials offer new possibilities for obtaining highly dispersed noble metal catalysts. Ordonez and his colleagues (2000) investigated the activity of eight commercial catalysts, which were Pd on alumina, Ni on SiO_2, Pt on alumina and activated carbon, Ru on alumina and also Rh on alumina for the hydrodechlorination of dichloromethane (DCM), chloroform (CLF), carbon tetrachloride (CTC), trichloroethane (TCA), trichloroethylene (TCE) and tetrachloroethylene (TTCE). They reported that Pt catalysts yielded the highest conversion especially for unsaturated molecules such as TCE and TTCE. CTC is the most reactive compound, presenting very high conversions for all the catalysts tested. CLF, TCE and TTCE conversions are more than 90% for Pt/C, and slightly lower for Pt/alumina and Pd catalysts. The highest selectivity for CLF hydrodechlorination was obtained from the Pt catalysts.

The comparisons of Pd on various zeolites (ZSM-5 and Y types) and Pd on MCM-41 in the dehalogenation reaction for groundwater treatment containing various halogenated compounds were carried out by Schuth et al. (2000). The resistance of the catalyst against poisoning from the anionic species was improved by embedding 1% w/w Pd in a hydrophobic support material. The first order reaction rates of the mesoporous MCM-41 catalysts were much faster than that of zeolites. However, in the presence of sulfite, all catalysts were deactivated with the exception of zeolite Y; in addition, MCM-41 was not tolerant when subjected to anionic poison.

Furthermore, Lopez (2003) observed that supported palladium catalysts show high activity and stability for the hydrodechlorination of chloroaliphatic compounds, such as CLF, TTCE, TCE and dichloroethylene. The influence of process parameters such as temperature, pressure, hydrogen flow and the nature of solvent on both activity and stability of this catalyst has been also studied. It was found that higher temperatures lead to higher initial activity, but faster deactivation; increasing hydrogen flow rates produces higher activity and stability of the catalyst, whereas pressure and solvent have no significant effects.

Similarly, the activity and selectivity of different kinds of supports, such as SiO_2, Al_2O_3, SiO_2-Al_2O_3, TiO_2, ZnO and MCM-48 on the detoxification of chloroform via the hydrodechlorination reaction were studied by Chayanan (2003). The activity order based on supported 0.5% Pd was ranked as $Al_2O_3 \approx SiO_2 \approx$ MCM-48 > TiO_2 > SiO_2-Al_2O_3 > ZnO. The higher activity was dependent upon an increase of percent metal loading. Compared with Ni, Pd catalysts performed both activity and stability higher for the same support and same amount for metal counting. In an evaluation of deactivation, Ni/MCM-48 presented a significant tendency to deactivation by coking, while the lowest tendency of coking was dedicated to Pd/MCM-48. Another kind of MCM family, MCM-41 was also used as a support of the hydrodechlorination reaction. The MCM-41 containing surface area of approximately 700-1000 m^2 g^{-1} and a uniform pore diameter of 29.5 Å was used as one of the supports for the hydrodechlorination of chloroform (Sirisak, 2003). Four kinds of metal catalysts, Ni, Pd, Pt, and Rh, were loaded on the MCM-41 particles using the incipient wetness impregnation and ion exchange method. The reaction was

carried out in a pulse reactor under atmospheric pressure with the temperature range of 100-200 °C. Parameters like metal loading, types of metals and supports were studied. It was found that the good dispersion of the catalyst on the support was obtained from the ion exchange method; however, even the impregnations, the conversions of the hydrodechlorination for all catalysts were satisfactory. The palladium catalyst provided highest level of activity compared to the other three metals and the most suitable metal loading was 1% by weight. The order of catalytic activity was Pd ~ Rh > Pt > Ni. The optimal temperature for favorable activities was around 150-200 °C, where the conversion of chloroform was enhanced up to 95-100%.

At present, it has been recognized that the techniques of catalyst preparation play an essential role on the dispersion of metal over the support surface as well as the activity of the catalyst. Many authors have attempted to find out the best catalyst preparation in order to improve the performance of catalyst. Schuth and others (2000) investigated the incipient wetness impregnation and ion exchange for Pt on MCM-41, and the direct introduction of Pt during the synthesis of MCM-41. High Pt contents (up to 80% of incorporation) were achieved using the direct incorporation of Pt via the synthesis gel. A neutral Pt precursor $[Pt(NH_3)_2Cl_2]$ results in the formation of the Pt crystallites embedded in the pores. Metal dispersion by incipient wetness impregnation or ion exchange of $[Pt(NH_3)]^{2+}$ gives larger crystallites, with a distribution of 2 and 20 nm but poor dispersion compared to the former. Another effective technique for tailoring catalyst over support surface was introduced by Tanaka and his coworkers (2002). Use of the sol–gel process and complexing agents such as ethylene glycol and acetyl acetone in the preparation of Pd/SiO_2 catalysts are quite effective for dispersing palladium highly into the silica. This high dispersion of the palladium is derived from the complexing agents that surround the palladium and tie between the palladium and the silica support.

Although, the noble metals exhibit a very good performance level in the catalytic reactions, the drawback of using these metals is deactivation. In hydrodechlorination, some authors mentioned that the most important of deactivation is poisoning by the HCl formed in the reaction [Chang and Gampine cited in Ordonez et al., 2001]; whereas other authors stated that the deactivation is mainly caused by

coking [Centi, 2001 and Finocchio et al., 2002]. In Ordonez et al.'s (2001) work, the carbonaceous deposits indicated the poor performance of carbon-supported catalysts. These cokes have low molecular weight and low density, thus occupying more volume and blocking active sites in higher concentrations. Eventually, this effect results in the collapse of microporous structure and leads to a reduction in the activity of the catalysts. Ordonez also found that on the same support the weight losses determined from the Thermogravimetry method (TG) were higher in the case of the Pt catalyst that presented the fastest deactivation while Pd showed lower carbon loss.

In summary, palladium is extensively used as the active component in several industrial catalytic applications, especially for the conversion of environmentally unfriendly chemicals in gaseous emissions due to its excellent performance in the conversion of some hydrocarbons and halocarbons, high thermal stability and low volatility of Pd species [Ordonez, 2000]. Like platinum, palladium requires low temperatures in the oxidation of hydrocarbons and other organic chemicals. The activity of palladium is generally better than that of platinum in the conversion of methane. The resistance of palladium to thermal and hydrothermal sintering is also better than that of platinum, but its behavior in the presence of poisons, such as sulfur containing pollutants or lead is worse. However, palladium is cheaper than platinum. The basis of cost, performance, and stability considerations makes palladium the preferable choice in the field of catalysis. The largest use of palladium for the cleanup of emissions from stationary sources is in the field of the catalytic oxidation of hydrocarbons. Several types of practical applications have been investigated in the conversion of methane catalytic combustion, reduction of greenhouse gas emissions, destruction or conversion to less harmful chemicals of chlorinated hydrocarbons, oxidative destruction of halocarbons and the elimination of other pollutants from gaseous emissions [Centi, 2001].

6.5 Experimental

6.5.1 Material and Chemicals

- RH-MCM-41 material synthesized by this work described in Chapter IV.
- Silica (SiO_2), received from Asia Catalysis Society, Japan.
- Silica-alumina (SiO_2-Al_2O_3), received from Asia Catalysis Society, Japan.
- Nitrogen gas with purification of 99.99%, purchased from Thai Industrial Gases Co., Ltd.
- Hydrogen gas with purification of 99.999%, purchased from Thai Industrial Gases Co., Ltd.
- Trichloromethane (chloroform) with a purification of 99.5%, purchased from Kanto Chemical.
- Palladium acetate [$Pd(OAc)_2$], purchased from Wako Pure Chemical Industries, Ltd.

5.5.2   Methodology

5.5.2.1 Catalyst Preparation

The oxide supports such as silica (SiO_2), silica-alumina (SiO_2-Al_2O_3) were used in this work. For the study of the hydrodechlorination of CLF over molecular sieve MCM-41, the palladium that embedded the RH-MCM-41 support with different loadings was prepared by means of incipient wetness impregnation. This method is rapid and simple to handle, and also provides sufficient metal distributions. To avoid waste of the active ingredients, the precursor of the catalyst was impregnated onto the surface of the support by incipient wetting with the volume of the precursor solution close to the pore volume of the support.

The RH-MCM-41 synthesized from rice husk silica possessed a pore volume of 0.93 cm^3 g^{-1} and BET specific surface area of (800 ± 8) m^2 g^{-1}. Palladium acetate [$Pd(OAc)_2$] was utilized as a catalyst precursor. The Pd loading over RH-MCM-41

was in different loading of 0.5, 1.0 and 3.0 wt%. The preparation of these catalysts was described as the follows:

1. The known amount of metal precursor $Pd(OAc)_2$ was dissolved in the minimum volume of dilute HCl and the solution was diluted to 25 mL by adding methanol. The calculation of the exact amount of $Pd(OAc)_2$ is shown in the Appendix (A).

2. The solution was slowly dropped onto the RH-MCM-41 support. During the process, RH-MCM-41 was shaken in order to obtain a homogeneous mixture.

3. The catalyst was dried for 12 h at 110 °C in hot air oven and then calcined for 6 h at 550 °C under the flowing of air.

4. The catalyst was removed from the furnace, cooled to room temperature, and stored in a desiccator.

5.5.2.2 Catalyst Characterizations

The distinctive crystalline patterns of the catalysts were detected by powder X-ray diffraction spectroscopy (XRD). The dispersion of palladium over the RH-MCM-41 support was determined by hydrogen chemisorption. An elemental analysis of the catalysts was measured by X-ray fluorescence spectroscopy (XRF).

5.5.2.2.1   Powder X-ray Diffraction Spectroscopy (XRD)

The XRD patterns were recorded by the Rigaku diffractometer, with low angle scanning at 2θ in a range of 2-10° and for high angle, 10-60°. The X-ray was generated from $CuK\alpha$ crystals with a current of 30 mA and a potential voltage of 25 kV. The scan speed for low-angle and high-angle measurement was set at 1° and 2° min^{-1}, respectively.

5.5.2.2.2 Hydrogen Chemisorption

Hydrogen chemisorption was measured with a flow reactor connected with an online gas chromatograph. A certain amount of sample was placed in a u-tube reactor and flowed with 30 mL min^{-1} of hydrogen gas at 450 °C for 1 h to get rid of moisture and then the temperature was reduced to 400 °C. Afterwards, nitrogen gas which was trapped the moisture was introduced through the CuO column at 214 °C in order to remove oxygen from nitrogen gas stream. The oxygen-free nitrogen was then trapped the moisture before being purged through the reactor to remove hydrogen from the surface of the catalysts. The clean-up process was conducted at room temperature until no changes of hydrogen effluent were observed on the TCD chromatogram. Nitrogen containing a 10% hydrogen balance was introduced periodically into the reactor. The chemisorbed hydrogen was recorded by an integrator and the dispersion of palladium on the surface of support was calculated from the hydrogen isotherm on a basis of a stoichiometry of one hydrogen molecule per two metal atom which is mentioned in Appendix (B).

5.5.2.2.3 X-Ray Fluorescence Spectroscopy (XRF)

The elemental compositions of prepared catalysts were analyzed by XRF Shimadzu EDX 700. The sample was transformed to a pellet by pressing at 200 kN m^{-2} and then placed on a sample holder before measurement.

5.5.2.3 Hydrodechlorination of Chloroform

The catalyst evaluation tests were performed in a fixed bed glass reactor connected through an on-line gas chromatography. The schematic of the instrument setting is presented in Figure 6-4. The reactor consisted of a 0.6 cm diameter and 20 cm length with a glass wool frit. The 20 mg of ground catalysts were placed in the glass reactor inside a tubular electric furnace, and equipped with a concentric thermocouple to measure the catalyst bed temperature. Prior to catalytic evaluation, each catalyst was reduced at 450 °C for 2 h under H$_2$ at a flow rate of 35 ml min^{-1}.

The 0.8 μl of CLF was injected manually by using a micro syringe. The calculated concentration of CLF was 5.71 mg $(L\,h)^{-1}$ (density of CLF 1.48 g mL^{-1}). The reaction was carried out in the temperature range of 100-200 °C. The reaction products were analyzed by using an on-line gas chromatograph (Shimadzu 14B) with a Gaskuropack column and the Thermal Conductivity Detector (TCD) was used to analyze the downstream gases. The GC conditions were set as shown in Table 6-3. Peak assignment was performed by the Chromatopac Shimadzu C-R6A. The blank test without Pd catalysts was conducted in similar manner and the calibration curve was produced for quantitative analysis. In the exit stream, hydrogen chloride, a by-product of the reaction, can be easily neutralized with the basic solution such as sodium hydroxide.

Table 6-3 Gas chromatography conditions for hydrodechlorination of CLF.

GC parameters	Conditions
Initial temp of column	80 °C
Final temp of column	200 °C
Injection temp	100 °C
Detector temp	200 °C
Initial time	3 min
Final time	13 min
Program rate	5 °C min^{-1}
Column	Gaskuropack54 (4m, 3.2mm I.D.)
Carrier gas	hydrogen
Flow rate of carrier gas	35 mL min^{-1}

Data analyser

Vent

Injection port

Temperature controller

TCD

Furnace

Reactor

Gas Chromatograph

H₂

N₂

Six port valves

Temperature controller

Vent
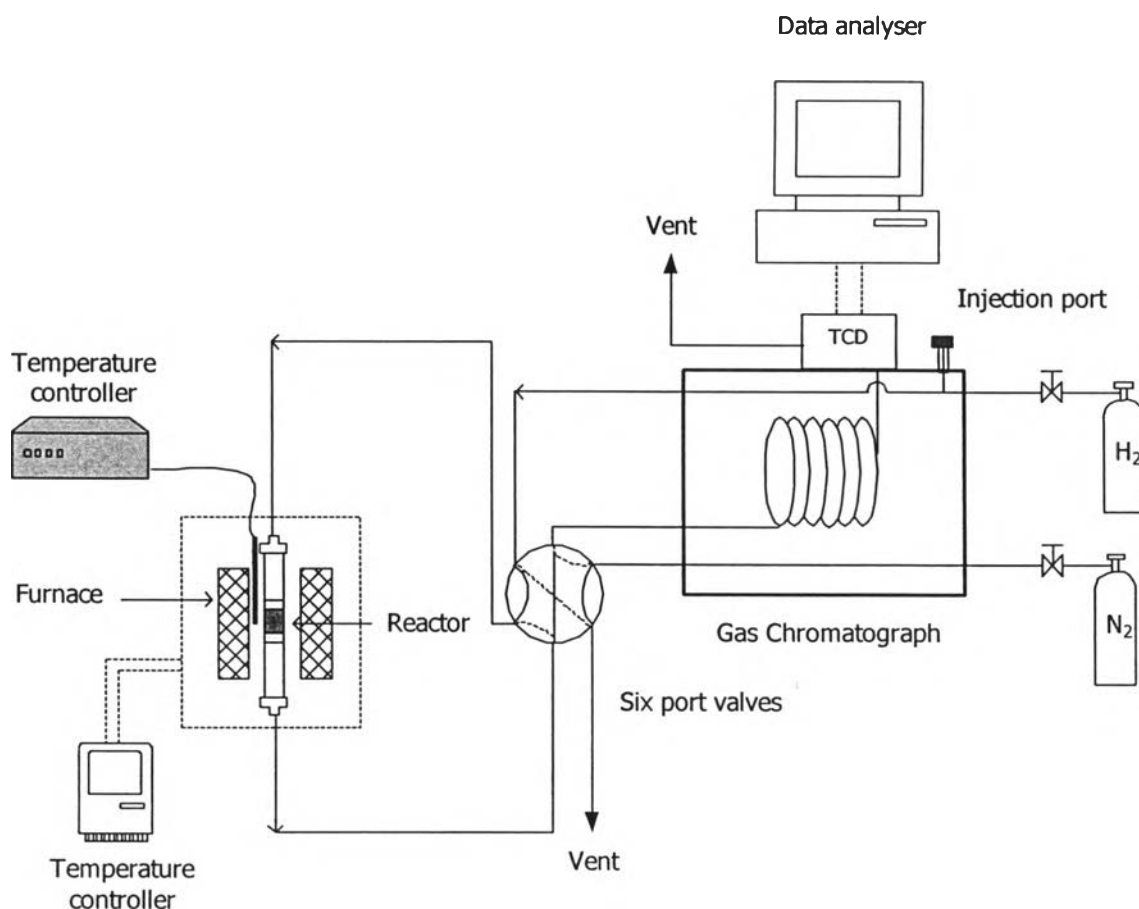
Figure 6-4 Schematic of hydrodechlorination test.

6.5.3 Results and Discussion

6.5.3.1 Catalyst Characterizations

6.5.3.1.1 XRD Results

The low-angle XRD diffraction pattern for Pd/RH-MCM-41 is shown in Figure 6-5. The patterns of the silica matrix featured the 2θ of Bragg peaks at 2.6, 4.3, 4.9 and 6.5, which were recognized as the identical finger print of MCM-41. The characteristics of palladium appeared at high angle scanning observed at 42, 48 and 58 degree [Tanaka, 2002] as seen in Figure 6-6. The crystalline peaks due to metallic palladium (for example, Pd (111) and (200) around $2\theta = 42$ and 48, respectively) become sharper with an increase in the amount of catalyst loading. This high intensity

of the peak indicated the presence of agglomeration of non-dispersive palladium over the pore surface of the MCM, which was found to be consistent with the results from the XRF characterization mentioned next.
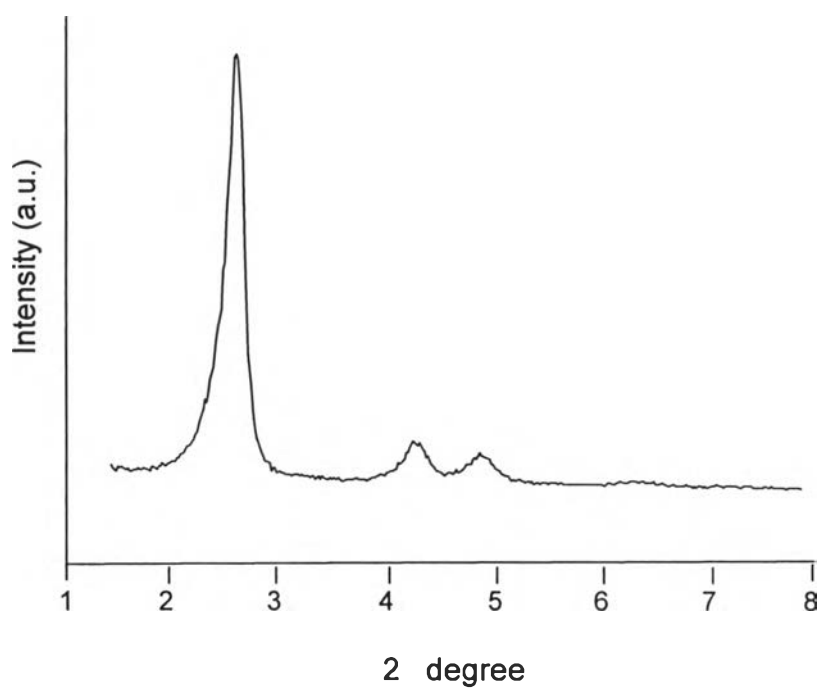
Figure 6-5 XRD pattern of Pd/RH-MCM-41 at low-angle region.
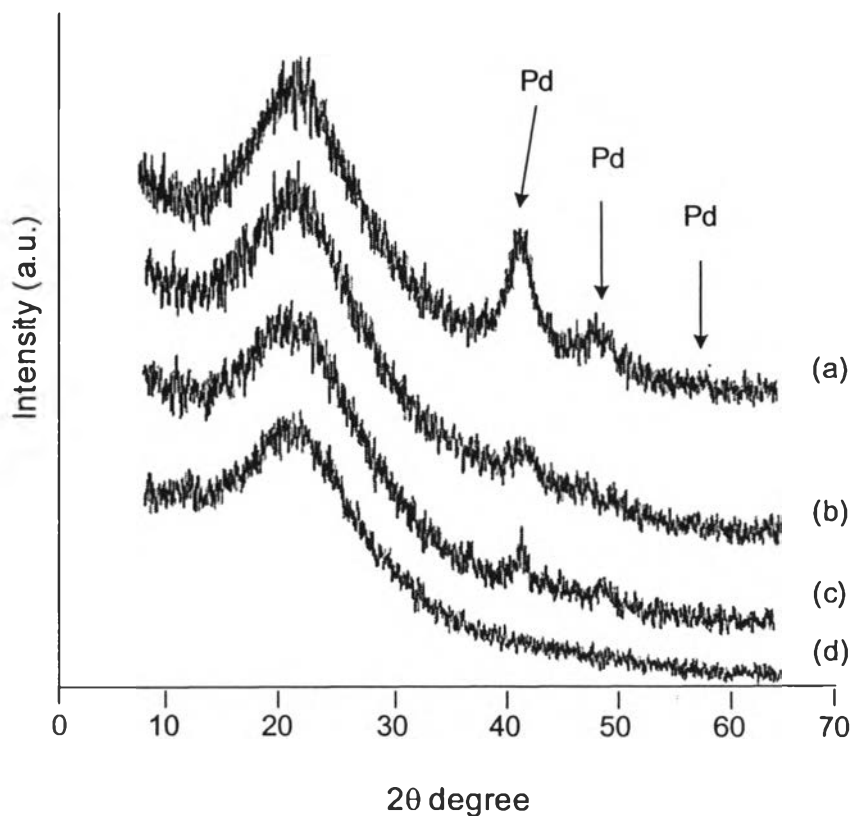
Figure 6-6 High-angle XRD results for various loading of Pd/RH-MCM-41; (a) 3 wt%, (b) 1.0 wt%, (c) 0.5 wt% and (d) 0 wt%.

6.5.3.1.2 XRF Results

Table 6-4 illustrates the composition of palladium and silica contained in the prepared samples. It was observed that the percentages of palladium measured by the XRF analysis seemed to be higher than the calculated amount. This could be explained by the tendency of moisture absorption which was due to the hydrophilicity of the RH-MCM-41 support during the preparation of the catalysts.

Table 6-4 Metal composition of the Pd/RH-MCM-41 catalysts at different loading, analyzed by XRF characterization.

Catalysts	SiO$_2$ wt%	Pd wt%
0.5wt%Pd/MCM41	98.901	0.471
1.0wt%Pd/ MCM41	97.237	1.099
3.0wt%Pd/ MCM41	96.339	2.763

6.5.3.1.3 Hydrogen Chemisorption Results

The percentage dispersions of palladium on the catalyst supports prepared by an incipient wetness method and their BET surface area are presented in Table 6-5. The Pd/RH-MCM-41 except 3.0 wt% loading provided better dispersions of palladium over the support than Pd/SiO$_2$ and Pd/SiO$_2$-Al$_2$O$_3$. This could be understandable due to the relationship of the surface area and the dispersion of the catalyst. A large surface area facilitates the diffusion of the precursor solution into the porous support, which is in agreement with the obtained results. The BET surface area of RH-MCM-41 supports was much higher than that found in silica and silica-alumina supports. However, in the case of high loading, the dispersion of palladium showed the reverse result. The influence of surface area was less significant than the preparation method used. All catalysts employed in this work were prepared by an incipient wetness, which has proved to be inefficient when high loading is required. This is because the solubility of the precursor is usually insufficient to achieve the required concentration.

Table 6-5 Dispersions of palladium over the silica, silica-alumina and RH-MCM-41 supports measured by hydrogen chemisorption at room temperature and their BET surface area.

Catalysts	BET surface area (m^2 g^{-1})	Dispersion (%)
0.5wt% Pd/SiO$_2$	310	17.0
0.5wt% Pd/SiO$_2$-Al$_2$O$_3$	400	21.4
0.5wt% Pd/RH-MCM-41	800[*]	47.6
1.0wt% Pd/RH-MCM-41	800[*]	43.9
3.0wt% Pd/RH-MCM-41	800[*]	23.4

Note: [*] the surface area for support RH-MCM-41 itself.

6.5.3.2 Conversions of CLF

A blank test was carried out by pulsing CLF through either a pack of quartz beads or RH-MCM-41 particles under the studied temperature range. An integrator detected only two peaks of input and output (after changing the polarity of the gas chromatograph). The amount of effluent presented the same as that of chemical injected. This implied that there was no reaction particular to hydrocarbon cracking taken place over those conditions and over the catalyst support, RH-MCM-41, itself. This result confirmed that cracking would not be favorable at the low temperature condition.

Catalyst metal of Pd was used as an active phase loaded onto RH-MCM-41 and two other kinds of general supports like SiO$_2$ and SiO$_2$-Al$_2$O$_3$. In this study, the loading of 0.5, 1.0 and 3.0 wt% Pd was tested. Tests were also carried out between 100-200 °C. Figure 6-7 presents the activity of CLF over the studied catalysts and temperature ranges. Consider the same loading of 0.5% of Pd, it was found that, for

all t emperature r anges, t he H DC o f C LF b y P d over S iO$_2$ a nd S iO$_2$-Al$_2$O$_3$ s upport provided lower activity than that over RH-MCM-41. At the low temperature of 100 °C, the conversions were of 15.6, 6.0, and 5.7% for Pd/RH-MCM-41, SiO$_2$-Al$_2$O$_3$, and SiO$_2$ respectively. However, for 200 °C, the activity by all of them presented higher to 83, 37, and 23% for Pd/RH-MCM-41, SiO$_2$ a nd SiO$_2$-Al$_2$O$_3$, respectively. The higher activity of Pd/RH-MCM-41 over others might be due to significantly large surface area of support, which provided surface for more dispersion of the metal. Evidence of that was shown in the dispersion result by the TPD of H$_2$. It was found that the dispersion of Pd over RH-MCM-41 was about 47.6%, while 17.0 and 21.4% for Pd/SiO$_2$, and Pd/ SiO$_2$-Al$_2$O$_3$, respectively as shown in Table 6-4. Obviously, good dispersion of catalysts contributed to the number of reactive sites over the surface that led to the high conversion of the products.

Moreover, the conversion of CLF increased with increasing reaction temperatures, exhibited as an S-curve. This was because hydrodechlorination is the exothermic reaction. Additionally, the S-curve indicated that the reaction rate over the porous RH-MCM-41 catalysts would be controlled by the slowest step in sequence of the reaction which was affected by the diffusion rate of the reactants into the mesopores.

Consider at the same support in different loading of Pd, The conversion was found i n t he o rder o f (3.0 % wt P d/RH-MCM-41) > (1.0 w t% P d/MCM-41) $\approx$ (5.0 wt% Pd/MCM-41). The 3.0 wt% loading provided approximately a 20-30% higher conversion compared to the others. It was demonstrated that higher loading gave higher conversion of products. However, all catalysts used in this experiment were prepared by using incipient wetness impregnation, which is found to be ineffective when high loading is required. For high temperatures typically (200 °C), activity of different loadings of Pd over RH-MCM-41 were not proved to be significantly different (81, 8 2, a nd 9 0% f or 0 .5, 1 .0, a nd 3 .0 % wt l oading, r espectively), w hich implied that an increase in reactivity of catalysts does not rely on the loading of the metal precursor.
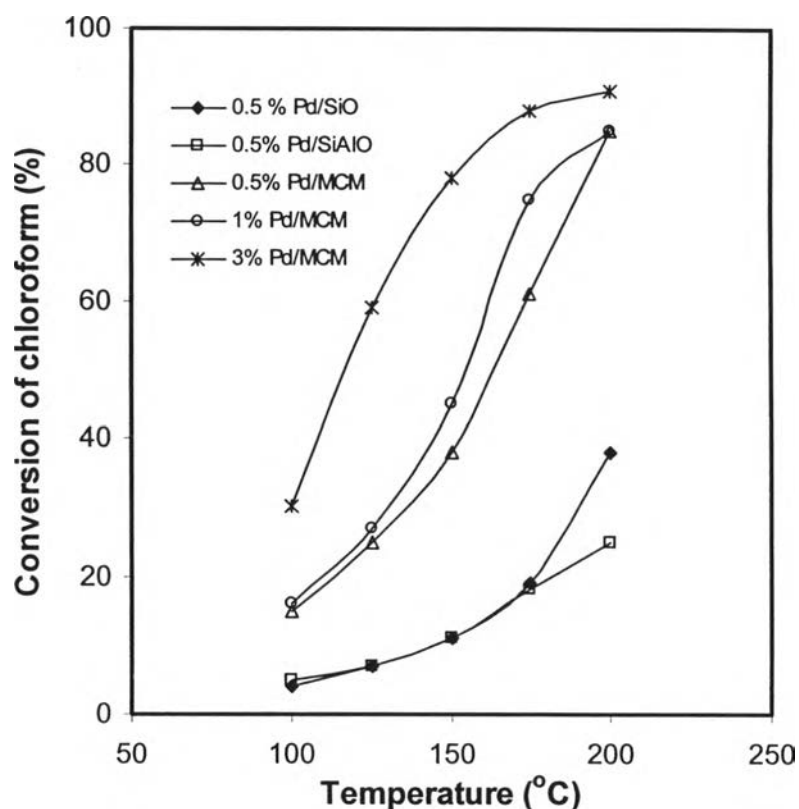
Figure 6-7 Conversions of CLF for the prepared catalysts: 0.5 wt%, 1.0 wt% and 3.0 wt% Pd/RH-MCM-41, 0.5 wt% Pd/SiO$_2$ and 0.5 wt% Pd/SiO$_2$-Al$_2$O$_3$ at various reaction temperatures.

6.5.3.3 Selectivity of CLF on Hydrodechlorination

While chloroform is dechlorinated, it could be substituted by either hydrogen or methyl radical to produce methane or ethane, respectively. Moreover, the dehydrogenation and polymerization would also take place over the acidic metal catalyst of Pd. Therefore, light hydrocarbons like methane, ethane, ethylene, propane, propylene, etc. could be produced along with the reaction of hydrodechlorination. Among those products, methane and ethane are desirable products. Other products produced from polymerization are undesirable products since they would cause

coking over the surface of catalyst. The selectivity to methane and ethane then is one of the considerable factors in selecting a suitable catalyst.

Figures 6-8 to 6-12 illustrate the product distributions obtained from the effluent of chloroform passing through 0.5wt% Pd/SiO_2, 0.5wt% Pd/SiO_2-Al_2O_3 and 0.5wt%, 1.0 wt% and 3.0 wt% Pd/RH-MCM-41, respectively. In all cases, a major product of the HDC of CLF was methane. Other hydrocarbon by-products of low molecular weight hydrocarbons ($C_2 - C_5$) were also found. Greater portions of C_2 and C_3 than C_4 and C_5 were detected. Besides, selectivity to methane declined, while by-products increased as temperature increased.
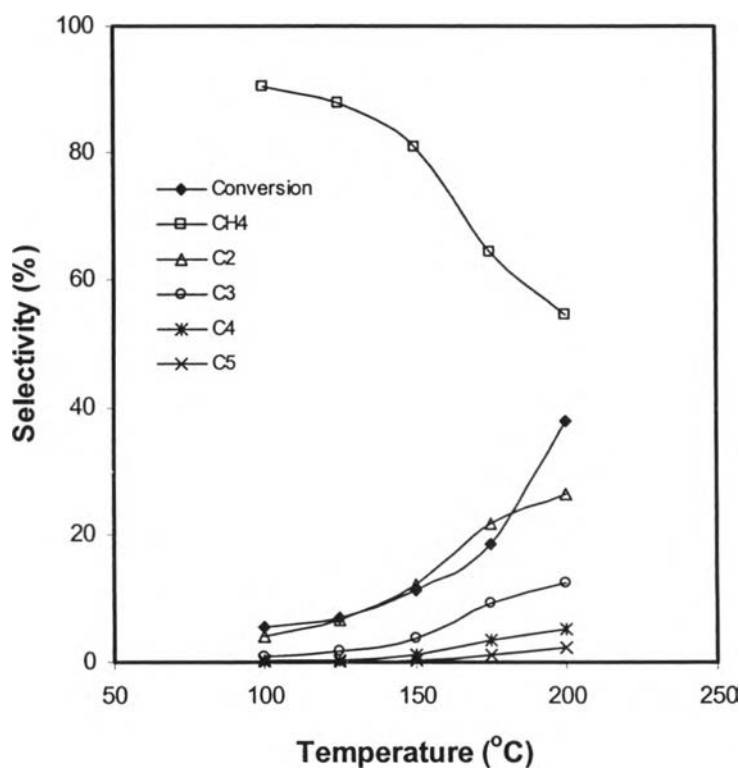
Figure 6-8 Conversion of CLF and hydrocarbon selectivity over a 0.5 wt% Pd/SiO_2 catalyst.
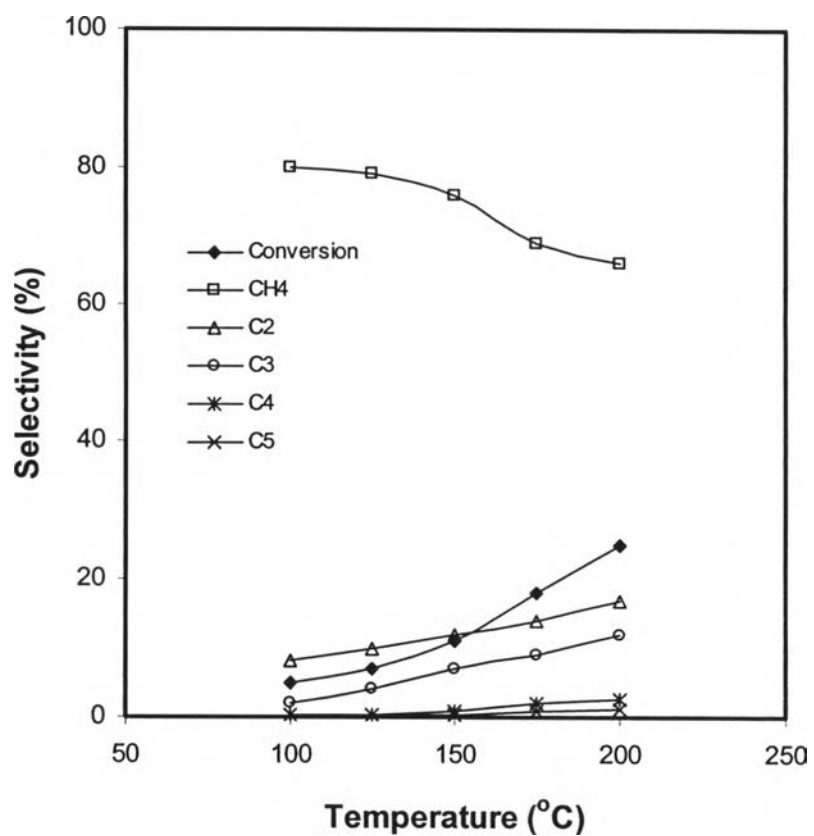
Figure 6-9 Conversion of CLF and hydrocarbon selectivity over a 0.5wt%Pd/SiO$_2$-Al$_2$O$_3$ catalyst.
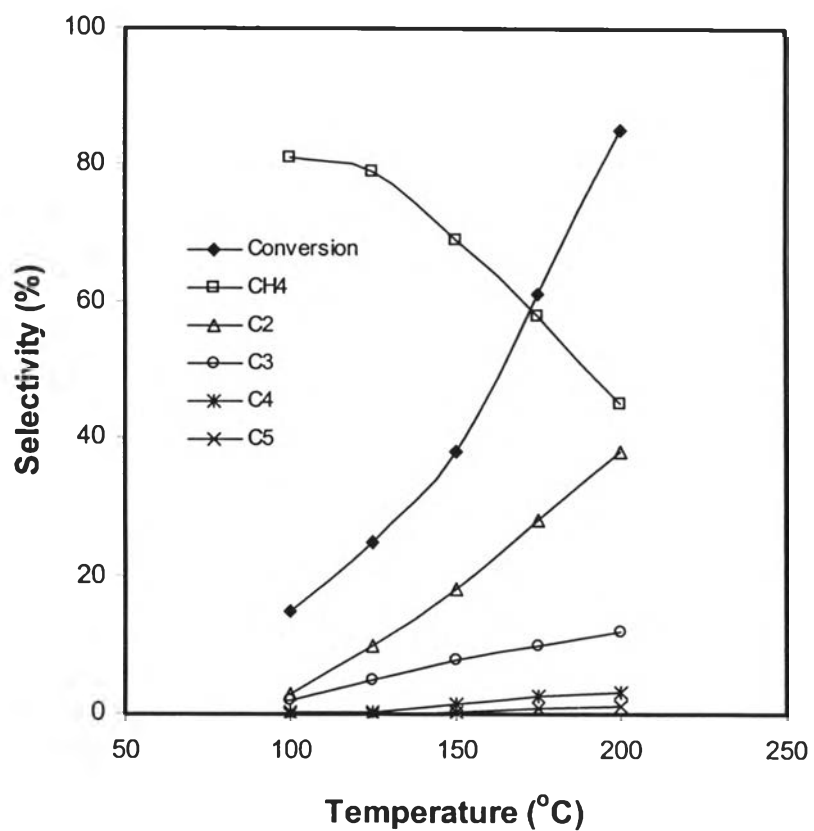
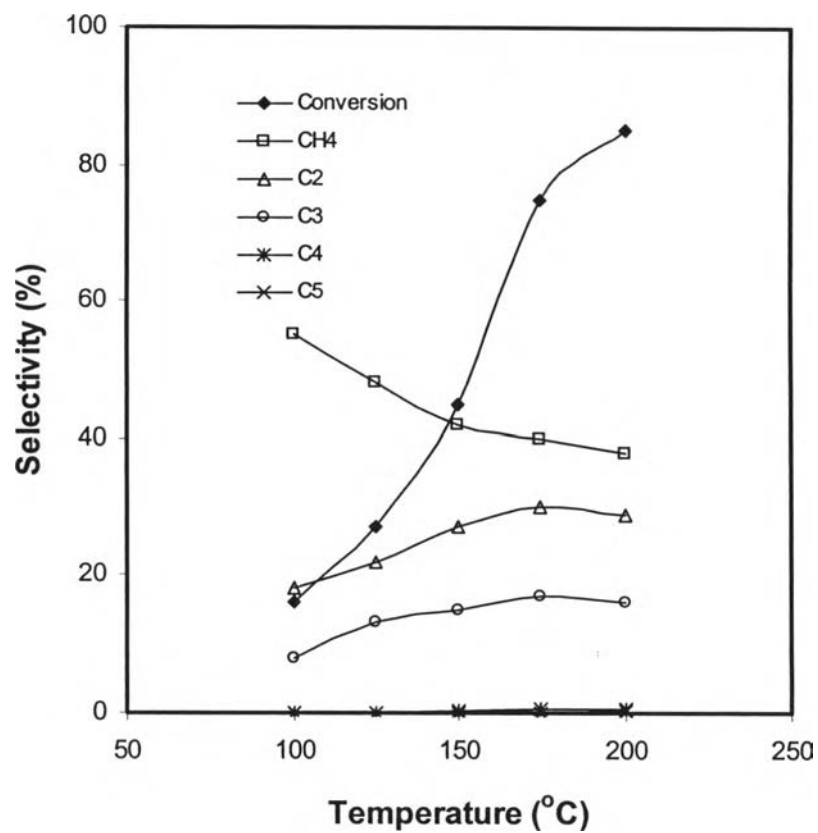**Figure 6-10** Conversion of CLF and hydrocarbon selectivity over a 0.5wt% Pd/RH-MCM-41 catalyst.

Figure 6-11 Conversion of CLF and hydrocarbon selectivity over a 1.0wt% Pd/RH-MCM-41 catalyst.
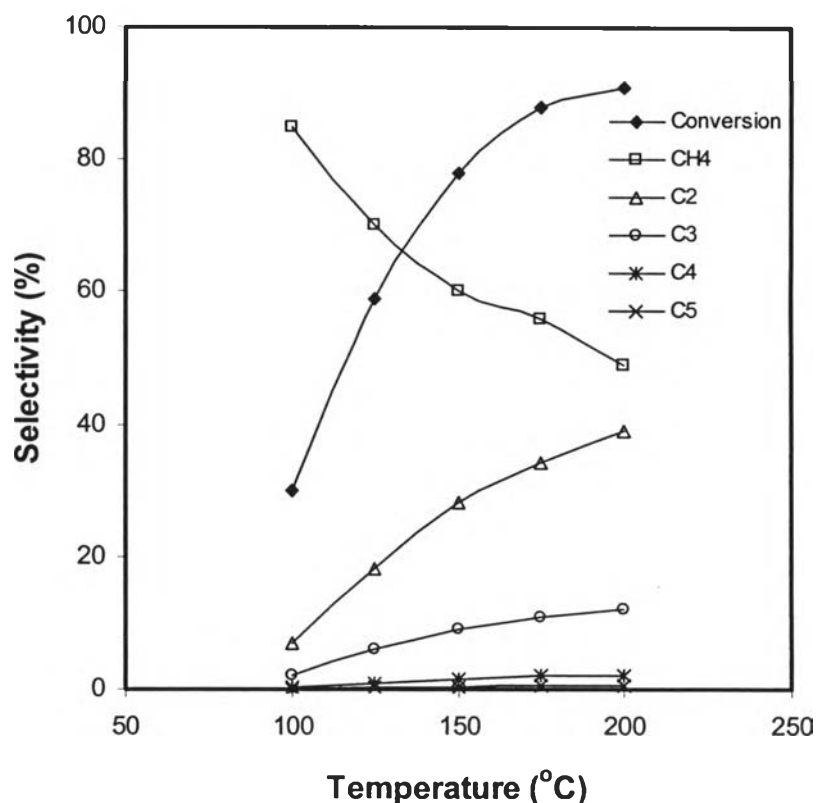
Figure 6-12 Conversion of CLF and hydrocarbon selectivity over a 3.0wt% Pd/RH-MCM-41 catalyst.

6.5.3.4 Anderson-Schulz-Flory Product Distributions and Deactivation

The life period of catalyst is an important parameter to consider before practical use. In general, the test of longevity has been carried out in a flow reactor for such a long period as well as activity and selectivity were recorded along time on stream. However, to compile with the time limitation, the Anderson-Schulz-Flory product distribution consideration was presented in order to estimate catalyst longevity. All reaction products can be indicated as carbon number. The plot of Shulz-Flory is done by log (Wn/n%) versus carbon number. Figures 6-13 to 6-15 illustrate the ASF plots of all studied temperatures (100-200 °C) for 0.5wt% Pd/SiO$_2$, 0.5wt% Pd/SiO$_2$-Al$_2$O$_3$, and 0.5wt% Pd/RH-MCM-41, respectively.

All figures presented similar trends of product formations. At low temperatures (100-125 °C), C_6 and C_7 are not found in the effluent. It was found that the slope became less as the temperature increased. The well-defined product dispersion patterns indicated that higher carbons were formed through the polymerization of surface C_1 species similar to the Fischer-Tropsch reaction. Merely carbonaceous products of C_1 to C_7 were generated from side reactions. When the temperature increased, higher molecular weight species such as C_6 and C_7 could be observed.
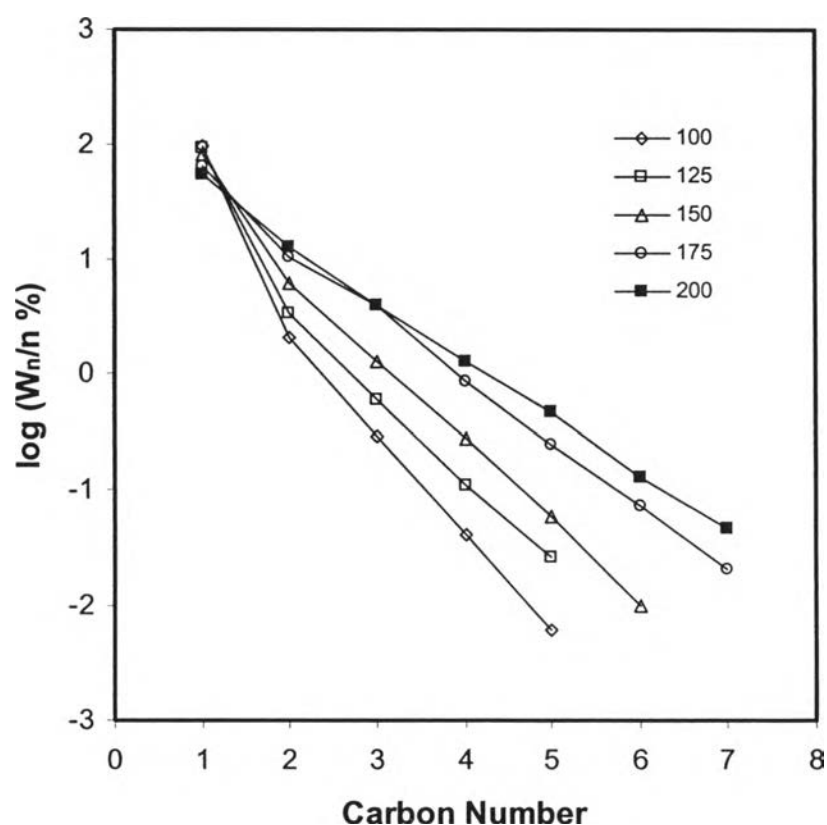
Figure 6-13 Schulz-Flory plots for hydrocarbons formed in the hydrodechlorination of CLF over a 0.5 wt% Pd/SiO$_2$ catalyst.
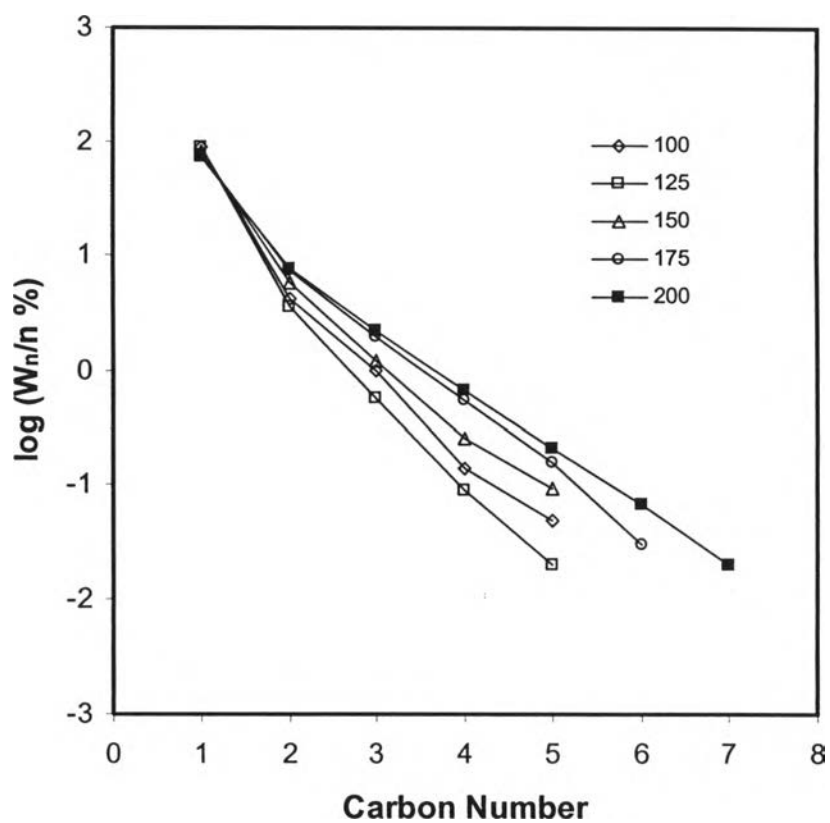
Figure 6-14 Schulz-Flory plots for hydrocarbons formed in the hydrodechlorination of CLF over a 0.5 wt% Pd/SiO$_2$-Al$_2$O$_3$ catalyst.
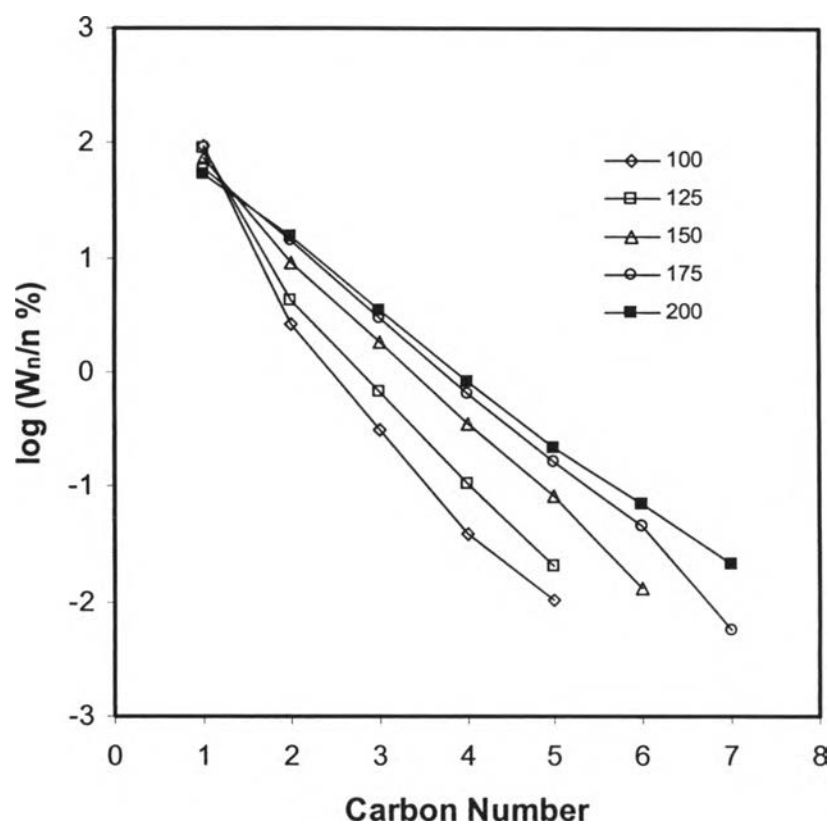
Figure 6-15 Schulz-Flory plots for hydrocarbons formed in the hydrodechlorination of CLF over a 0.5 wt% Pd/RH-MCM-41catalyst.
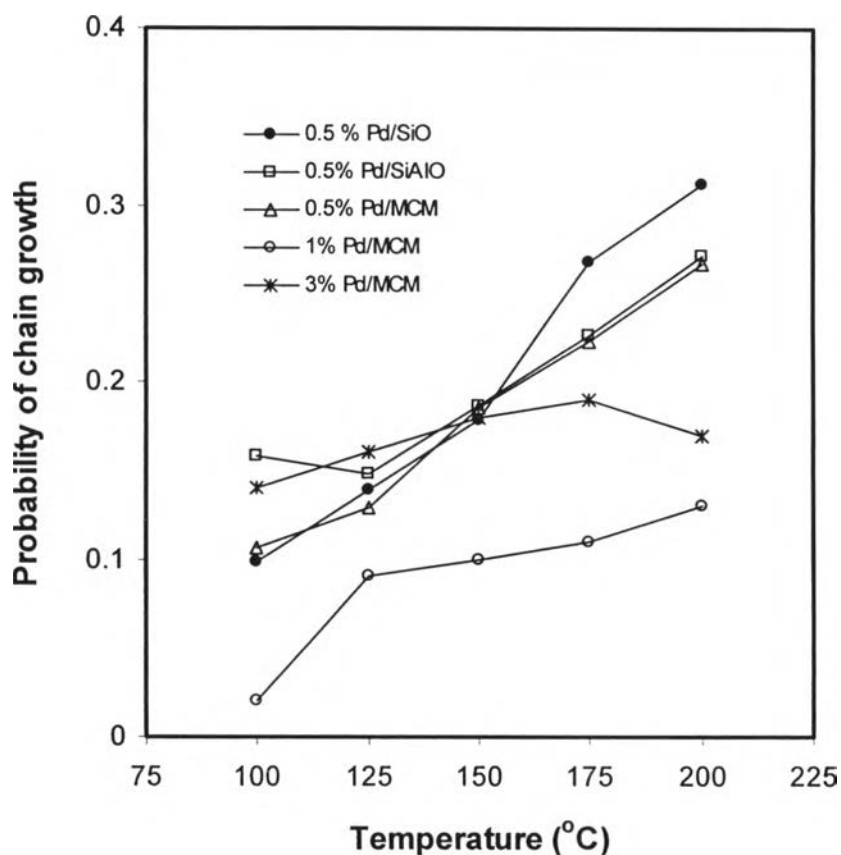
Figure 6-16 Probability of the chain-growth of hydrocarbons produced from the hydrodechlorination of CLF.

During high temperature catalytic reactions and in the presence of palladium, the reactive palladium sites contribute to the chemisorption of methane molecules or – CH_x species, and then the active carbon bonds may gradually polymerize to form various kinds of high molecular-weight carbonaceous materials, following the reaction below:

$$n(-CH_2-) \longrightarrow n(-CH_x) + H_2 \text{ (excess)} \longrightarrow (CH_x)_n \quad \ldots\ldots\ldots(6\text{-}8)$$

The reaction continues until the catalyst is deactivated. The deposits of high molecular weight hydrocarbons on the surface brought about a decline in the reactivity, caused by the coking phenomena. The cokes caused the reverse effect of the blockage inside the pores and a reduction in the active surface area.

The probability of chain growth was calculated from the slope of each line. Figure 6-16 shows the probability of chain growth (α) for the hydrodechlorination of CLF over the prepared catalysts at the reaction temperatures of 100, 125, 150, 175 and 200 °C. An increase in the reaction temperature as well as the reactivity resulted in the higher probability of chain growth. This indicated that the formation of cokes depended on a change in temperature. To reduce the coking effect, the low-temperature reaction is recommended but a lower product conversion should be taken in to account. Different from other catalysts, the RH-MCM-41 supported catalysts showed a slightly lower probability of chain growth. However, the graphs did not clarify the relationship between the metal loading and the metal dispersion on the α value. From the experimental data, only the 1.0 wt% Pd/RH-MCM-41 performed at a much lower α value than the others. This could be inferred to the longevity of the catalysts over the HDC reaction. In other words, the life-time of the 1.0 wt% Pd/RH-MCM-41 used in the HDC of CLF might be longer compared to the others. The reaction continued proceeding as long as the formation of cokes interrupted the reactivity of the catalysts, and deactivation occurred.

5.5.3.4 Proposed Mechanism for Hydrodechlorination of CLF

The proposed mechanism of the hydrodechlorination of chloroform in the presence of a Pd catalyst is demonstrated in Figure 6-17. The adsorption of hydrogen molecules takes place at the active sites of palladium over the RH-MCM-41 support. The palladium, acting as Brønsted acid, causes breaking of bond in the hydrogen molecules, forming individual hydrogen atoms. In the presence of activation energy, the chlorine atoms of $CHCl_3$ molecules could be replaced step by step with the hydrogen atoms yielding the product of carbon compounds as described above. The deactivation in the hydrodechlorination reaction could occur by means of coking. The carbons compounds with high molecular weight could be formed in the process of polymerization of some unsaturated derivatives such as those presented in the **5.4.3.1** reaction (8). These compounds lead to the blockage of pores and the reduction of active surface.
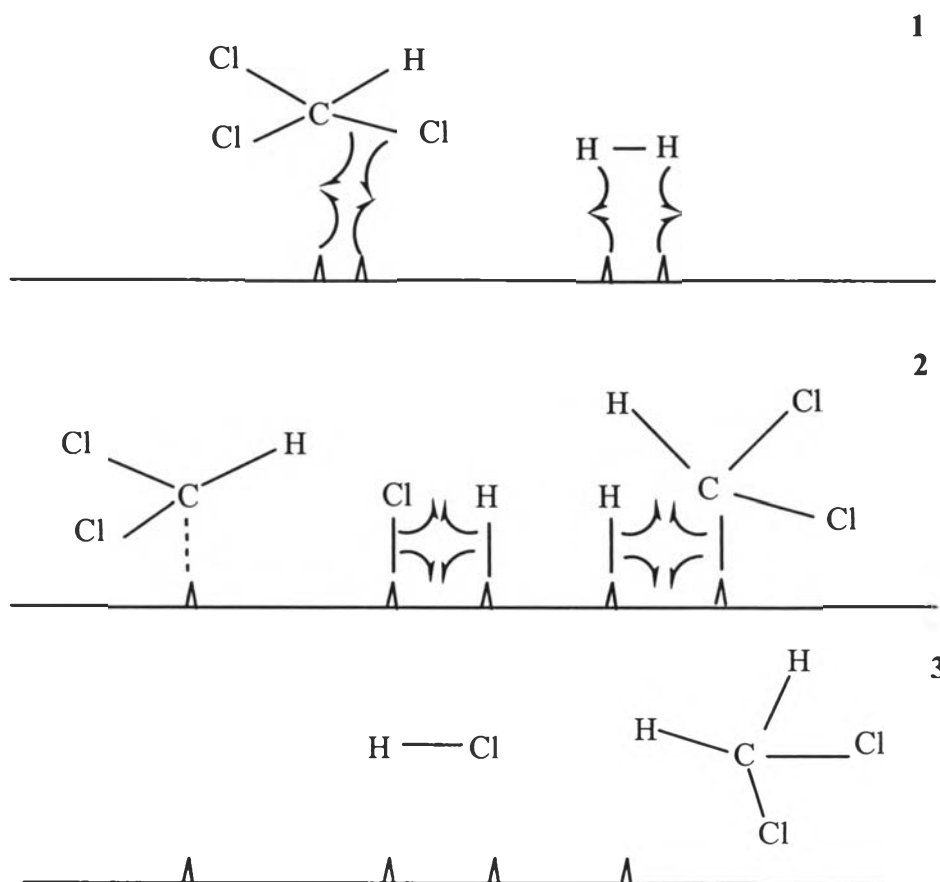
Continue mechanism with the similar manner

Figure 6-17 Proposed mechanism of the hydrodechlorination for chloroform ($CHCl_3$) over Pd/RH-MCM-41 surface.

6.6 Summary

Catalytic hydrodechlorination is an effective treatment in the abatement of CLF by transformation of CLF to methane, a major product of the reaction, and some environmental friendly hydrocarbons. The capability of catalysts on product conversion and selectivity depends considerably on reaction temperature, the amount of metal loading, dispersion of palladium and the catalyst support materials. High reaction temperature, high metal loading and good metal dispersion give a raise of product conversion. In comparison with commercial silicas, the catalytic activity was in the order of Pd/RH-MCM-41 > Pd/SiO$_2$ ≈ Pd/SiO$_2$-Al$_2$O$_3$. The optimal temperature

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for favorable activities of Pd/RH-MCM-41 was around 150-200 °C, where the conversion of CLF was enhanced up to 80-90 % higher than that exhibited by a Pd supported on the others. Accordingly, the RH-MCM-41 material is suggested to be the best support for palladium embedment used for the hydrodechlorination of CLF. This is relevant to its excellent properties of a high surface area associated with its uniform pore size. The product distributions determined by the ASF demonstrated the temperature dependence of the formation of oligomers (C_2-C_7) performed by polymerization. An increase in the reaction temperature resulted in the higher probability of chain growth or less product selectivity. Among all catalysts, the 1.0 wt% Pd/RH-MCM-41 exhibited the lowest tendency of coking and longer lifetime than the others for the hydrodechlorination of CLF.