

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Petrochemical industry is a basic industry of which products are used as raw materials in other industries. In the refining industry, light olefins have been increasing in demand as premier building blocks for reformulated gasoline and for petrochemicals. Among petrochemicals, light olefins, especially ethylene and propylene are produced at large scale due to a great demand for downstream plants to produce their derivatives. Generally, demand for ethylene derivatives refers to total demand for polyethylene, polyvinylchloride, ethylene glycol and styrene monomer that are represent in equivalent amount of ethylene. Demand for propylene derivatives mostly refers to total demand for polypropylene, acrylonitrile and oxo-alcohol.<sup>1</sup> Fast growing of petrochemical industry increases from greater demand for intermediate petrochemical substances.

Chemistry Division of Manufacturing Industries Bureau has forecasted demand trends for petrochemical products such as ethylene and propylene until 2007. Table 1.1 shows changes in global demand for ethylene derivatives in equivalent tons of ethylene. Global demand for ethylene derivatives in 2001 was 92.1 million tons of ethylene, a 3.9% increase from the previous year. Global demand for ethylene derivatives in 2002 was 95.6 million tons of ethylene, a 3.9% increase from the previous year. Since then the global demand seems to increase sharply till 2005. After 2005, the demand is increasing at slower rate than before. Average yearly growth rate of global demand for ethylene derivatives is about 5.0%. Table 1.2 shows global and regional demand for ethylene derivatives. In some regions such as Western Europe and North America, demand for ethylene derivatives does not significantly

increase or even decrease in Japan. However, a big rise in demand in China affects to lift overall global demand. Table 1.3 shows global and regional demand for propylene derivatives comparing. As shown in Table 1.3, the global demand for the main propylene derivatives is expected to rise 6% from the 2001 level of 36.9 million tons to 52.3 million tons in 2007. The average annual rate of demand growth for this period is expected to be 6.9 in Asia, 5.5% in North America and 3.7% in Western Europe. Demand for China alone is expected to rise by 10.3%. Demand for the raw material propylene is expected to rise from the 2001 level of 54.7 million tons, a 6.1% rise from the previous year, to 70 million tons in 2007, which would be an average annual increase of 4.2%.

**Table 1.1** Changes in global demand for ethylene derivatives ( in equivalent tons of ethylene )

	2001	2002	2003	2004	2005	2006	2007	Average Growth rate 01-07
Demand <sup>a</sup> volume	92.1	95.6	100.5	106.0	112.0	117.3	123.3	-
Yearly <sup>b</sup> Growth rate	3.9	3.9	5.1	5.5	5.6	4.8	5.1	5.0

(Unit; a=million tons, b=%)

**Source:** Forecast of global supply and demand trends of petrochemical products,  
<http://www.meti.go.jp> [2002, October 30]

**Table 1.2** Global and regional demand for ethylene derivatives (in equivalent tons of ethylene)

	Global <sup>a</sup> Total	Asia <sup>b</sup>							Western <sup>b</sup> Europe	North <sup>b</sup> America	Middle <sup>b</sup> East
		South Korea	Taiwan	China	ASEAN	India	Japan	Total			
Demand											
2001	92.1	3.6	2.6	12.4	4.3	2.2	5.9	32.0	21.5	24.2	2.0
2007	123.3	5.0	3.0	20.3	6.3	3.6	5.7	45.5	25.4	31.5	3.6
Increase											
2001-2007	31.2	1.4	0.4	7.9	2.0	1.4	-0.2	13.5	3.9	7.3	1.6
Yearly Growth Rate 2001-2007	5.0	5.7	2.6	8.6	6.5	9.0	-0.5	6.0	2.9	4.5	10.0

(Unit; a=million tons, b=%)

Source: Forecast of global supply and demand trends of petrochemical products,  
<http://www.meti.go.jp> [2002, October 30]

**Table 1.3** Global and regional demand for propylene derivatives ( in equivalent tons of propylene)

	Global <sup>a</sup> Total	Asia <sup>b</sup>							Western <sup>b</sup> Europe	North <sup>b</sup> America	Middle <sup>b</sup> East
		South Korea	Taiwan	China	ASEAN	India	Japan	Total			
Demand											
2001	36.9	1.6	1.1	5.6	2.0	1.2	3.3	15.2	8.8	7.5	1.0
2007	52.3	2.3	1.3	10.0	2.8	1.9	3.7	22.6	11.0	10.4	1.7
Increase											
2001-2007	15.4	0.7	0.2	4.4	0.8	0.7	0.4	7.4	2.2	2.9	0.7
Yearly Growth Rate 2001-2007	6.0	6.7	3.2	10.3	5.6	7.9	1.8	6.9	3.7	5.5	8.5

(Unit; a=million tons, b=%)

Source: Forecast of global supply and demand trends of petrochemical products,  
<http://www.meti.go.jp> [2002, October 30]

It is important to develop a process of light olefins manufacture especially using the catalytic reaction. One of interest is olefin metathesis where an olefin is transformed to another type of olefins.<sup>2</sup> Olefin metathesis is often found simultaneously occurring during the naphtha cracking process in refinery plants. Common heterogeneous catalysts industrially in use are supported metal oxides of molybdenum, tungsten, and rhenium on amorphous silica and/or alumina.<sup>3</sup> However, the process provides a rather low value of olefin conversion of 30-40% with not high selectivity to formation of light olefins.<sup>4</sup> Therefore, this project proposes to study a novel catalyst which is supported tungsten oxide on SBA-15 for metathesis of 1-hexene. SBA-15 was recently discovered in 1998<sup>5</sup> and it was found as a hydrothermally stable ordered hexagonal mesoporous material with large surface area. It has not been reported about synthesis of the supported  $WO_3/SBA-15$  for olefin metathesis. This is the first report of such an area. As a substrate, 1-hexene is selected due to it is the lightest liquid olefin to avoid the cross metathesis where the reaction takes place between two different types of olefins. The cross metathesis causes formation of several types of olefins and results in lower product selectivity.

## 1.2 Objectives

To prepare and characterize supported tungsten catalysts for metathesis of 1-hexene and study the effect of temperature and tungsten loading on their catalytic performance.

## 1.3 Scope of Work

Synthesize SBA-15 by Stucky<sup>5</sup> method for using as support to prepare  $WO_3/SBA-15$  catalysts over the range of 1-10% by weight of  $WO_3$ . The catalysts are used to catalyze metathesis of 1-hexene in gas phase.

## 1.4 Literature Reviews

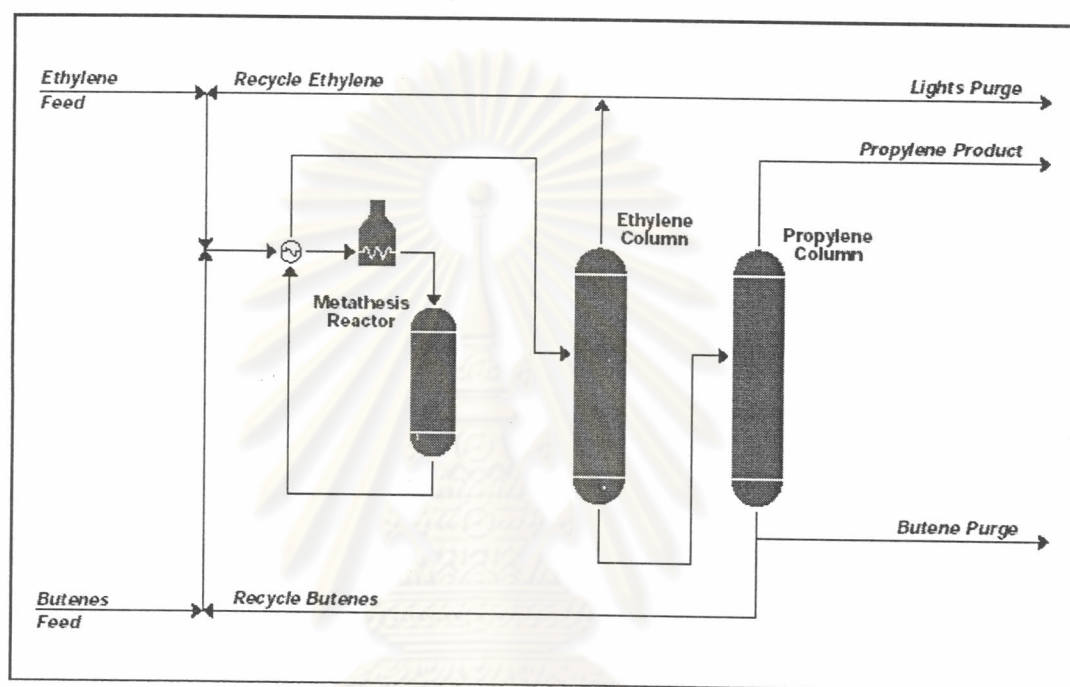
Propylene is obtained mainly from naphtha steam cracking (globally about 65%) as a co-product with ethylene, and as a co-product from gasoline-making from fluid catalytic cracking (FCC) at refineries.<sup>1</sup> Relatively small amounts are produced by propane dehydrogenation and by coal gasification via Fischer–Tropsch chemistry. Strong global demand for propylene, however, presently outpaces supply from these conventional sources. Propylene is used about 60% for making polypropylene, and further for producing acrylonitrile, oxo alcohol, acrylic acid, etc.<sup>6</sup>

Olefin metathesis is applied to industries in order to produce high capacity of olefin.<sup>7</sup> For example, an alternative route to propylene is by applying the metathesis reaction for the conversion of a mixture of ethylene and 2-butene into propylene. A process, called the Phillips triolefin process,<sup>8</sup> which utilizes a heterogeneous catalyst system, was originally developed by Phillips Petroleum Co., USA, and operated from 1966 to 1972 for the conversion of propylene into ethylene and butene, due to less propylene demand at that time. The Phillips process in the reverse direction, equation 1.2, is now offered by ABB Lummus Global, Houston (USA), for license as olefins conversion technology (OCT) for the production of propylene.



Figure 1.1 shows a simple process flow diagram of the OCT process.<sup>9</sup> Fresh C<sub>4</sub>'s plus C<sub>4</sub> recycle are mixed with ethane feed plus recycle ethylene and sent through a guard bed to remove trace impurities from the mixed feed. The feed is heated before entering the metathesis reactor. The reaction takes place in a fixed-bed reactor over a mixture of

$\text{WO}_3/\text{SiO}_2$  (the metathesis catalyst) and  $\text{MgO}$  (an isomerization catalyst) at  $>260^\circ\text{C}$  and 30-35 bar. 1-Butene in the feedstock is isomerized to 2-butene as the original 2-butene is consumed in the metathesis reaction.



**Figure 1.1** The OTC process (reversed Phillips Triolefin Process)<sup>9</sup>

The conversion of butene is above 60% per pass and the selectivity to propylene is  $>90\%$ . The reactor is regenerated on a regular basis. In 1985, the Lyondell Petrochemical Co. started to operate a plant in Channelview, Texas (USA) for the production of 136,000 tons per year of propylene.<sup>2,7,8</sup> In their process, part of the ethylene from ethane-cracking units is dimerized to 2-butene, using a homogeneous nickel catalyst developed by Phillips, which reacts with the rest of the ethylene to produce propylene. The process has been retrofitted to the company's steam cracker in Channelview.

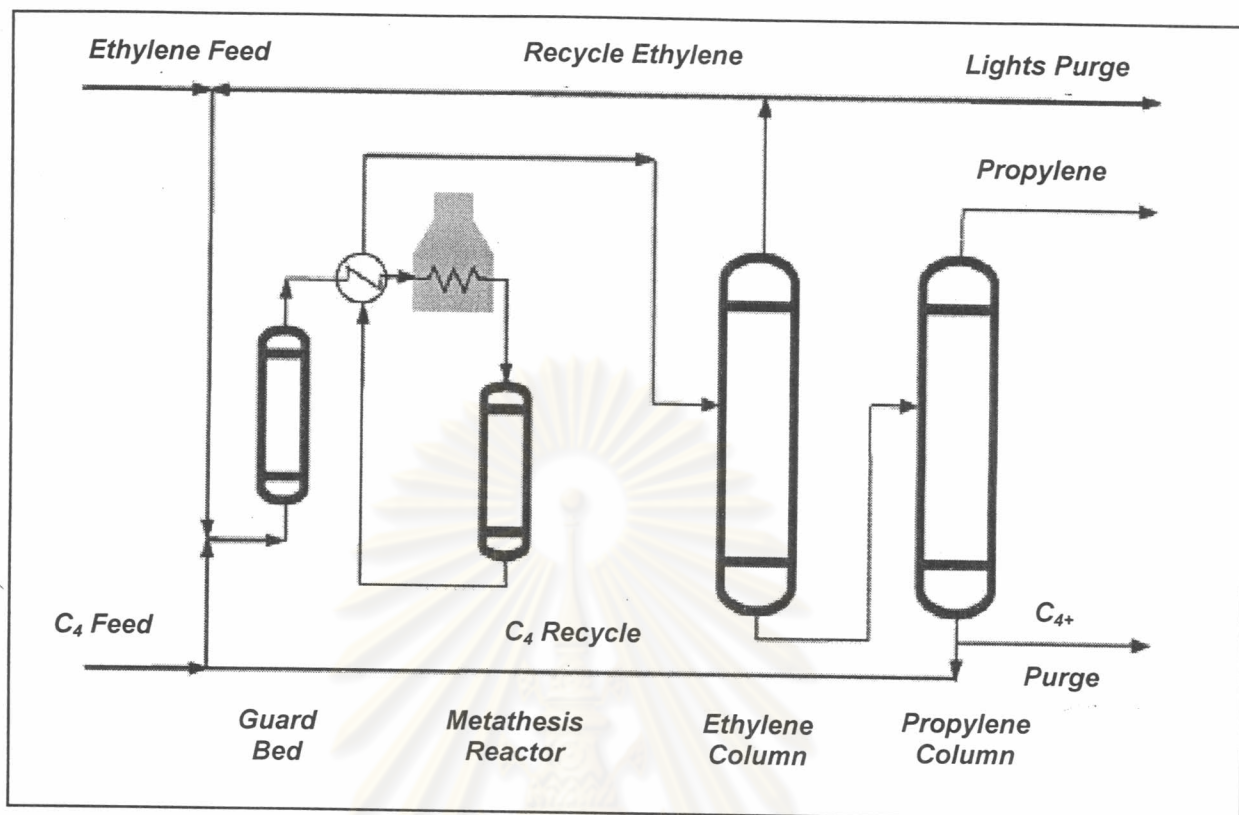
In particular, naphtha steam crackers with an integrated metathesis unit are an interesting alternative for producing more propylene. BASF FINA Petrochemicals brought on

stream a world-scale steam cracker plant in Port Arthur, Texas (USA), which will integrate the OCT process to enhance the production of propylene in relation to ethylene. This plant produces 920,000 tons per year of ethylene and 550,000 tons per year of propylene when the metathesis unit is added, it will adjust the output to 830,000 tons per year of ethylene and 860,000 tons per year of propylene.

Mitsui Chemicals will install the OCT process to meet increasing propylene demand in Asia. The propylene capacity of its olefins plant at its Osaka Works in Japan will be increased by 140,000 tons per year. Completion of the project is expected, the new unit will be the first plant installation in Japan to produce propylene using the OCT process. By this revamp, the propylene to ethylene production ratio can be raised from 0.6 to >1.0. The OCT process will also be used at Shanghai Secco Petrochemical, which is building a 900,000 tons per year naphtha cracker integrated with an OCT unit to produce a total of 590,000 tons per year of propylene at Caojing, China.

PCS (Petrochemical Corp., Singapore), a joint venture between Shell Chemicals and Sumitomo Chemical, will use OCT (metathesis technology) to increase the propylene output at its olefin units by 200,000–300,000 tons per year. Nippon Petrochemicals plans to increase the propylene capacity at its cracker with 100,000 tons per year, most likely using metathesis technology.

The Institut Français du Pétrole (IFP) and the Chinese Petroleum Corporation (Kaoshiang, Taiwan) have jointly developed a process for the production of propylene, called Meta-4,<sup>7,8</sup> as shown in Figure 1.2. In their process, ethylene and 2-butene react with each other in the liquid phase in the presence of a  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst at 35 °C and 60 bar. The (equilibrium) conversion is 63% per pass.<sup>6</sup>



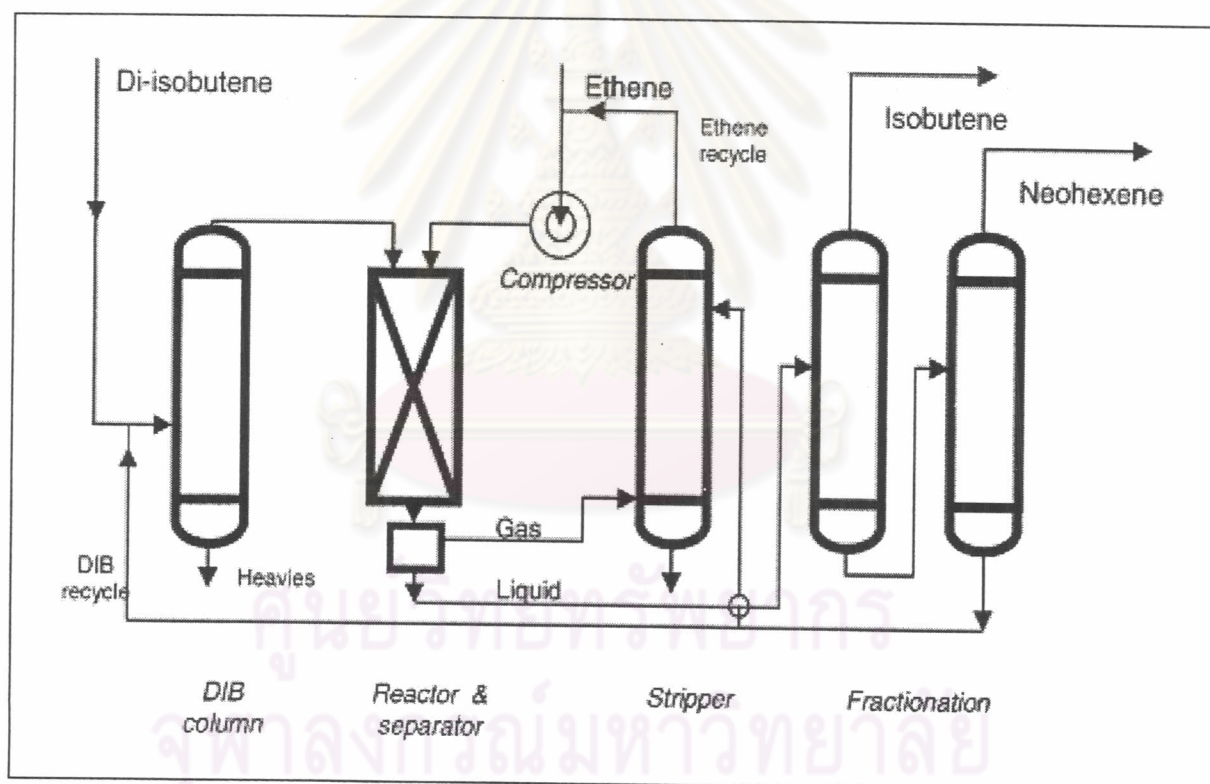
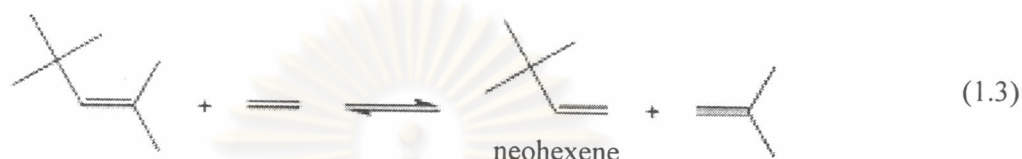
**Figure 1.2** Propylene production with Meta-4 process<sup>8</sup>

A semi-works unit using the OCT process for the metathesis of butene to produce 3-hexene, which is then isomerized into 1-hexene (a high-value comonomer used in the production of polyethylene), together with ethylene and propylene, is under construction at Sinopec's olefin plant in Tianjin (China), and will be started up in 2003.

Neohexene (3,3-dimethyl-1-butene) is an important intermediate in the synthesis of Tonalide®, a synthetic musk perfume. It is also used to make Terbinafine®, an anti-fungal agent. A neohexene unit located within Chevron Phillips Chemical Company LP's Houston Chemical Complex with a capacity of 1400 tons per year.<sup>10</sup> The process is based on the dimer of isobutene, which consists of a mixture of 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene. Cross-metathesis of the former with ethylene yields the desired product as shown in equation 1.3. The latter is not wasted since a dual catalyst can be used to ensure that it is isomerized to 2,4,4-trimethyl-2-pentene as this gets used up by metathesis. With a 1:3 catalyst



mixture of  $\text{WO}_3/\text{SiO}_2$  and  $\text{MgO}$  an average conversion of the di-isobutene of 65–70% and a selectivity to neohexene of ~85% is achieved at 370 °C and 30 bar (molar ratio ethene/di-isobutene = 2). The co-product isobutene is recycled to an isobutene dimerization reactor.



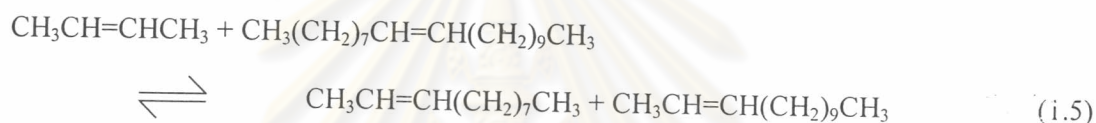
**Figure 1.3** The neohexene process; DIB: di-isobutene<sup>10</sup>

Figure 1.3 shows the process scheme of the neohexene process. Commercial di-isobutene is first fractionated to remove an oxidation inhibitor, which would otherwise poison



In the second step, these lighter and heavier alkenes undergo double-bond isomerization over a solid potassium metal catalyst to give an equilibrium mixture of internal alkenes.

In the third step, this mixture is passed over an alumina supported molybdate metathesis catalyst, resulting in a statistical distribution of linear internal alkenes with both odd and even numbers of carbon atoms via cross-metathesis reactions such as reaction 1.5. This yields about 10–15 wt.% of the desired C<sub>11</sub>–C<sub>14</sub> linear internal alkenes per pass, which are subsequently separated by normal distillation.



The isomerization and metathesis catalysts operate at 100–125 °C and 10 bar. The remaining lower (<C<sub>11</sub>) and higher (>C<sub>14</sub>) alkenes are recycled. The product consists of >96% of linear internal C<sub>11</sub>–C<sub>14</sub> alkenes. These can then be converted into detergent alcohols, via a hydroformylation process, or into detergent alkylates.<sup>2</sup> Shell Chemicals operates a SHOP unit at Stanlow (UK) with a capacity of 270,000 tons per year and three large-scale SHOP units at Geismar, Louisiana (USA) with a total capacity of 920,000 tons per year of higher olefins. The third SHOP unit at their Geismar location was brought on stream in 2002 for the production of 320,000 tons per year of higher olefins. This expansion brought Shell Chemicals' total worldwide production capacity to 1,190,000 tons of linear alpha and internal olefins per year; these are sold under the trade name Neodene®.<sup>11</sup>

One of the characteristics of Fischer–Tropsch synthesis is insufficient selectivity. Efforts have to be made to bring the products obtained in line with the market requirements. Based on existing and suggested process technologies, applications of the olefin metathesis reaction to convert less desirable olefins to more useful ones are under consideration. An

example of the conversion of low value olefins to high value olefins that can be employed in further downstream processes, is the conversion of low value C<sub>7</sub> α-olefins to internal C<sub>12</sub> olefins, which can be used as detergent alcohol feedstock. Besides the normal heterogeneous (tungsten) catalysts for the metathesis of such α-olefins, the highly active ruthenium complexes are very attractive, due to their robustness to air, water and oxygenates, high reaction rates and selectivities. An extremely active ruthenium-based catalyst is the second-generation Grubbs-type catalyst [RuCl<sub>2</sub>(=CHPh)(H<sub>2</sub>IPr)(PCy<sub>3</sub>)] with a turnover number (TON) of >640,000 at ambient temperature for the metathesis of 1-octene, and an initial turnover frequency (TOF) exceeding 3,800 s<sup>-1</sup> at 60 °C.<sup>11</sup> This high activity is because of the steric bulk of the ligand and superior electron-donating properties. Therefore, non-productive metathesis of the internal olefin formed during the reaction is less possible due to this increased steric bulk, which also might slow down decomposition pathways. A point of high interest is that degradation products of these ruthenium catalysts can be highly active and selective double-bond isomerization and hydrogenation catalysts. In this way via, e.g. first isomerization and then metathesis, interesting conversions of low-value olefins to high-value olefins can be accomplished.<sup>2</sup>

Not only in the petrochemical industry, but also in the oleochemical industry there are many interesting possibilities for olefin metathesis.<sup>17</sup> The metathesis of unsaturated natural fats and oils and their derivatives offers new synthesis routes from cheap feedstocks to valuable new or existing chemical products from renewable resources with high chemoselectivity. Efficient homogeneous and heterogeneous catalysts have been developed and it is to be expected that their use will lead to commercial applications for the production of polymers, agrochemicals, pheromones, fragrances, pharmaceutical intermediates, etc.

In the polymer field ring-opening metathesis polymerization (ROMP) of cycloalkenes is an attractive process for making linear polymers when based on cheap monomers or

possessing special properties compensating for a high price. Several industrial processes involving homogeneously catalyzed ROMP have been developed and brought into practice.<sup>12</sup>

Use of metathesis in industrial has been directly correlated to improvement in activity of catalysts. The metathesis reaction is catalyzed both in heterogeneous and homogeneous phases. Traditionally, the high tonnage technologies employing alkene metathesis depended on heterogeneous catalysis. Because of heterogeneous catalysts offer the two major advantages of greater thermal stability and ease of separation of products from catalyst.

Generally, the heterogeneous catalysts are metal oxide on supporting materials or solid matrix that can stand high temperature and pressure.<sup>13</sup> This type of catalyst for metathesis, molybdenum-on-aluminum, was known since metathesis reaction have been discovered. Since then, other petrochemical companies tried the experiment with this catalyst type. Addition of third component was involved to improve activity of catalysts. Peters and coworker<sup>7</sup> assigned in 1960 to Standard Oil Co. of Indiana, that propylene combined with molybdenum oxide on alumina treated with triisobutyl aluminum yields ethylene and butanes. Moreover, in 1964, Banks *et al.*<sup>4</sup> of Phillips Petroleum, reported the disproportionation of propylene to ethylene and butenes using molybdenum hexacarbonyl supported on alumina.

In term of support, besides the alumina, silica and silica-alumina were also used as support. It was shown in the study by Aritani *et al.*,<sup>14</sup> MoO<sub>3</sub> catalyst on various amorphous supports were tested in metathesis of propylene. It was found that when silica-alumina was used as supported, the activity was higher than using silica or alumina alone. Homs *et al.*<sup>15</sup> studied supports for WO<sub>3</sub> to use as catalyst for metathesis of propylene. Total conversion of propylene obtained from WO<sub>3</sub>/SiO<sub>2</sub> was higher than WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> at the same condition. The previous works indicated that influence of each type of support affected to catalytic activity for metathesis reaction. In addition, Onaka *et al.*<sup>16</sup> have studied on HMS in term of developing a new high surface area silica support for molybdenum-based metathesis catalysts.

metathesis catalysts. It demonstrates that HMS impregnated with molybdenum oxide ( $\text{MoO}_3/\text{HMS}$ ) showed high activity for metathesis of 1-octene to ethylene and 7-tetradecene.

Studying and improvement of catalysts on different supporting materials has been a major focus of current research. It was shown that designing a heterogeneous catalyst involves both the proper control of the surface chemistry and a rigorous control of the surface geometry at the micro-, meso- and macroscales.<sup>17</sup> This is because high surface areas or high active phase dispersions as well as fast mass transfer of the reactants and products to and from catalytic sites are required from any active catalyst. It is, therefore, clear that the new materials designated as mesoporous molecular sieves have introduced a new definition in the conception of catalysts.

Since the discovery of surfactant-organized silicas and silicates in the early 1990s, there has been extensive research in the field, motivated by the promise of these materials as catalyst supports. In discussing catalytic applications, reference will, however, be made to three kinds of relevant materials obtained followed different synthetic procedures. The first one is so-called M41S family of silica and aluminosilicates introduced by the Mobil group<sup>18</sup> which includes hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50 phases. The preparation of M41S materials involves ionic surfactants as structure directing agents. Especially MCM-41, several researchers have focused on the study of it in preparation of industrial catalysts. Then, Inagaki and co-worker<sup>19</sup> reported the synthesis of hexagonal mesoporous materials namely FSM-16 (Folded Sheets Mesoporous Material) from a layered polysilicate by using ionic surfactants as structure directing agents similar to that for MCM-41 preparation.

The second one was introduced by the group of Pinnavaia<sup>20</sup> who produced mesoporous material using two neutral routes based on hydrogen bonding and self assembly of non-ionic primary amines and oligomeric silica precursors. The hexagonal mesoporous silica (HMS and

MSU) produced by this technique are less ordered, showing a worm-hole like pore structure, than mesoporous materials produced with ionic surfactants. They have, however, a monodispersed pore diameter, thicker pore walls, a higher thermal stability. In addition, the mesopores of HMS being shorter allow a faster diffusion of reactants.

Finally, the Santa Barbara group<sup>5</sup> has contributed largely to the development of the mesoporous materials. SBA-15 was synthesized by using amphiphilic triblock copolymers (poly(ethylene glycol) - poly(propylene glycol) - poly(ethylene glycol)) as the structure-directing agents. These materials have long range order of hexagonal, large monodispersed mesopores and thicker walls which make them more thermally and hydrothermally stable than previous materials. The advantages of the thicker walls is the ability to form stable crystal nuclei of the constitutive oxide within the walls.



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย