

CHAPTER I

INTRODUCTION

1.1 Statement of Problems

In the petrochemical industry, light olefins have been steadily increasing in demand. From a petrochemical consideration, ethylene and propylene are desired olefin products that were produced from various processes¹ such as catalytic cracking, dehydrogenation, methanol to olefin (MTO) and metathesis. Metathesis or disproportionation is the useful process to produce olefins since 1960s. Figure 1.1 shows the growth of ethylene and propylene demand. It indicated that from 1990-2004, propylene demand becomes greater than ethylene. In addition, the growth rate of propylene production is forecasted to surpass ethylene production in 2005. More than 80% of the propylene is used in petrochemical application; polypropylene (PP) consumes more than 50% of this usage. Predicted annual growth of PP is estimated at 5.1% over the next 15 years. The trend of propylene demand will drive up propylene prices, currently at a level of 0.80 times of ethylene prices.²

To maximize propylene production, olefin manufacturers have several possible options. Three possible solutions can be used to raise the propylene yield while maintaining ethylene output²:

- (1) Add a propane dehydrogenation unit

Propane dehydrogenation accounts for 2% of the total propylene production. This process operates at high temperatures and is thermodynamically limited reaction. The

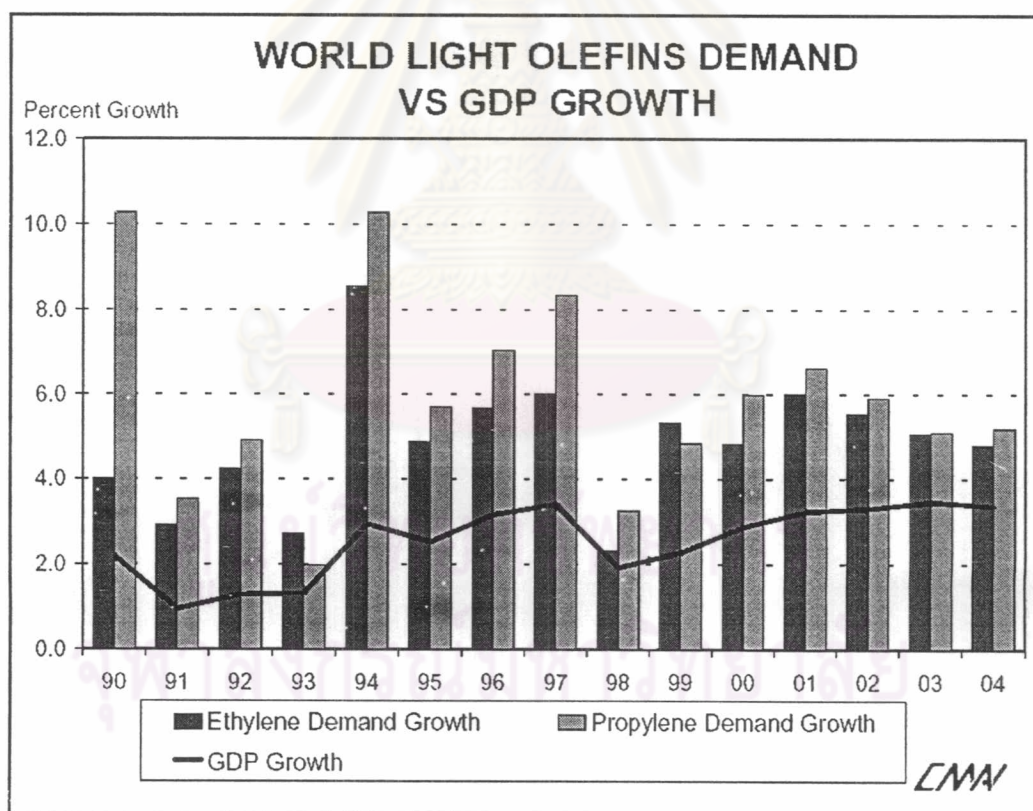
major problem of the process came from the fact that the separation of hydrogen, propylene and propane is difficult and the operation cost is high.

(2) Recover propylene from fluidizing catalytic cracking (FCC) unit

The lack of stream cracker propylene can be counterbalanced by recovering from refinery FCC unit. Although FCC propylene recovery process can be used, it required adding a super-fractionation column.

(3) Install an ethylene/butene metathesis unit

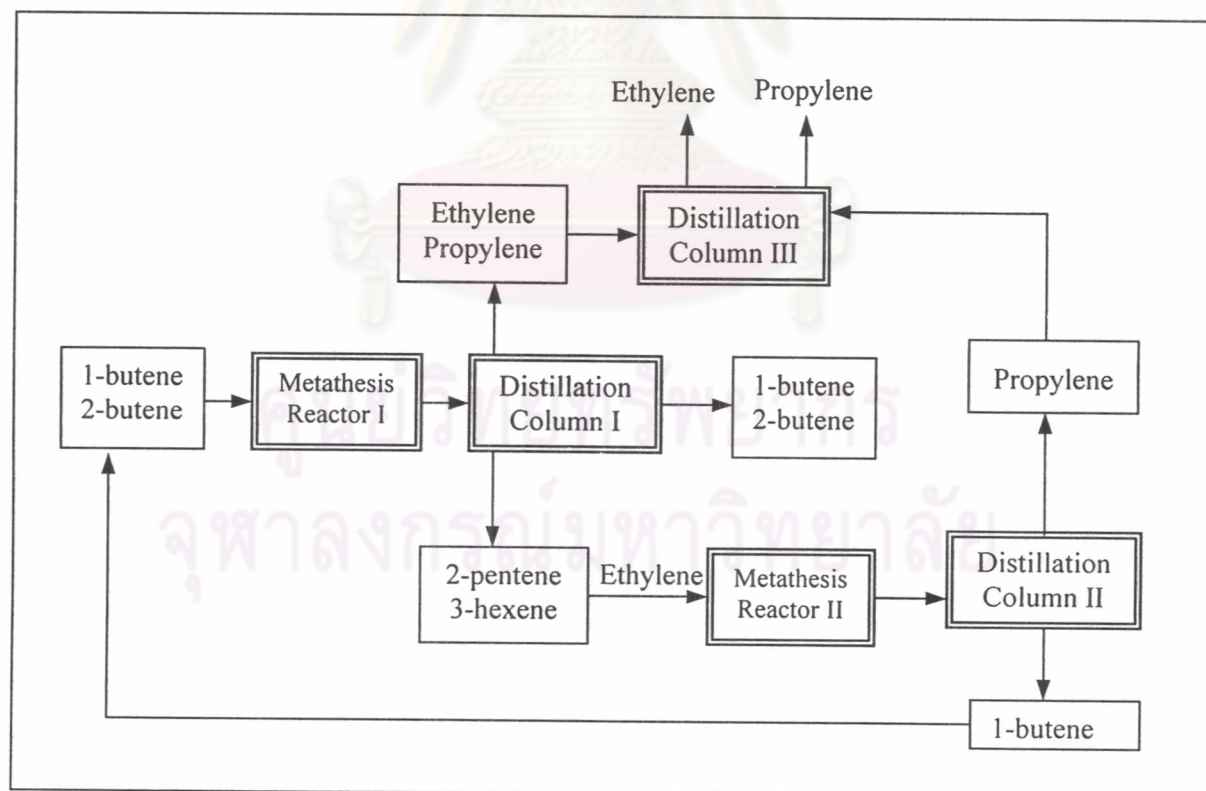
Metathesis reaction is an alternative route that can eliminate the raw C₄ cracker cuts and increase propylene production by cross-metathesis between ethylene and butene.



Source : CMAI NEWS, Febuary, 2000 (<http://www.cmaiglobal.com/news>)

Figure 1.1 World light olefin demand.

In fact, butenes from C_4 stream are mixed C_4 components comprising 1-butene, *cis/trans* 2-butene, isobutene, n-butane and also iso-butane.¹⁻³ It is found that impurities in feed butene play role on side reaction in the system. Recovery of by-products and turning to desirable olefins are the useful alternative way for industrial application. In the reaction system of propylene production *via* cross-metathesis between ethylene and butene, hexene and pentene were major by-products.³ Self-metathesis of 1-butene produced 3-hexene and ethylene while cross-metathesis of 1-butene and 2-butene produced 2-pentene and propylene. However, the by-products can be separated by distillation prior to cross-metathesis with ethylene again. For example, Schwab *et al.*⁴ revealed the process for recovery of 3-hexene and 2-pentene, yielding propylene and 1-butene as a result by cross-metathesis with ethylene as shown in Scheme 1.1. It also indicates that only butenes can be used for metathesis for producing light olefins.



Scheme 1.1 Schematic production of olefin with pentene and hexene recovery starting from butenes.⁴

Supported tungsten and also rhenium or molybdenum are well known as active catalysts for alkene metathesis⁵. Although the rhenium-based catalyst operated at low temperature that had higher cycle-length, the cost of Re-based catalyst was extremely high, and it requires higher regeneration temperature than that for tungsten-based catalyst. Metathesis reaction also did not work when rhenium content was low.^{2,6}

The preparation of metathesis catalysts can be easily achieved by impregnation method, metal active species were dispersed on the surface of supporting material. In addition, properties of supporting materials, such as surface area and acidity, play a significant role on the activity of a catalyst. Nowadays, discovery of new supporting material gain attention of catalysis application. Utilization of microporous zeolite or other mesoporous materials is the alternative way for replacing low surface-area amorphous supports. Thus, in this work, catalytic activities of tungsten-based catalyst on various supports are studied for metathesis reaction in order to produce light olefins. Both modern and conventional supports are to be studied. HMS and Al-HMS are the most interesting candidates due to their high surface area of 600 m²/g or more while that of ZSM-5 is about 400 m²/g and conventional amorphous support, alumina and silica-alumina, have the least value of surface area.

1.2 Objectives

- (1) To synthesize and characterize various supported tungsten catalysts for metathesis of 1-hexene.
- (2) To investigate the effect of support by comparison in their activities.
- (3) To study the effect of temperature and tungsten loading.

1.3 Literature Reviews

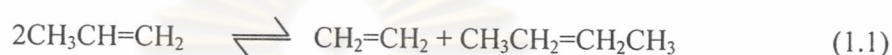
1.3.1 Development of Metathesis Process for Industrial Applications

There are various commercial applications of olefin metathesis⁷ : (i) the production of polymerization-grade propylene *via* cross-metathesis between ethylene and 2-butene. In fact, the reverse process is the first industrial application of olefin metathesis. The metathesis of propene produces high-purity ethylene and 2-butene, called the Philips Triolefin Process, which was in operation in 1966; (ii) the production of neohexene, an important intermediate in the manufacture of synthetic musks *via* cross-metathesis of diisobutene and ethylene. It is the useful one in application of metathesis in fine chemistry; (iii) the Shell Higher Olefins Process (SHOP), a large scale industrial process incorporating olefin metathesis for converting ethylene to detergent-range olefins; (iv) the production of several kinds of polymers produced *via* metathesis of cyclic olefins, such as cyclooctene, norbornene and dicyclopentadiene. In addition, the synthetic application for the metathesis reaction also concerned the metathesis of acyclic olefins containing heteroatom functional groups. This would allow single-step synthesis of various mono- and bifunctional derivatives of hydrocarbon with well-defined structure. Some of applications of metathesis are reviewed below.

(a) Production of Ethylene and Butene

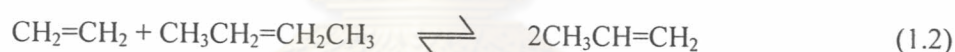
Schneider and Frölich firstly discovered the olefin metathesis reaction in 1931 when they observed that ethylene and butene were formed during pyrolysis of propylene.⁸ Thirty year later, Banks and Bailey discovered that this reaction could be catalyzed by molybdenum oxide supported on alumina.⁹ In the 1960s, Philips Petroleum³ performed the Triolefin process using propylene as a reactant to produce ethylene and butene as

shown in Equation (1.1). During 1966 and 1972 an industrial plant with a capacity of 30,000 tons butene per year was operated by Shawinigan in Canada. The reaction was catalyzed using $\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$ catalysts, using the consideration of the reaction temperature of 120-210°C at the pressure of 25-30 bars. This condition yield 40% conversion of propylene. This process can use WO_3/SiO_2 as well but high operating temperature of 500°C was required and propylene conversion was approximately 42%.



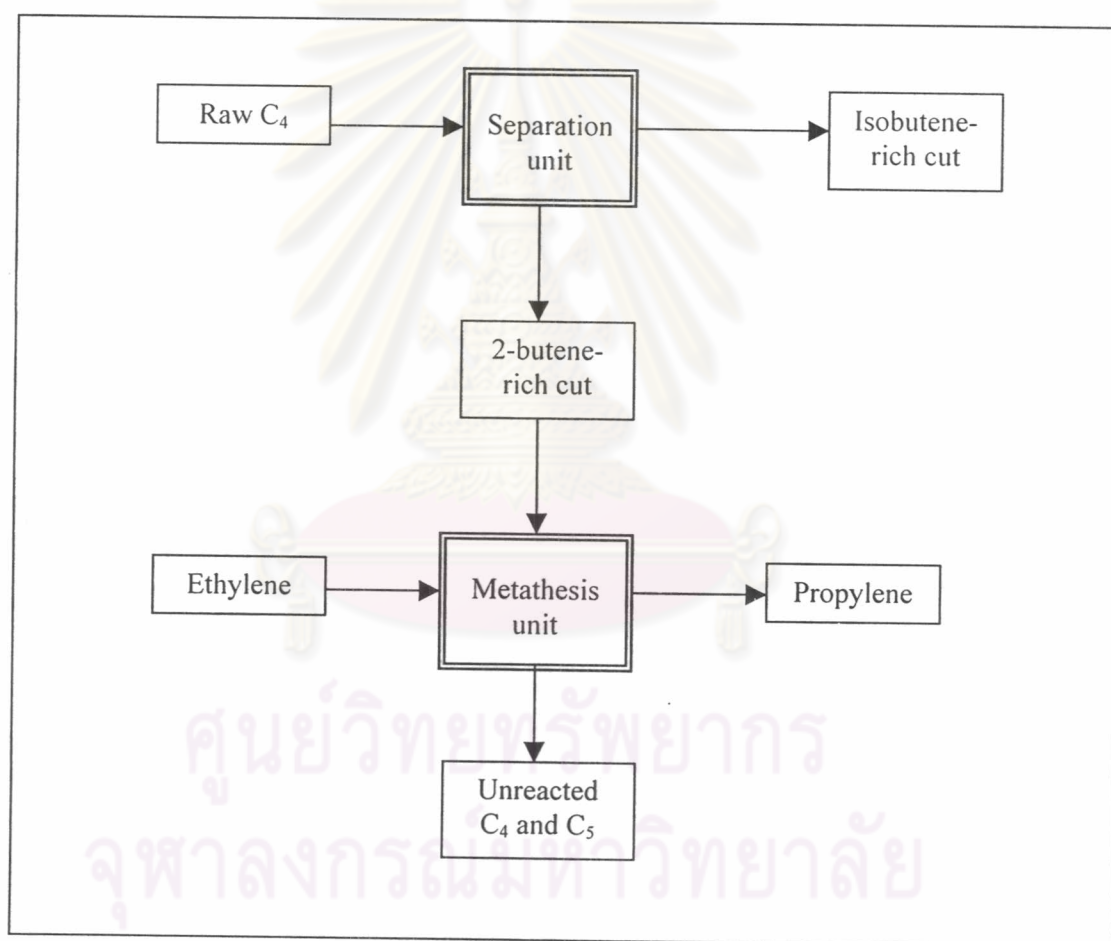
(b) Production of Propylene

When the propylene global demands rapidly grow, reverse direction process of the Triolefin process is more attractive as shown in Equation (1.2).



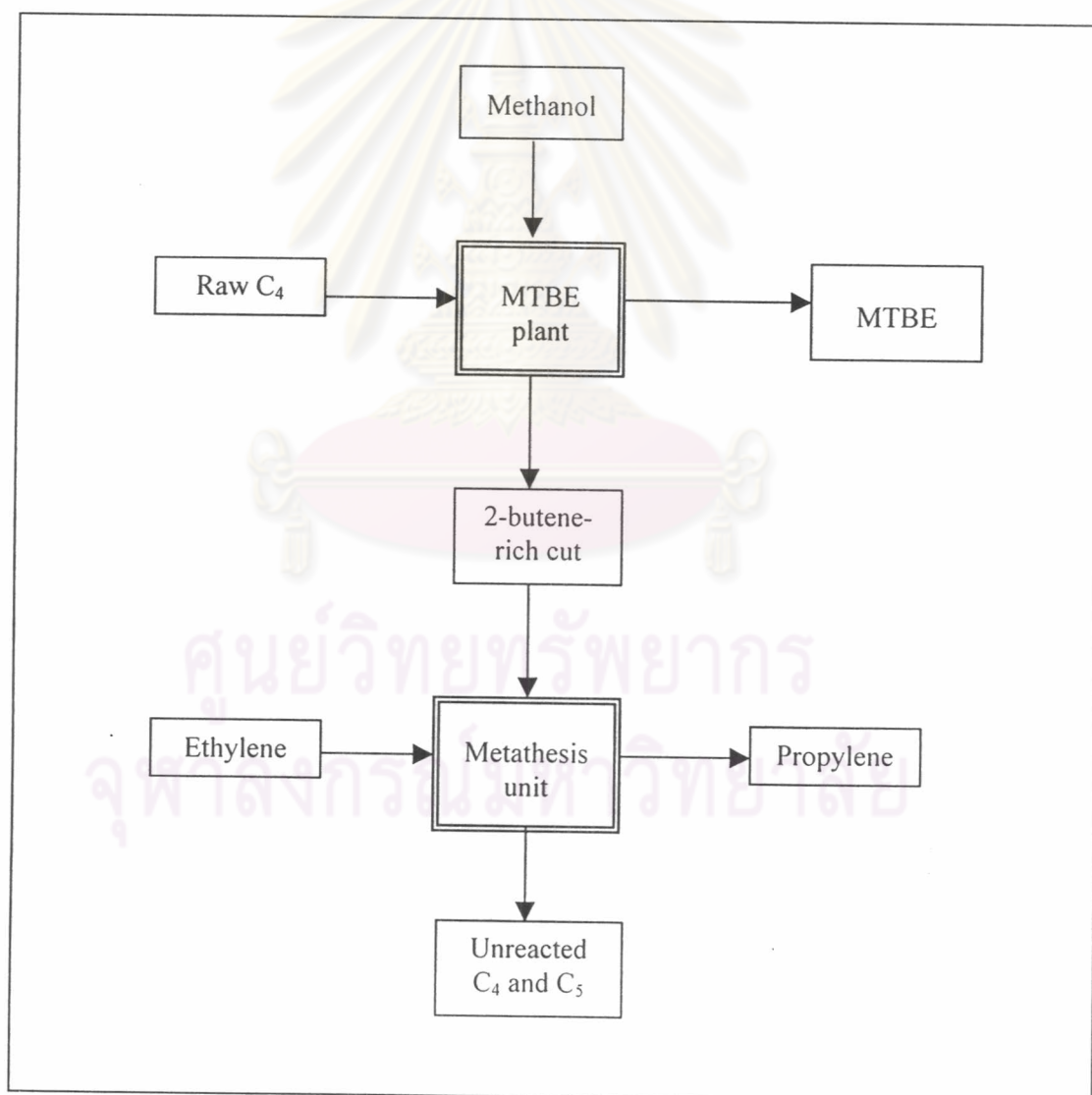
In 1985, Lyndell Petrochemical, Texas (USA), operated a propylene production plant with a capacity of 136,000 tons per year using only ethylene as reactant.^{1,3,10} Ethylene was initially dimerized to 2-butene, then 2-butene was reacted with additional ethylene in metathesis step to produce propylene. Thus, the development of catalyst in metathesis reaction attracted researchers until British Petroleum (BP) discovered a rhenium catalyst, in form of rhenium oxide supported on alumina ($\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$), which was active for low temperature metathesis. In fact, this reaction was operated either at high temperature or the gas phase (150-350°C) with molybdenum or tungsten supported catalyst or at low temperature (50°C) with rhenium-based catalyst working in gas or liquid phase.

The manufacture of polymerization-grade propylene from ethylene and 2-butene in continuous process called Meta-4 was developed jointly by Institut Français du Pétroleum (IFP) and the Chinese Petroleum Corporation (CPC) in Taiwan.^{3,10} Ethylene and 2-butene reacted with each other in the liquid phase in the presence of a $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ at the temperature of 35°C and the pressure of 20 bar. Scheme 1.2 shows the enhancement of propylene production using metathesis unit in the Meta-4 process.



Scheme 1.2 Propylene production using ethylene/butene metathesis unit in the Meta-4 process.³

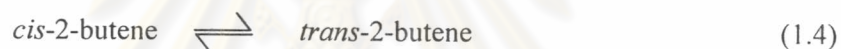
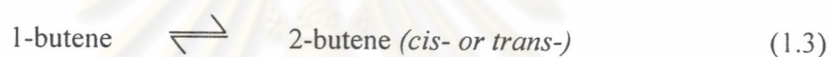
Iso-butene was separated from raw mixed C₄ feed at separation unit. Then 2-butene-rich cut was reacted with ethylene at metathesis unit to produce propylene. If iso-butene was present, it can be reacted with ethylene generating propylene and 2-methyl-2-butene. This side reaction should be minimized because polymerization of 2-methyl-2-butene could take place.² However, isobutene is the important reactant in MTBE (methyl *tert*-butyl ether) production so the Meta-4 process is advantageously combined with MTBE plants. After raw C₄ reacted with methanol, 2-butene feed was served to metathesis unit as shown in Scheme 1.3.



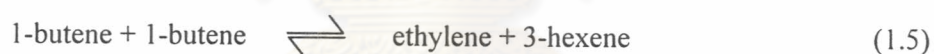
Scheme 1.3 Combining of MTBE production with the Meta-4 process.³

Although, cross-metathesis of butene and ethylene can be applied to produce propylene in the reaction system, side reaction of reactants can take place.^{2,11} For example, isomerization of 1-butene yields isomerization product like 2-butene in form of *cis*- and *trans*-2-butene, self-metathesis of 1-butene yields ethylene and 3-hexene. Further more, when 2-butene reacts with 1-butene, 2-pentene usually occurs as by-product in the system as shown in equation 1.3-1.6 respectively. It showed that under normal operation, pentene and hexene were major by-products.

Isomerization of butene :



Self-metathesis of 1-butene :



Cross-metathesis of 1-butene and 2-butene



Stereoisomerization of 2-butene in Equation 1.4 and cross-metathesis of 1-butene and 2-butene in Equation 1.6 were studied over $\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ by Engelhardt *et al.*¹² It was found that the rate of isomerization was higher for *trans*-2-butene than *cis*-2-butene. It made selective formation of *trans*-2-pentene product when *trans*-2-butene underwent cross-metathesis with 1-butene.

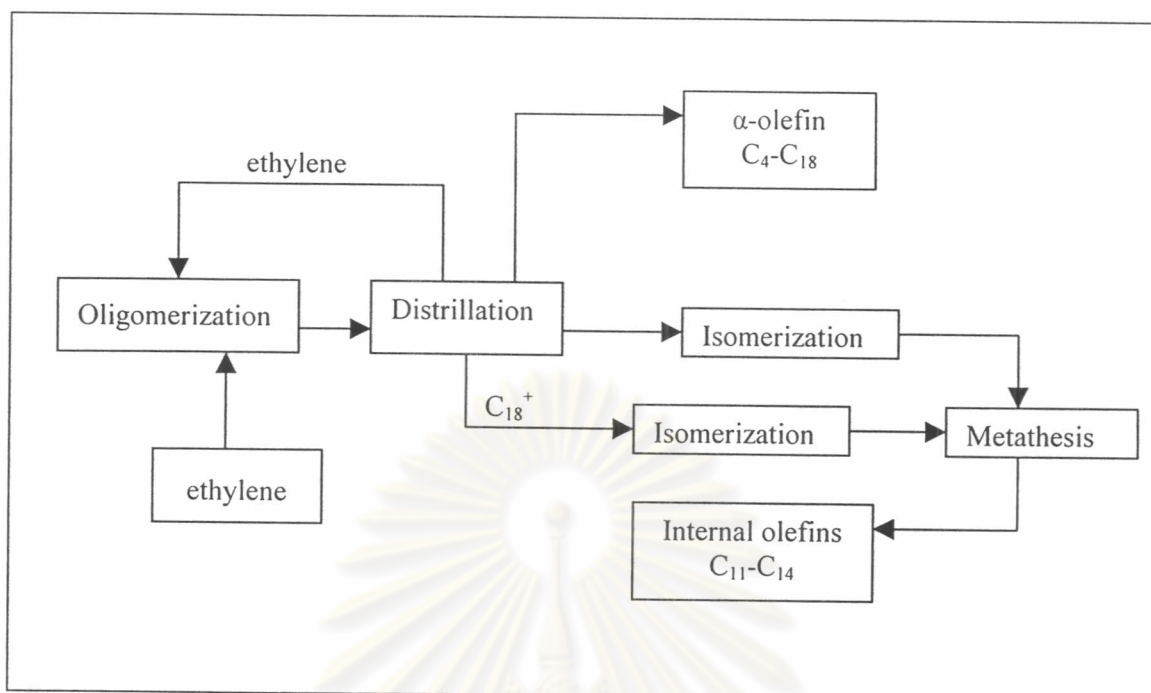
It can be concluded that propylene can be produced from metathesis of ethylene only^{1,3} and also generated from butene feed only.⁴ However, the large amount of butene and mixed C_4 in industrial and also difficulty to separate its component

economically by simple distillation due to their close boiling points. It makes relative low economical value of them. Thus, the metathesis reaction using butene is a challenge for light olefin production.

(c) **Production of α -Olefin and Detergent Range of Alkenes**

In 1977, a large-scale of 320,000 ton-per-year industrial plant incorporating olefin metathesis called the Shell Higher Olefins Process (SHOP)^{1,5} was firstly operated in USA for converting ethylene to produce detergent-range alkenes. It indicates that metathesis process can be applied for petrochemical process to meet changing of market requirement and also make flexibility in using of raw material.

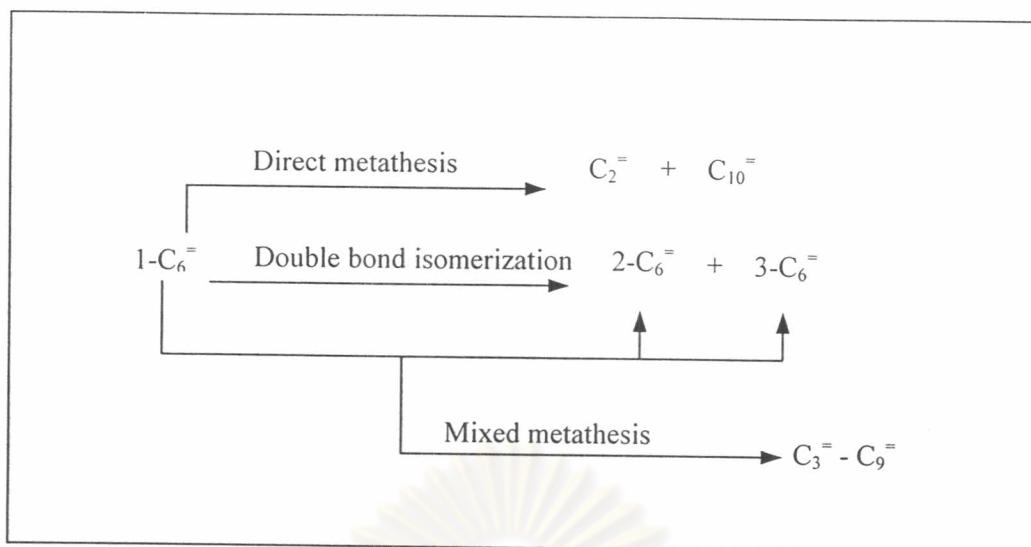
The first commercial catalytic process is a combination of ethylene oligomerization, isomerization and metathesis. In the first step, the ethylene oligomerization is catalyzed by a Ni complexes which is dissolved in 1,4-butanediol so the nonpolar α -olefin products being almost insoluble in this diol. This catalyst solution can easily separated form the insoluble product in a high-pressure separator. In a series of distillation towers, different α -olefin cuts are isolated. The desired alkenes are those with C_4 - C_{18} were separated and can be used for different purposes. In the second step, the remaining lower and heavier alkenes (the $C_{18}+$ fractions) were combined to isomerize to internal linear alkenes by a catalyst such as Na/K on Al_2O_3 or MgO in the liquid phase. In this step 90% of the α -olefin were converted to internal alkenes which are subsequently subject to the metathesis reaction in the third step. Metathesis of the lower and the higher internal alkenes gave a mixture of alkenes with odd and even carbon chain lengths. The mixture comprised about 11-15% of the desired C_{11} - C_{14} linear internal alkene (detergent – range) which were separated by distillation. The metathesis step took place at the temperature range from 100-125°C and the pressure of 10 bar on molybdate supported on Al_2O_3 .



Scheme 1.4 Shell Higher Olefins Process (SHOP).⁵

1.3.2 Metathesis of 1-alkene

To explore possibilities of the use of alkene metathesis in industrial processes, it is important to have information about the reactivity of various alkenes. In self-metathesis of 1-alkenes the reaction rate decreased with increasing carbon chain length and also less reactive than internal alkenes due to branching close to double-bond decrease the double reactivity from steric hindrance.¹³ However, 1-alkenes become internal alkenes *via* isomerization. For example, isomerization of 1-hexene usually occurred, yielding internal alkenes like 2-hexene and 3-hexene. Isomerization of 1-hexene took place in parallel with metathesis, it makes 2-hexene and 3-hexene participate actively in the total reaction of hexenes.¹⁴ Consequently, in addition to ethylene (C₂[°]) and decene (C₁₀[°]), olefin ranging from propylene (C₃[°]) to nonene (C₉[°]) were obtained as product *via* mixed metathesis, which can be illustrated by Scheme 1.5.



Scheme 1.5 Metathesis of 1-hexene in a presence of isomerization.¹⁴

Yihua *et al*¹⁴ reported metathesis of 1-hexene at 200°C under rhenium and molybdenum oxide catalysts supported on alumina. It was found that the molybdenum catalyst (MoO_3/Al_2O_3) was highly active for isomerization and the products were $C_3= - C_9=$ olefins, indicating that for the MoO_3/Al_2O_3 catalyst, the metathesis reaction took place mainly as mixed metathesis. In case of Re_2O_7/Al_2O_3 catalyst, it displayed a different behavior. The metathesis product from of 1-hexene was higher than using of MoO_3/Al_2O_3 as catalyst. However, MoO_3/Al_2O_3 can be improved in activity by adding small proportion of Re_2O_7 as a bicomponent catalyst. It can be concluded that in the metathesis reaction of 1-alkenes with isomerization, the metathesis pathway becomes more complicated and further reaction of reactive products in the system can take place.

For higher alkenes such as 1-octene and 1-decene, long-chain alkenes with symmetric internal position of the double bond can be produced *via* self-metathesis. The products are potentially useful intermediates in the manufacture of synthetic fatty acids and other special chemicals. Cross-metathesis of two higher alkenes with different chain lengths produces, besides their self-metathesis products, also long-chain asymmetric internal alkenes. It has been reported that products from cross-metathesis

between 1-octene and 1-decene or 5-decene product from self-metathesis of 1-hexene can be used for the production of synthetic lubricants.^{13,15}

1.3.3 Development of Metathesis Catalysts

The metathesis reaction is catalyzed both in heterogeneous and homogeneous phases. A wide variety of transition metal compounds can be applied for metathesis catalysts and the most successful are based on Re, W and Mo. Heterogeneous catalysts generally consist of a transition metal oxide or an organometallic complexes, deposited on an inorganic oxide support. In some cases, a promoter or cocatalyst like the non-transition metal compound was added to increase the activity of catalyst.¹⁰

Metal oxide catalysts for alkene metathesis are usually prepared on supporting materials because they were favorable for industrial in case of heterogeneous catalyst. There are many strategies to prepare the catalysts by dispersing metal species on a support and impregnation method is useful one. Generally, supports for preparing metathesis catalysts are amorphous materials; for example, silica, alumina and silica-alumina. Thus, use of crystalline porous material as a support is the alternative way because their high surface area and molecular sieve properties are advantages. From these reason, zeolite supports were gain interesting. For example, Hamdan *et al.*¹⁶ studied the activities of rhenium-impregnated zeolite Y in metathesis of 1-hexene in liquid phase and high selective to 5-decene. However zeolites are microporous materials, the application was limited by the narrow pore size.

Discovery of new supporting materials makes the potential to develop of metal supported catalyst for the metathesis reaction and other reactions. Mesoporous molecular sieve were material discovered and became an alternative way for use as supports due to their higher surface area and larger pore size than conventional supports. In 1992, scientists form Mobil Research and Deveolpment Cooperation discovered M41S¹⁷ silica

and aluminosilicate mesoporous molecular sieves. These materials are prepared hydrothermally in the presence of surfactant supramolecular templates. One of the members of the M41S family is referred to MCM-(Mobil Composition of Matter) 41 and exhibits a hexagonal array of cylindrical pores, whose diameter can be tailored within the range from 1.5-10 nm by changing the conditions of the synthesis procedure. After discovery of MCM-41, several researchers have been focused on the study of for hexagonal mesoporous material synthesis in different strategies. In 1993 Inagaki *et al.* reported the synthesis of mesoporous materials namely FSM-16 from a layered polysilicate (Folded Sheets Mesoporous Material)¹⁸. In 1994 Pinnavaia *et al.*¹⁹ were successful in synthesis of new hexagonal mesoporous called HMS (Hexagonal Mesoporous Silica) by neutral templating route using primary amine as template. In 1998 Stucky *et al.*²⁰ reported about mesoporous with straight hexagonal structure called SBA-15 (Santa Barbara no.15) synthesized using triblock-copolymer as template. Nowadays the researches about mesoporous material stills go on because of their potential application in catalyst development.

Hexagonal Mesoporous Silica (HMS) is one of interest hexagonal mesoporous materials because it can be synthesized in neutral condition. Environmentally synthesis route also make HMS attended as good support material. Tanev and Pinnavaia²¹ proposed a neutral templating mechanism in which the preparation was carried out in the presence of neutral inorganic precursors and uncharged surfactant such as primary amines. In this case, hydrogen bonding interaction was a driving force for the cooperative organization of the organic inorganic-mesophase. Although HMS has a short-range order with smaller scattering domain sizes than MCM-41 of which wall thickness and textural mesoporosity was higher.²² HMS materials is very promising as catalyst and catalyst supports. The framework composition may be easily to be modified by incorporating heteroatoms such as titanium²², aluminium and others²³⁻²⁴ which induce desirable catalytic properties. Due to high surface area and significant thermal stability, HMS molecular sieves are suitable

as supports for catalytically active species. Onaka *et al*²⁵ reported that MoO₃ on pure silica HMS support showed higher catalytic activity than amorphous silica support in metathesis of 1-octene. It was indicated that surface area of supports play an important role on metathesis activity.

In addition, acidity of support also affects the activity of the metal supported catalyst in olefin metathesis. Aritani *et al*²⁶ reported the catalytic activity of MoO₃ catalyst on various amorphous supports in metathesis of propylene. It was found that when silica-alumina was used as support, the activity was higher than using silica or alumina alone. Schekler-Nahama *et al*⁶ studied the influence of Lewis acidity of rhenium oxide supported on alumina. It was found that the initiation of the metathesis was essentially governed by Lewis acidity with the increasing of rhenium loading due to the presence of an aluminium perrhenate on the surface. Moreover, Mol *et al.*¹⁰ found that the catalytic performance of Re₂O₇/Al₂O₃ in the range of lower rhenium loading (<10%wt Re₂O₇) can be greatly improved by the using of SiO₂-Al₂O₃ as a support. When SiO₂-Al₂O₃ was used as a support, in contrast to Re₂O₇/Al₂O₃, the catalytic activity was decreased with increasing rhenium content. At the high rhenium loading, rhenium was reacted with silanol group, resulting in inactive rhenium center, as it is known that Re₂O₇/SiO₂ has no activity in olefin metathesis.^{10,13} According to Homs *et al.*²⁸, the catalytic activity of WO₃/support in metathesis of propene was depending on type of supporting materials. WO₃/SiO₂ yielded higher total conversion and metathesis conversion than WO₃/Al₂O₃ did at the same condition.

From these results, properties of supports influence the activity of metal oxide catalysts. Different metal oxides have different catalytic behavior on different supports in the same reaction. For example, Re₂O₇/SiO₂ is inactive in metathesis of propylene while WO₃/SiO₂ and Re₂O₇/Al₂O₃ are active catalysts.