

# CHAPTER I

## INTRODUCTION

### 1.1 Statement of Problem

The development of olefin chemistry after World War II is closely related to the vigorous growth in petrochemistry. Light olefins, *i. e.* ethylene, propylene and butylene used as petrochemical feedstock, are produced by a steam cracking process of olefins. There are two 'basic factors in the growth of olefin chemistry'<sup>1</sup>. First, the rising demand on gasoline of the world, which is used not only as a feed but also as alkylated gasoline. Second, the expansion of petrochemistry, based on crude oils and inexpensive olefins, led to the development of cracking processes for olefin manufacture. Therefore, chemical researches are mainly focused on the development of new catalysts for the conversion of inexpensive olefins to light olefins. Figure 1.1 shows the growth of demand and demand forecast of ethylene during 1995-2005, where EBZ is ethylbenzene, EDC is ethylene dichloride, EO is ethylene oxide and EG is ethylene glycol. These are monomers used to produce polymers in downstream petrochemical industry. It has been observed that the demand of ethylene is increased since 1995.

Olefin metathesis is a process of converting two olefins to olefins *i. e.* a conversion of ethylene and butylene to produce propylene, and it is being used dramatically in the specialty chemical market. In addition, it can adapt the availability and flexibility to the global demand and manufacturing processes. The ethylene share from naphtha cracking mixtures could, for example, be increased at the

cost of propylene, thereby simultaneously producing additional butylene feedstock for dehydrogenation to butadiene.

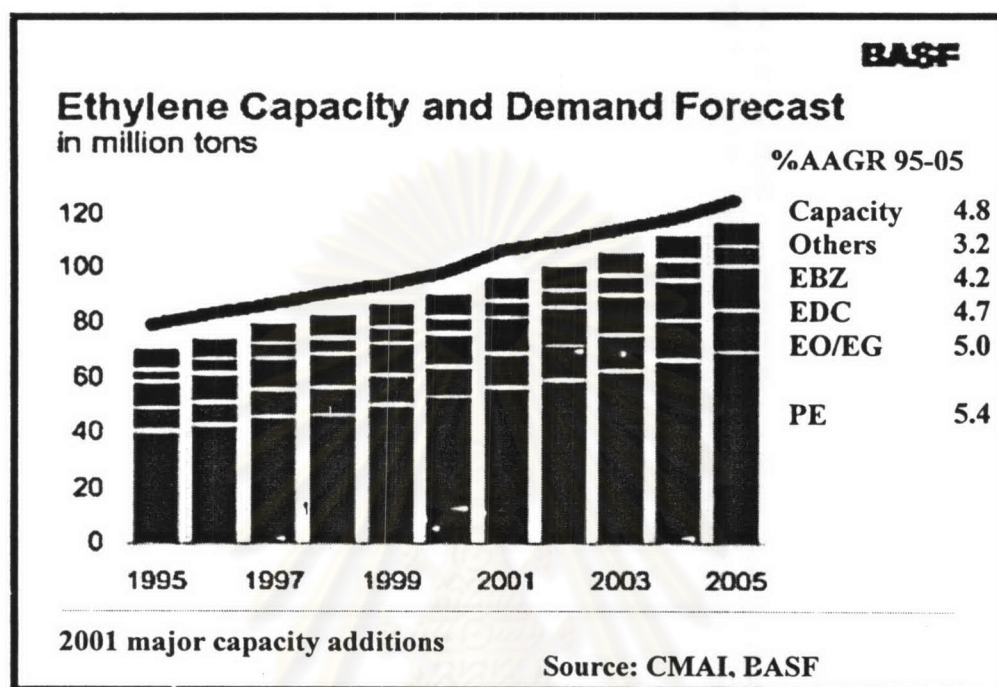


Figure 1.1. Ethylene capacity and demand forecast in 1995-2005.<sup>1</sup>

It can also be used in the combination with ethylene oligomerization in countries where natural gas cracking is favored to increase, otherwise, an inadequate supply of higher olefins. Other opportunities for metathesis include synthesis of otherwise inaccessible diolefins and ring-opening polymerizations of cycloolefins.

### 1.1.1 Development of Metathesis Process for Industrial Applications

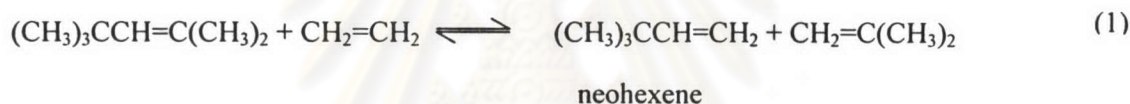
The olefin metathesis reaction was firstly discovered in 1931 by Schneider and Frölich when it was observed that ethylene and butylene were formed during pyrolysis of propylene at 1130 K<sup>2</sup>. In the 1960s, the first industrial application of olefin

metathesis as the Triolefin Process was operated by Phillips Petroleum<sup>19</sup> using propylene as a reactant to produce ethylene and butylene. During 1966 and 1973 an industrial plant with a capacity of 30,000 tons butylene per year was operated by Shawinigan in Canada. The reaction condition depends upon the catalyst employed. With Co-molybdate catalysts, the reaction temperatures of 120-210°C at 25-30 bars are sufficiently enough to obtain propylene conversion of *ca.* 40%. The operating temperature of 450-500°C is required for WO<sub>3</sub>/SiO<sub>2</sub> and propylene conversion at 500°C is approximately 42%. Nowadays, it is more attractive to use the Triolefin Process in the reverse direction as the strong global demand for propylene outpaces supply from conventional sources. Lyondell Petrochemical, Texas (USA), has already been operating a 136,000 ton-per-year plant since 1985. Ethylene is initially dimerized to 2-butylene, which then reacts with additional ethylene in a metathesis step to produce propylene.<sup>1</sup> A rhenium catalyst in the form of Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> was formed firstly developed by British Petroleum (BP) for metathesis processes. The catalyst was found more active than the previous catalysts and it was, in principle, already active at room temperature. The Institut Francais du Pétrole (IFP) and the Chinese Petroleum Corporation (Taiwan) have jointly developed a continuous process,<sup>3</sup> called Meta-4, in which ethylene and 2-butylene react with each other in the liquid phase in the presence of a Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at 35°C and 60 bar.<sup>4,5</sup> A large-scale, 320,000 ton-per-year industrial plant incorporating olefin metathesis called the Shell Higher Olefins Process (SHOP) was firstly operated in 1977 in USA for converting ethylene to detergent-range alkenes. After that, many plants have begun the operation and by 1993, the worldwide capacity for  $\alpha$ -olefins by the SHOP process has grown to about 10<sup>6</sup> tons per year.



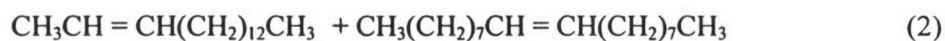
### 1.1.2 Metathesis in Fine Chemistry

Besides the industrial applications, metathesis reaction is also valuable and can be applied for fine chemistry<sup>6</sup> and oleochemistry (*i. e.* making products from natural fats and oils of vegetable and animal origin).<sup>7</sup> Since 1969, Phillips Petroleum has commercially operated a 1,400-tons-per-year plant for the production of neohexene (3,3-dimethylbut-1-ene), an important intermediate in the manufacture of synthetic musks, *via* cross-metathesis of  $\beta$ -di-isobutylene (2,4,4-trimethylpent-2-ene) with ethylene (ethenolysis), using a  $\text{WO}_3/\text{SiO}_2$  metathesis catalyst.<sup>8</sup> The reaction is represented in equation 1.



The coproduct isobutylene can be recycled to an isobutylene dimerization reactor, which backed to be a reactant in reaction 1.1. Neohexene is used to make a class of synthetic musks known as bicyclic musks. These musks simulate macrocyclic musks and have excellent odor and fixative properties.<sup>9</sup>

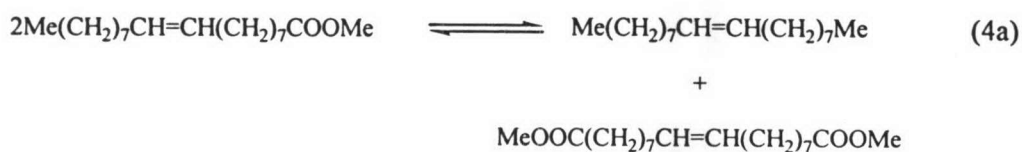
In 1985, Banasiak, D.S.<sup>10</sup> has attempted to synthesize biologically active compounds such as insect pheromones using metathesis reaction. The conventional synthetic routes to these pheromones are often multistep sequences, which causes pheromones too expensive for widespread use.<sup>10</sup> The interesting results have been obtained in a few steps by cross-metathesis between 2-hexadecene and 9-octadecene in the presence of the catalyst  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  (Equation 2) to produce 9-tricosene.

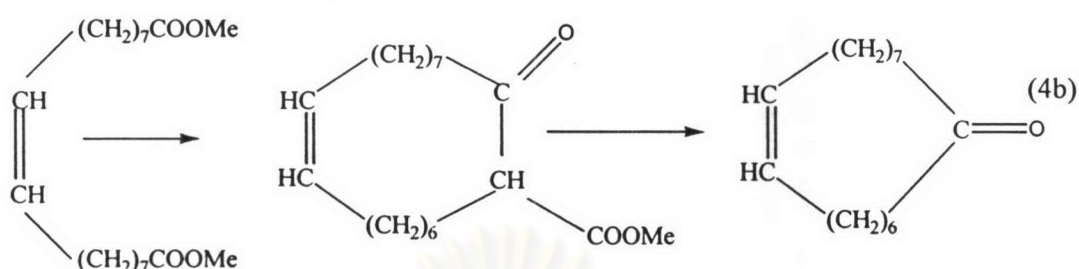


Cyclic alkenes can be dimerized to larger cyclic dienes that are used as intermediates in the synthesis of fine chemicals. Warwel *et al.*<sup>11</sup> synthesized 1,9-cyclohexadecadiene using dimerization of cyclooctene over a  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{Me}_4\text{Sn}$  catalyst at temperature of 35-50°C (Equation 3).

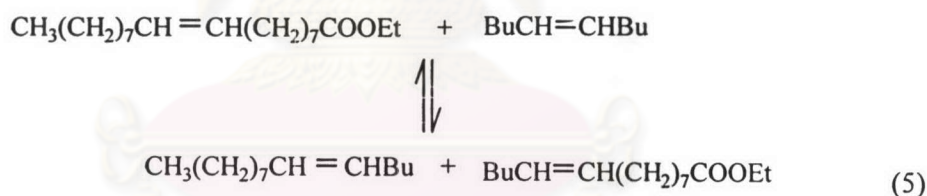


Unsaturated fatty acid esters are very promising and cheap feedstocks for metathesis. For this reason, the metathesis reaction is very interesting in the field of oleochemistry. For example, methyl oleate (methyl *cis*-9-octadecenoate) is an attractive functionalized olefin because of its ready availability and the utility of the metathesis products. The products of methyl oleate from metathesis<sup>12</sup> and cyclocondensation reaction have intense musk odor, which is very attractive for perfume components (Equations 4a and 4b).





Cross-metathesis reactions are useful for the production of fine chemicals such as synthetic perfumes, prostaglandin intermediates, and insect pheromones. The cross-metathesis of ethyl oleate with 5-decene in the presence of  $\text{MoO}_3/\text{SiO}_2/\text{cyclopropane}$  catalyst<sup>14</sup> results in a *cis/trans* mixture of ethyl 9-tetradecenoate, an insect pheromone precursor (Equation 5).



Metathesis reaction is catalyzed in both heterogeneous and homogeneous phases. The reactions generally use catalysts, based on molybdenum, tungsten, or rhenium. In a liquid phase, soluble halides or carbonyls are reduced to lower valency states by the simultaneous presence of organometallic compounds and activated using oxygen-containing promoters. In a gas phase, catalysts are oxides, sulfides or carbonyls of the above-mentioned metals on supports with large surface areas such as silica or alumina.<sup>14</sup> Therefore, in order to improve the efficiency of the catalysts, most industrial researches are mainly focused on the enhancement of surface activity, identification of promoters and additives, and recovery or regeneration of catalysts.



Generally, supports can be distinguished into three types:<sup>15</sup> (a) an amorphous solid. This type of solid has random pores, and more or less impervious to reactant molecules, so that the reaction takes place at irregular surface, perhaps in pits or pores; (b) sheets or layers (lamella), which are separated by interlamellar regions where any useful activity resides; and (c) the three-dimensional structure comprises a regular array of channels in which molecules of appropriate dimensions can fit. Silica and alumina fall into the first category, clays and graphite are the second, and zeolites are the third.

**Table 1.1.** Properties of solid supports

Support	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MCM-41
Acid-base property	Basic	amphoteric	Low acidic
Surface area <sup>26</sup>	80-700 m <sup>2</sup> /g.	80-350 m <sup>2</sup> /g.	>1000 m <sup>2</sup> /g.

Microporous and mesoporous inorganic solids have found great importance as catalysts and sorption media because of their large internal surface area. Well-known members of the microporous class providing excellent catalytic properties are zeolites, which are a crystalline aluminosilicate network. However, their applications are limited by the relatively small pore opening. Until 1992, the Mobil Oil research group has introduced a new family of mesoporous silicate material<sup>16,17,18</sup> called MCM (Mobil Composition of Matter) 41. This inorganic solid has high surface area regular hexagonal arrays of uniform pore sizes within the mesoporous region (15-100 Å), and various different types of shape selectivity for products, and reactants. In order to apply mesoporous silica as catalysts, many metal ions such as Al, Ti, V, Cr, Mn, Mo and W have been attempted to incorporate into MCM-41.

Rhenium based catalyst supports such as amorphous silica or alumina has been well known for their high activity on the propylene metathesis reaction when compared with Mo and W. However, the price of rhenium catalyst is very expensive and it may not be worthwhile for industrial application. Because of its similarity in the chemical property as rhenium and the cheap price, tungsten has been gained much attention on metathesis of olefins, but only few researches has been reported on the incorporation of tungsten into the framework structure of supports. Therefore, this study is aimed to incorporate tungsten into the framework structure of high surface area support MCM-41 and to test the synthesized catalyst using olefin metathesis.

## 1.2 Objectives

- (1) To synthesize W-MCM-41 and  $\text{WO}_3/\text{MCM-41}$  as catalysts for olefin metathesis.
- (2) To compare the catalyst activity of W-MCM-41 and  $\text{WO}_3/\text{MCM-41}$  catalysts in olefin metathesis of 1-hexene.

## 1.3 Literature Reviews

The olefin metathesis reaction was firstly reported by Banks and coworkers from Phillips Petroleum.<sup>19</sup> Reactants such as propylene, 1-butylene, 1-pentene, and 1-hexene were passed over molybdenum hexacarbonyl-alumina catalyst at 120°C, 34 bar and 1 to 2 WHSV, and gave conversions of 25% for propylene, 10% for 1-butylene, 60% for 1-pentene and 54% for 1-hexene respectively. Tungsten hexacarbonyl on the alumina catalyst gave conversions of 7% for 1-butylene and 44% for 1-pentene. In addition, the propylene conversions were the highest with 7-12% molybdena catalysts. The addition of 2 to 4% cobalt oxide to molybdena-alumina catalysts reduced coke formation and gave the conversion of propylene about 40%.



Tungsten oxide and molybdena based catalysts have received considerable attention due to their high metathesis activity and because tungsten and molybdenum are similar in chemical structure. For heterogeneous catalyst, it has been widely accepted that analogous metal carbene species are formed on the surface of oxidic catalysts<sup>20</sup>. Ramos *et al.*<sup>20</sup> compared series of alumina-supported Mo- and W-based catalysts with a wide range of  $\text{MO}_3$  (M = Mo,W) loadings in the metathesis of propylene. The selectivity to metathesis products at the reaction temperature of 500 °C, propylene feed at 20 ml/min for  $\text{WO}_3$  and  $\text{MoO}_3$  catalysts varied as a function of the metal oxide content. The catalyst of 3% by weight  $\text{WO}_3/\text{Al}_2\text{O}_3$  exhibits its activity to form product mixture of ethylene/butylene ratio close to that using the 3% by weight  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst. However, this ratio decreased markedly with increasing metal oxide content. This indicates that after the metathesis reaction, dimerization of ethylene takes place and isobutylene is the main component of the  $\text{C}_4$  fraction. The 15% by weight  $\text{WO}_3/\text{SiO}_2$  catalyst has a high selectivity ( $\approx 92\%$ ) to a metathesis reaction, which compared with 15% wt  $\text{WO}_3/\text{Al}_2\text{O}_3$  at the reaction temperature of 500°C.

Maksimowski *et al.*<sup>21</sup> described the catalytic activity in 1-pentene metathesis using the  $\text{WOCl}_4$ /silica-alumina system with different cocatalysts. It was found that  $\text{Et}_3\text{Al}$  was the best cocatalyst with the optimum conditions of 1-pentene:W = 50:1, cocatalyst :W = 3:1 at 60°C.  $\text{Me}_3\text{Al}$  and  $\text{Bu}_4\text{Sn}$  showed good performance, while  $\text{Et}_4\text{Sn}$  was only a weak cocatalyst and  $\text{Et}_4\text{Pb}$  did not activate catalysts. With increasing the reaction temperature, the conversions of 1-pentene to metathesis products were increased. Besides, the  $\text{WCl}_6$ /silica-alumina catalyst exhibited almost the same activity as the  $\text{WOCl}_4$ /silica-alumina system.

Aritani *et al.*<sup>22</sup> reported that 10 % wt.  $\text{MoO}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$  containing 28.6 %wt of  $\text{Al}_2\text{O}_3$  exhibited a conversion of propylene metathesis of 50.2% at 200°C without

reductive pretreatment and a conversion of 46.3% for  $\text{MoO}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$  containing 13.8 % by weight of  $\text{Al}_2\text{O}_3$ . On the other hand,  $\text{MoO}_3/\text{SiO}_2$ , and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts, which were prereduced with  $\text{H}_2$  at  $500^\circ\text{C}$  and then evacuated at the same temperature exhibited higher conversion than unreduced ones.

Ookuoshi *et al.*<sup>23</sup> reported a new silica support known as hexagonal mesoporous silica HMS for molybdenum-based olefin metathesis. The reaction exhibited much higher catalytic activity for metathesis of 1-octene in a liquid phase, compared with  $\text{MoO}_3$  on normal porous silica and  $\text{MoO}_3$  on  $\gamma$ -alumina. The catalytic activity was critically dependent on different kinds of alkylamines which were functioned as templating agents in the formation of HMS. The 7% by weight  $\text{MoO}_3$ -supporting HMS prepared from octylamine had the highest activity at  $50^\circ\text{C}$ , compared with different alkyl chain lengths (C12 and C16) of alkylamines. The yield of 7-tetradecene product at 16 h was approximately 44% and 77% selectivity.

Gil *et al.*<sup>24</sup> reported a 0.5% by weight  $\text{MoO}_3$  supported on Al-pillared montmorillonite, a new support which was obtained by exchanging the original interlayer cations of a smectite by polyoxocations, was test in the propylene metathesis and compared with activity to  $\text{MoO}_3/\text{SiO}_2$  and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  at  $250^\circ\text{C}$ . The pillared clay sample showed similar conversion decay with time was observed for 1 % by weight  $\text{MoO}_3/\text{SiO}_2$  and 1% by weight  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts, but these reference catalysts showed an initial specific activity per gram of Mo between 5 to 7 times higher and have a *trans/cis* ratio of 2-butene similar to the silica catalyst.

In 1996, Lehtonen *et al.* developed new tungsten-based catalysts for olefin metathesis.<sup>25</sup> Three tungsten complexes, 1:  $[\text{W}(\text{eg})_3]$ , 2:  $[\text{W}(\text{eg})(\text{pin})_2]$ , and 3:  $[\text{W}(\text{pin})_3]$ , which are stable in air and soluble in common organic solvents were used as precursors for the silica-supported tungsten oxide catalysts in the propylene metathesis. The results were compared with those of the reference catalysts prepared from  $(\text{NH}_4)_2\text{WO}_4$  and  $\text{WOCl}_4$ , respectively.

1:W(eg)<sub>3</sub>2:W(eg)(pin)<sub>2</sub>3:W(pin)<sub>3</sub>

(H<sub>2</sub>eg = ethane-1,2-diol, H<sub>2</sub>pin = 2,3-dimethylbutane-2,3-diol)

It was found that the reaction of propylene over these catalysts led to a mixture of ethylene, propylene, and *cis*-, *trans*-butylenes without isomerization or polymerization of products. The activities of catalysts 1: [W(eg)<sub>3</sub>] and 2: [W(eg)(pin)<sub>2</sub>] are more active than both of the reference catalysts and the catalyst 3: [W(pin)<sub>3</sub>] is nearly as active as the reference catalyst prepared from WOCl<sub>4</sub>. In addition, it has been suggested that ligands of the metal complexes play a role for the catalytic activity and only one labile ligand is necessary for the good activity.

Amigues *et al.*<sup>26</sup> reported the optimization of the Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst for the propylene metathesis that the reaction did not work at very low rhenium contents (1% or less) at the temperature of 35°C and 38 bar pressure. The catalyst containing 12.7% by weight Re produced 1% liquid oligomers from the side-reaction. These oligomers behave as diffusional barriers and block the active sites of the catalyst. Mol *et al.*<sup>27</sup> reviewed propylene metathesis over the supported rhenium oxide catalyst and concluded that the reaction activity increased exponentially with a Re<sub>2</sub>O<sub>7</sub> loading above 6% by weight. The highest activity is reached at the reaction temperature of 50°C and ~18% by weight Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub>.



Acidic properties of the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst was characterized by a combined study using Fourier transform infrared spectroscopy (FT-IR) and temperature-programmed desorption (TPD). The amounts of adsorbed pyridine on both Lewis and Brønsted acid sites in  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst decreased with increasing the evacuation temperature. The desorption temperature of pyridine on the Brønsted acid sites went up to  $300^\circ\text{C}$  and up to  $500^\circ\text{C}$  on the Lewis acid sites. Most of the acid sites were weak acid together with a few strong acid sites. The addition of small amounts of alkaline salt selectively poisons both strong Brønsted and Lewis acid sites and the effectiveness in poisoning Lewis acid sites depended mostly on alkaline cations, whereas anions played an important role in Brønsted acid sites.<sup>28</sup> Nahama F. *et al.*<sup>29,30</sup> studied the surface acidity of the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst, and the nature of the acidity implicated in the metathesis reaction. Characterization of the surface acidity by infrared spectroscopy and ammonia thermodesorption revealed that the initiation of the metathesis reaction is essentially governed by Lewis acidity exalted by the rhenium content and the calcination temperature. Increasing the rhenium content led to emphasis strong Lewis acidity of alumina at the expense of weak Lewis acidity of alumina, the appearance of Brønsted acidity. Besides, weak Brønsted acidity appearing above 14% by weight Re with pyridine adsorption seemed to be inefficient for the good processing of the reaction. Using infrared spectroscopy, it was pointed out by ammonia adsorption-thermodesorption that a band at  $1320\text{ cm}^{-1}$ , a characteristic peak of Lewis acidity of aluminium perrhenate, probably brought by the  $\text{Al}^{3+}$  ions of the perrhenate. Therefore it indicates the presence of an aluminium perrhenate on the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst surface.

The effect of promoters or cocatalysts on metathesis was studied by Kawai *et al.*<sup>31</sup>. 1-Alkene containing bromide was metathesized over the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst promoted with various kinds of alkylmetal cocatalysts. The catalytic activities of the reaction were greatly increased in the sequence of Bu-<Me-<Et- alkyl group and in

the metal sequence of Si,Al<<Ge<Sn. The most favorable catalyst system was the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst promoted with  $\text{SnEt}_4$  at  $60^\circ\text{C}$ . Klimov *et al.*<sup>32</sup> presented the other method for preparing rhenium-containing catalysts, in addition to the conventional impregnation method. It consisted of anchoring the rhenium tris-acetylacetonate  $\text{Re}(\text{C}_5\text{H}_7\text{O}_2)_3$  to the  $\text{Al}_2\text{O}_3$  surface. IR-spectroscopy showed the acetylacetonate ligands coordinated to rhenium remained intact in the surfaced compounds. And, addition of an organometallic compound as a cocatalyst exceeded the activity of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalysts prepared by impregnation. du Plessis *et al.*<sup>33</sup> investigated the influence of  $\text{Cs}^+$  and  $\text{PO}_4^{3-}$  on the metathesis activity. The results showed that the additions of  $\text{Cs}^+$  and  $\text{PO}_4^{3-}$  ions to the 3%wt.  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnMe}_4$  catalyst with a Sn:Re mole ratio of 2:1 caused an increase in the metathesis product yield of 1-octene, on the other hand, it increased isomerisation and cross metathesis activities of other catalysts.

The regenerability of tetraalkyltin-promoted rhenium-based catalysts on propylene metathesis,<sup>34</sup> was studied and characterized using temperature-programmed reduction (TPR) and metal-content analysis techniques. The results indicated that the loss of catalyst activity was due to  $\text{SnO}_2$  remaining behind on the catalyst surface and interacting with the rhenium oxide. A deactivated catalyst could also be partly restored by regenerating in a stream of oxygen, and renewing promoter. Each regeneration cycle resulted in some loss of activity.

Supported rhenium catalysts for alkene metathesis have been extensively studied. Most of the researches are focused on the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst even though other material such as  $\text{SiO}_2$  or  $\text{SiO}_2\text{-Al}_2\text{O}_3$  could also be used as the catalyst support.  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst is one of the best metathesis catalysts due to its high activity and selectivity. This means that the catalyst does not have acidity for double-bond shift isomerization and dimerization. The rhenium oxide on alumina was firstly reported in propylene metathesis by researchers of British Petroleum<sup>35</sup> in 1964. SiBeijn *et al.*<sup>36</sup> compared the activity of the  $\text{Re}_2\text{O}_7$  catalyst supported on phosphated  $\gamma\text{-Al}_2\text{O}_3$



with the  $\gamma\text{-Al}_2\text{O}_3$  catalyst in the propylene metathesis. FTIR-measurements supported that the active metathesis site of the  $\gamma\text{-Al}_2\text{O}_3$  supported  $\text{Re}_2\text{O}_7$  catalysts was an electron-deficient Re center. These sites were formed when  $\text{ReO}_4^-$  ions reacted with the more acidic OH groups to form Al-bonded  $\text{ReO}_4$  groups on the catalyst surface. The sharp increase in activity of  $\gamma\text{-Al}_2\text{O}_3$  supported  $\text{Re}_2\text{O}_7$  catalysts, was above a 6 % by weight  $\text{Re}_2\text{O}_7$  loading due to the relative increase in the number of electron-deficient Re centers at higher loadings. On the contrary, almost no activity was obtained at low  $\text{Re}_2\text{O}_7$  loading. The modification of  $\text{Al}_2\text{O}_3$  with  $(\text{NH}_4)_2\text{HPO}_4$  resulted in a more active  $\text{Re}_2\text{O}_7$  catalyst, as the more acidic OH groups on  $\gamma\text{-Al}_2\text{O}_3$  have reacted with the phosphate to form acidic P-OH groups. In the catalysts based on this support, the  $\text{ReO}_4^-$  ions have also reacted with the phosphorus-bonded OH groups, at low Re loadings.

Sheu *et al.*<sup>35</sup> studied series of alumina/aluminum borate (AAB) with various Al/B mole ratios as a catalyst support for the propylene metathesis. It was found that the  $\text{Re}_2\text{O}_7/\text{AAB}$  catalyst is more active, stable and regenerable than the conventional  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ . The optimum Al/B mole ratios are in the range of 4-10. Boron promotes the activity of  $\text{Re}_2\text{O}_7/\text{AAB}$  by maintaining Re at a desirable oxidation state for the formation of initial metal carbene and increasing support the acidity.

The metathesis of a cyclic olefins is catalyzed by a great variety of transition metal compounds. Recently, a few research have been focused on a non-transition metal compound. Jannini *et al.*<sup>37</sup> reported the metathesis of linear  $\alpha$ -alkenes (1-hexene, 1-octene, and 1-decene) in the presence of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  promoted with tetrabutyltin in a liquid phase at room temperature. The reaction condition was olefin/ $\text{Bu}_4\text{Sn}/\text{SiO}_2\text{-Al}_2\text{O}_3$  = 6.5 mmol/42-50 $\mu\text{mol}/500\text{mg}$ , heptane as a solvent and reaction time of 3-4 h. The conversion of 1-hexene to primary metathesis products was 7% and about 60% for 1-octene and 1-decene, which indicated the isomerization of 1-hexene.