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ZIEGLER-NATTA CATALYST ON MAGNESIUM CHLORIDE SUPPORT PREPARED FROM MAGNESIUM COMPLEX

Mr. Likhasit Sinthusai

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
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Thesis Title	ZIEGLER-NATTA CATALYST ON MAGNESIUM CHLORIDE SUPPORT PREPARED FROM MAGNESIUM COMPLEX
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ลิขสิทธิ์ สินธุไสย : ตัวเร่งปฏิกิริยาซิเกลอร์-แนตทาบนตัวยึดแมกนีเซียมคลอไรด์เตรียมจากสารเชิงซ้อนแมกนีเซียม (ZIEGER-NATTA CATALYST ON MAGNESIUM CHLORIDE SUPPORT PREPARED FROM MAGNESIUM COMPLEX) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. วิมลรัตน์ ตระการพฤกษ์, 82 หน้า

วิทยานิพนธ์ฉบับนี้เกี่ยวข้องกับการเตรียมตัวยึดแมกนีเซียมคลอไรด์ชนิดไม่เป็นระเบียบและภาวะที่เหมาะสมสำหรับการเตรียมตัวเร่งปฏิกิริยาซิเกลอร์-แนตทาบนตัวยึดแมกนีเซียมคลอไรด์จากสารเชิงซ้อนแมกนีเซียม สามารถเตรียมสารเชิงซ้อนแมกนีเซียมโดยการทำปฏิกิริยาของบิวทิลออกทิลแมกนีเซียมกับ 2-เฮกซิล-1-เฮกซานอล ทำปฏิกิริยาคลอริเนชันของสารเชิงซ้อนแมกนีเซียมด้วยสารให้คลอรีน พบว่าอัตราส่วนโดยโมลไทรเอทิลอลูมิเนียมต่อแมกนีเซียมที่เหมาะสมเป็น 0.5 ได้สังเคราะห์ตัวเร่งปฏิกิริยาซิเกลอร์-แนตทาโดยใช้อัตราส่วนโดยโมลไทเทเนียมต่อแมกนีเซียมที่ต่างกัน โดยใช้อัตราส่วนโดยโมลไทรเอทิลอะลูมิเนียมต่อแมกนีเซียมที่เหมาะสม ได้ประเมินประสิทธิภาพของตัวเร่งปฏิกิริยาด้วยผลผลิตพอลิเอทิลีนที่เกิดขึ้น ภายใต้ภาวะความดันแก๊สไฮโดรเจน 1 บาร์และ 3 บาร์ วัดอัตราการไหลหลอมของพอลิเมอร์ ซึ่งแสดงถึงการตอบสนองต่อแก๊สไฮโดรเจนของตัวเร่งปฏิกิริยา ได้คำนวณค่าความสมดุลแอคติวิตี (AB) ของตัวเร่งปฏิกิริยา นอกจากนี้ ยังได้ศึกษาถึงผลกระทบของเอทิลเบนโซเอท ซึ่งทำหน้าที่เป็นตัวให้อิเลคตรอนภายใน ต่อสมบัติของตัวเร่งปฏิกิริยา วิเคราะห์ปริมาณของไทเทเนียมและเอทิลเบนโซเอทที่ยึดบนผิวของแมกนีเซียมคลอไรด์ พบว่าเมื่อปริมาณเอทิลเบนโซเอทสูงขึ้น ปริมาณไทเทเนียมบนผิวแมกนีเซียมคลอไรด์จะลดต่ำลง สมบัติของตัวเร่งปฏิกิริยาสามารถปรับปรุงได้โดยการปรับสภาพหลังปฏิกิริยา ได้แก่ เวลาและอุณหภูมิการปรับสภาพ พบว่า ที่ภาวะความเข้มข้นไฮโดรเจนสูง ถ้าอุณหภูมิการปรับสภาพตัวเร่งปฏิกิริยาสูงกว่า 85 องศาเซลเซียส ตัวเร่งปฏิกิริยาไม่มีความว่องไว การทดลองแสดงให้เห็นผลการเลียนแบบรูปร่างของพอลิเมอร์ที่เตรียมขึ้นตามรูปร่างของตัวเร่งปฏิกิริยา พบว่าตัวเร่งปฏิกิริยาที่เตรียมขึ้นมีรูปร่างปกติและไม่ก่อปัญหาการเกาะผนังของถังปฏิกรณ์ พอลิเมอร์ที่ผลิตขึ้นจากงานวิจัยนี้มีการกระจายน้ำหนักโมเลกุลเทียบเท่าของพอลิเมอร์เชิงพาณิชย์

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต
ปีการศึกษา 2551 ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก W. Trakarnpruk
ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม Roman Strauß

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KEYWORD: ZIEGLER-NATTA CATALYST/HIGH HYDROGEN RESPONSE AND ACTIVITY BALANCE/ETHYLENE POLYMERIZATION

LIKHASIT SINTHUSAI: ZIEGLER-NATTA CATALYST ON MAGNESIUM CHLORIDE SUPPORT PREPARED FROM MAGNESIUM COMPLEX
THESIS PRINCIPAL ADVISOR: ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph.D., ROMAN HELMUTH ADAM STRAUSS, Ph.D., 82 pp.

This thesis involved the preparation of disordered $MgCl_2$ based support and the optimization of Ziegler-Natta catalysts on magnesium chloride support prepared from magnesium complex. Magnesium complex was prepared by reacting butyloctyl magnesium with 2-ethyl-1-hexanol. The chlorination reaction of magnesium complex was performed with chlorinating agent. It was found that optimum triethylaluminium (TEA)/Mg molar ratio was 0.5. Ziegler-Natta catalyst was synthesized under different Ti/Mg molar ratio using the optimum TEA/Mg molar ratio. The performance of catalyst was evaluated by polyethylene yield under hydrogen pressures of 1 bar and 3 bars. Melt flow index (MFI) of polymers was measured and represented hydrogen response of catalyst. Activity balance (AB) value of the catalyst was calculated. Furthermore, the effect of ethyl benzoate as internal donor (ID) on catalyst property was studied. Amount of Ti and ethyl benzoate fixed on $MgCl_2$ surface was determined. The higher ethyl benzoate content, the lower Ti amount was fixed on $MgCl_2$ surface. The property of the catalyst can be further improved by varying post reaction treatment: aging time and aging temperature. It was found that the catalyst was inactive under high hydrogen concentration in polymerization condition if the aging temperature was above 85°C. The replication effect of catalyst morphology on derived polymer particles morphology was shown. It was found that the produced catalyst showed regular shape and did not cause reactor fouling. Molecular weight distribution of polymer produced from this work is similar to that of commercial one.

Field of Study Petrochemistry and Polymer Science Student's signature.......................................
Academic year 2008 Principal Advisor's signature W. Trakarnpruk
Co advisor's signature Roman Strauß

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LIST OF ABBREVIATIONS

AB	Activity balance
APS	Average particle size
BD	Bulk density (g/cc)
BOMAG	Butyloctyl magnesium
CE	Catalyst efficiency (g PE/g cat)
DE	1,3-Diether
De	External electron donor
DIBP	Diisobutylphthalate
DPMS	Diphenyldimethoxysilane
EB	Ethyl benzoate
ESCR	Environmental stress crack resistance
FTIR	Fourier transform infrared spectroscopy
MFI	Melt flow index
MFR	Melt flow ratio
MPT	Methyl-p-toluate
MWD	Molecular weight distribution
PE	Polyethylene
TEA	Triethylaluminium
Z-N	Ziegler-Natta
mg	Miligram
ml	Mililiters
phr	Part per hundred
vol	Volume

CHAPTER I

INTRODUCTION

Demand for polymerization catalyst in the US is forecasted to expand 5.5 percent annually to $1.1 billion in 2009, with a volume of 215 million pounds. Growth will derive primarily from increased polymer production and expanding use of higher value Ziegler-Natta and single-site catalysts. These catalysts, which find their greatest use in rapidly growing, large volume polyolefins, yield plastic resins that offer a variety of performance and processing advantages. Ultimately, demand for polymerization catalysts is highly dependent upon the production of various polymers. In particular, rapid growth in the production of polyethylene will boost catalyst demand [1].

1.1 Statement of problems

Demand for Ziegler-Natta catalyst will increase 5.2 percent annually to $565 million in 2009. Ziegler-Natta catalysts, the industry workhorses for the last 30 years, will continue to be widely used, largely due to the development and commercialization of fourth and fifth generation Ziegler-Natta products. These newer catalysts make Ziegler-Natta technology more competitive with single-site catalyst, and will ensure its continued market domination for the foreseeable future.

In low pressure process for polyethylene production, the data for year 2006 show that Ziegler-Natta catalyst based on silica based support contributed to 32%, Ziegler-Natta catalyst based on non silica support 24%, Chrome gas phase 17%, Chrome slurry phase 23%, and solution process 4% [1].

Since the discovery of $TiCl_3$ catalyst by Ziegler and Natta in 1950, catalyst activity and stereospecificities were so low that a step for removing catalyst residue (de-ashing) was needed in the commercial production process for polyolefins. Without the de-ashing, the polyolefins would have been colored and would have caused corrosion of the mold machines. These were enormous efforts to increase activity. In 1968, Norio Kashiwa discovered $MgCl_2$-supported $TiCl_4$ catalyst which brought about a breakthrough and led to innovative improvement of the properties of polyolefins and a drastic cut of the production costs.

The achievements by $MgCl_2$-supported $TiCl_4$ catalyst boosted the growth of the polyolefin industries by replacing not only $TiCl_3$-catalyzed products but also other materials such as paper, wood, metal, or engineering plastics. The favored method for increasing the activity of Ziegler-Natta catalyst was to support the active species on the surface of inorganic materials with chemical reactions. A reaction of $TiCl_4$ with the hydroxyl group on such a support as silica, alumina, or Mg(OH)Cl was regarded as a good tool. However, the activities of these catalysts were at most five times as high as those of the $TiCl_3$ catalyst [2].

A new concept to enhance the activity of Ziegler-Natta catalyst is to generate the Ti active species with liquid $TiCl_4$ on $MgCl_2$ where $MgCl_2$ should have been finely ground. $MgCl_2$ crystals belong to the same hexagonal group as $TiCl_3$, and Mg^{2+}, and Ti^{4+} have similar ionic radii, 0.68 and 0.65 angstrom, respectively. However, it was very difficult to plate $MgCl_2$ with $TiCl_4$ because $MgCl_2$ has high crystallinity, low specific surface area and no reactive groups for $TiCl_4$. One way to destroy $MgCl_2$ crystallinity was accomplished by adding such compound as n-butanol or methyl acetate and controlled re-crystallization of $MgCl_2$ by removing the added compound. $TiCl_4$ was incorporated onto the $MgCl_2$ surface during crystallization when an excess amount of $TiCl_4$ was used to remove the added compound. $MgCl_2$-supported $TiCl_4$ catalyst demonstrated more than 100 times higher activities than the $TiCl_3$ catalyst [2]. On the other hand high surface area of $MgCl_2$ could be prepared by the chemical reaction of dialkylmagnesium with chlorinating agent, but little work has been conducted on that route. $MgCl_2$-support $TiCl_4$ catalyst not only enhanced the activity but also narrowed the molecular weight and compositions of polyethylene. The $MgCl_2$-supported $TiCl_4$ catalysts were not single-site catalysts, but they allowed the active species to approach the single-site nature. It became possible to control PE structures more precisely. So, it was possible to design a film-grade HDPE consisting of a high-molecular-weight part having a high content of a comonomer and a low-molecular-weight part possessing a low content of the comonomer to accomplish both high film strength and high processibility.

1.2 Objective of the thesis

1.2.1 To synthesize and characterize Ziegler-Natta catalyst supported on $MgCl_2$ which is obtained from magnesium complex.

1.2.2 To investigate the reaction conditions for polymerization of ethylene and characterize the polyethylene.

1.3 Scope of the thesis

In this thesis, Z-N catalyst on magnesium chloride support was prepared via chemical reaction route through the steps of:

A) Reacting of butyloctyl magnesium with 2-ethyl-1-hexanol to obtain soluble magnesium complex. Viscosity of this complex was reduced with triethyl aluminium (TEA) in toluene.

B) Disordered $MgCl_2$ was prepared by chlorination of magnesium complex with chlorinating agent such as $TiCl_4$. Ethyl benzoate (EB) was used as morphology control agent.

C) Titanation step with $TiCl_4$.

D) Aging step

E) Decantation step

The invented catalyst was aimed to improve hydrogen sensitivity and activity balance under high and low H_2 concentration. Morphology of $MgCl_2$ and supported catalyst ($MgCl_2/TiCl_4$) was controlled by internal donor such as ethyl benzoate. In addition, the internal donors could control the amount of Ti fixed on $MgCl_2$ support. Isolated active sites of catalyst can enhance hydrogen response.

The following parameters were studied for catalyst preparation.

- Effect of TEA/Mg molar ratios
- Effect of Ti/Mg molar ratios
- Effect of EB/Mg molar ratios
- Effect of aging time
- Effect of aging temperature

Properties of Z-N catalysts were characterized by using infrared spectroscopy (IR), scanning electron microscopy (SEM), gas chromatography, and particle sizer. The catalysts were used for ethylene polymerization. Performances of the invented catalysts were examined with activity and hydrogen response balance (AB value). Properties of the resulted polymers were characterized by using melt flow indexer (MFI), scanning electron microscopy (SEM), particle sizer, gel permeation chromatography (GPC), and cone & plate rheometer.

CHAPTER II

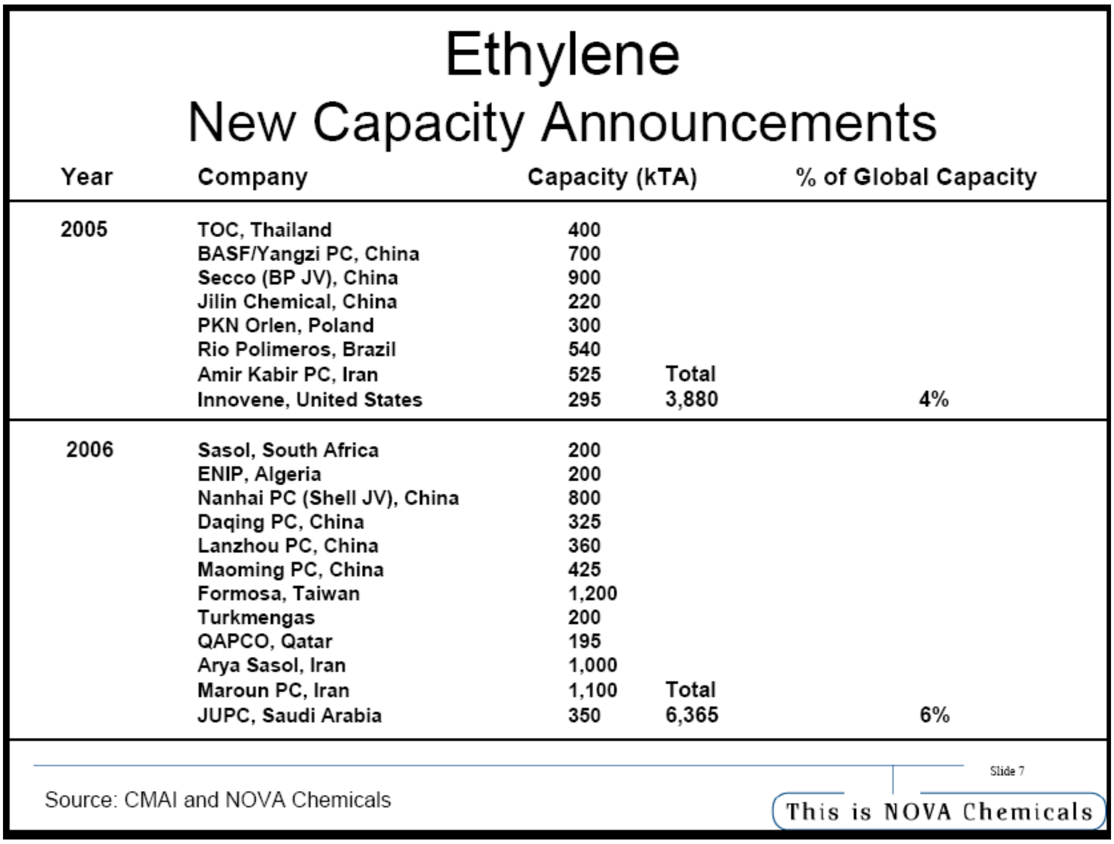
THEORY

2.1 Background

The Ziegler-Natta (Z-N) catalyst has been used in the olefin polymerization since it is discovered in 1950. Heterogeneous Z-N catalysts are the main systems among polyethylene catalysts and they are responsible for the production over tens of million tonnages of polyethylene per year. The process type besides the control of the polymerization conditions allows product with special properties to be obtained, which has been motivating the continuous study of these catalysts until now.

Due to broad range spectrum of physical properties of polyethylene, it became the largest tonnage commercial polymer, and the largest outlet for ethylene gas from petrochemical industry. From CMAI and NOVA chemical report, growing of ethylene is about 4-6% by annual from 2005 to 2008 and growing of polyethylene is also in the same level of ethylene. The key to its adaptability lies in its semi-crystalline morphology, which can be controlled by manipulating molecular and processing variables. Altering its molecular weight, co-monomer type, and co-monomer content can regulate toughness, hardness, clarity, and other physical properties characteristics. Manipulation of polyethylene prior to and during crystallization also influences its solid-state properties.

Polyethylene is sustainable commodity plastic. Growing of polyethylene is paralleled with ethylene in 2005 - 2008. Global new capacity of ethylene and polyethylene are growth about 4-6% annual. Among this growing, Middle East is the new biggest ethylene and polyolefins producer due to the fact that they have competitive in down stream and up stream. Growing of ethylene and polyethylene were shown in figure 2.1.



Ethylene

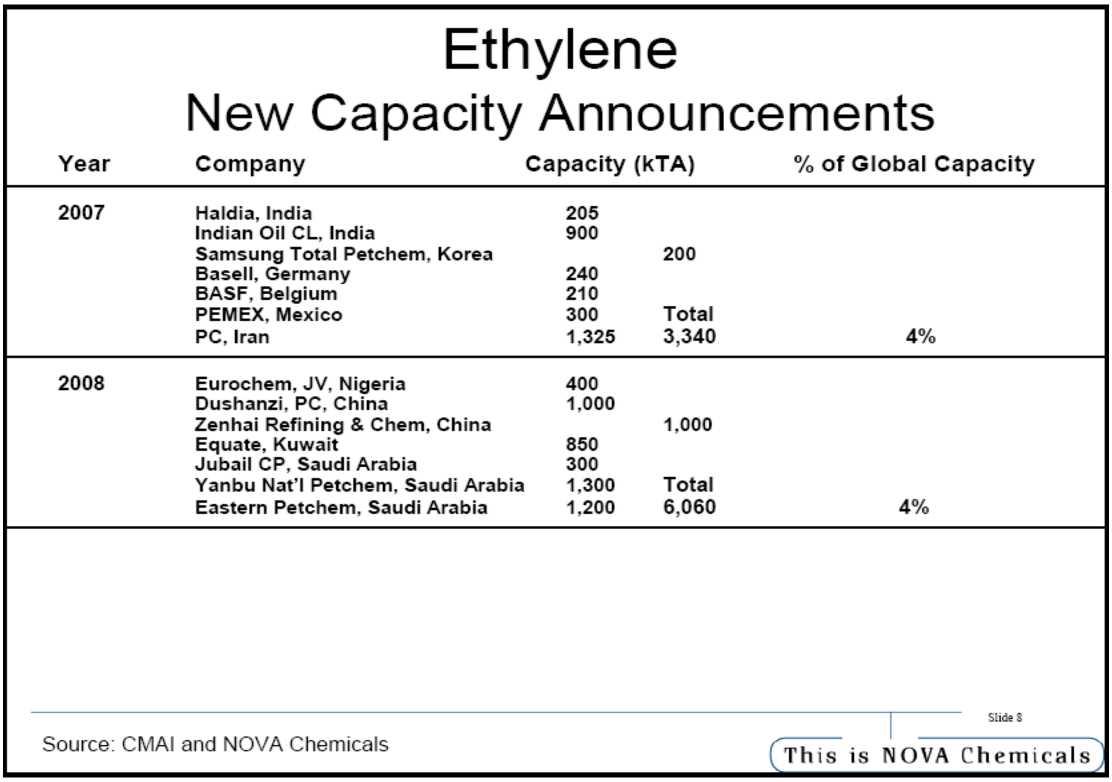
New Capacity Announcements

Year	Company	Capacity (kTA)		% of Global Capacity
2005	TOC, Thailand	400		
	BASF/Yangzi PC, China	700		
	Secco (BP JV), China	900		
	Jilin Chemical, China	220		
	PKN Orlen, Poland	300		
	Rio Polimeros, Brazil	540		
	Amir Kabir PC, Iran	525	Total	
	Innovene, United States	295	3,880	4%
2006	Sasol, South Africa	200		
	ENIP, Algeria	200		
	Nanhai PC (Shell JV), China	800		
	Daqing PC, China	325		
	Lanzhou PC, China	360		
	Maoming PC, China	425		
	Formosa, Taiwan	1,200		
	Turkmengas	200		
	QAPCO, Qatar	195		
	Arya Sasol, Iran	1,000		
	Maroun PC, Iran	1,100	Total	
	JUPC, Saudi Arabia	350	6,365	6%

Source: CMAI and NOVA Chemicals

Slide 7

This is NOVA Chemicals



Ethylene

New Capacity Announcements

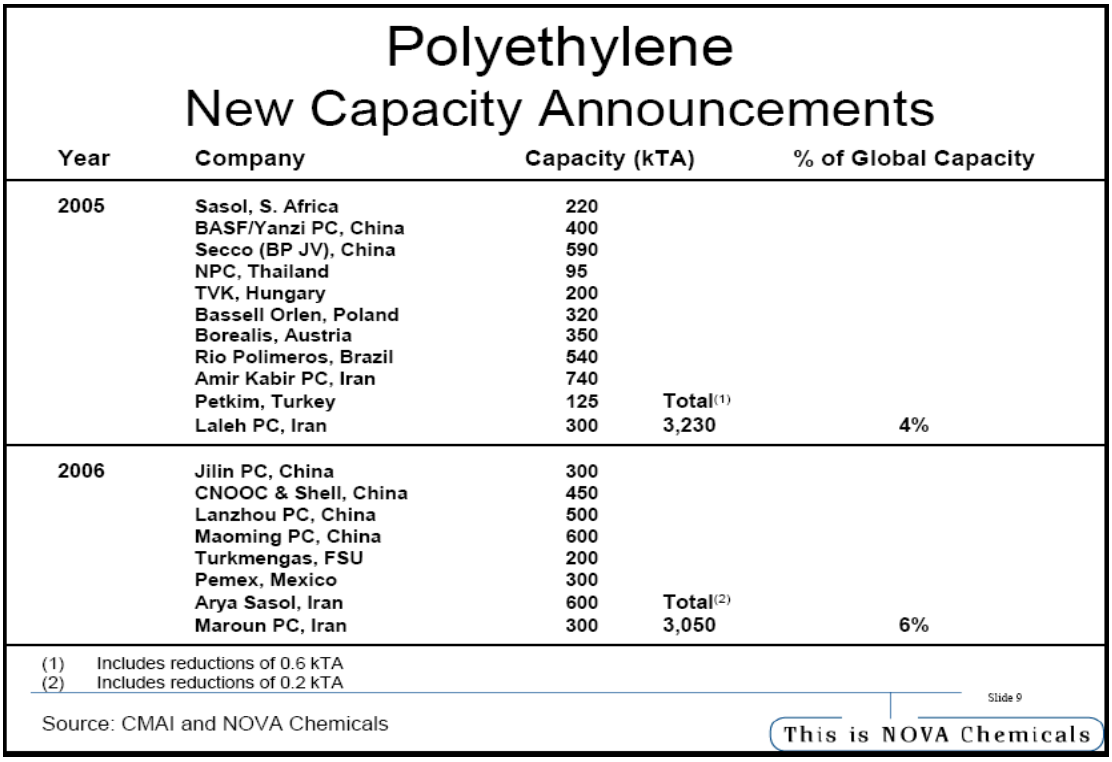
Year	Company	Capacity (kTA)		% of Global Capacity
2007	Haldia, India	205		
	Indian Oil CL, India	900		
	Samsung Total Petchem, Korea		200	
	Basell, Germany	240		
	BASF, Belgium	210		
	PEMEX, Mexico	300	Total	
	PC, Iran	1,325	3,340	4%
2008	Eurochem, JV, Nigeria	400		
	Dushanzi, PC, China	1,000		
	Zenhai Refining & Chem, China		1,000	
	Equate, Kuwait	850		
	Jubail CP, Saudi Arabia	300		
	Yanbu Nat'l Petchem, Saudi Arabia	1,300	Total	
	Eastern Petchem, Saudi Arabia	1,200	6,060	4%

Source: CMAI and NOVA Chemicals

Slide 8

This is NOVA Chemicals

Figure 2.1. Ethylene and polyethylene new announcements in 2005 – 2008.



Polyethylene
New Capacity Announcements

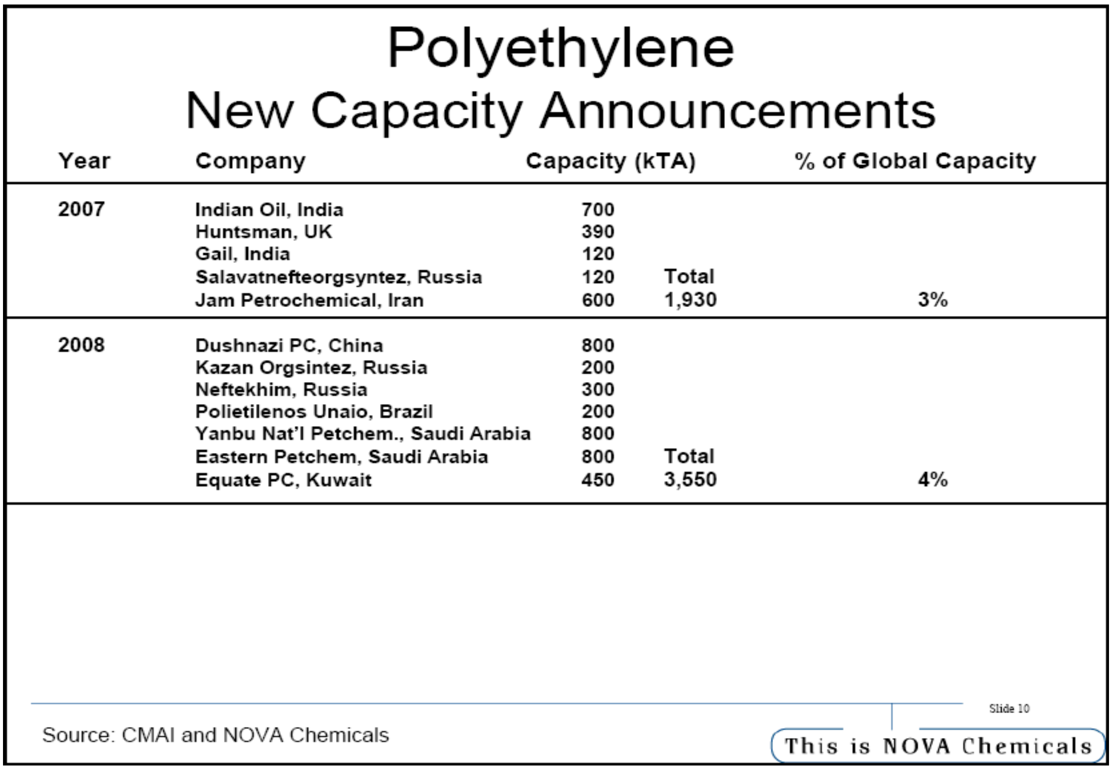
Year	Company	Capacity (kTA)		% of Global Capacity
2005	Sasol, S. Africa	220		
	BASF/Yanzi PC, China	400		
	Secco (BP JV), China	590		
	NPC, Thailand	95		
	TVK, Hungary	200		
	Bassell Orlen, Poland	320		
	Borealis, Austria	350		
	Rio Polimeros, Brazil	540		
	Amir Kabir PC, Iran	740		
	Petkim, Turkey	125	Total(1)	
	Laleh PC, Iran	300	3,230	4%
2006	Jilin PC, China	300		
	CNOOC & Shell, China	450		
	Lanzhou PC, China	500		
	Maoming PC, China	600		
	Turkmengas, FSU	200		
	Pemex, Mexico	300		
	Arya Sasol, Iran	600	Total(2)	
	Maroun PC, Iran	300	3,050	6%

(1) Includes reductions of 0.6 kTA
(2) Includes reductions of 0.2 kTA

Slide 9

Source: CMAI and NOVA Chemicals

This is NOVA Chemicals



Polyethylene
New Capacity Announcements

Year	Company	Capacity (kTA)		% of Global Capacity
2007	Indian Oil, India	700		
	Huntsman, UK	390		
	Gail, India	120		
	Salavatnefteorgsyntez, Russia	120	Total	
	Jam Petrochemical, Iran	600	1,930	3%
2008	Dushnazi PC, China	800		
	Kazan Orgsintez, Russia	200		
	Neftekhim, Russia	300		
	Polietilenos Unaio, Brazil	200		
	Yanbu Nat'l Petchem., Saudi Arabia	800		
	Eastern Petchem, Saudi Arabia	800	Total	
	Equate PC, Kuwait	450	3,550	4%

Slide 10

Source: CMAI and NOVA Chemicals

This is NOVA Chemicals

Figure 2.1. (Cont.) Ethylene and polyethylene new announcements in 2005 – 2008.

2.2 The advent of high density polyethylene

Prior to the major discoveries of Karl Ziegler's research group in West Germany and the researchers of Phillips Petroleum in the United States, short chain branching polyethylene had been produced by Imperial Chemical Industries (ICI) in 1936. Then, the pilot plant was established in 1937 and commissioned in 1942. The classes of polymerization of catalysts can be distinguished:

1. Phillips-type catalysts, which are composed of a chromium oxide supported on an amorphous material such as silica (e.g. Cr/SiO_2).

2. Ziegler-Natta catalysts, which consist of a combination of titanium trichloride and an alkylaluminium chloride, mostly supported on $MgCl_2$ (e.g. $TiCl_3$-$Al(C_2H_5)_3/MgCl_2$); an

3. Single site metallocene catalysts, which are bis-cylopentadienyl derivatives of either Zr, Hf or Ti combination with methylaluminoxane (e.g. Cp_2ZrCl_2-$[MeAlO]_n$).

4. Constrained geometry catalyst (CGC), a catalyst containing a pendant arm on the cyclopentadienyl ring which can chelate to the metal center through a lone pair of nitrogen atom. The donor atom can either occupy a vacant coordination site in the neutral molecule or it can be free hence available to coordination with the active metal. The catalysts have received considerable industrial interest because of the ability both to polymerize ethylene to propylene containing long-chain branching and to copolymerize ethylene with α-olefins to give polymers containing high proportions of α-olefins e.g. $(C_5R_4CH_2CH_2NMe_2)TiCl_3$ (R = Me), $(C_5H_4SiMe_2N^tBu)M(CH_2Ph)_2$(M = Ti, Zr). When activated with $B(C_6H_5)_3$, $B(C_{12}F_9)_3$ and $[Ph_3C]^+[B(C_6F_5)_4^-$, these compounds formed very active catalysts for ethylene and propylene polymerization, yielding ultrahigh molecular weight linear polyethylene and high molecular weight, atactic polypropylene.

5. The recently most advance post metallocene or non-metallocene, which is supra-molecular control over the long range molecular polymer chains (e.g. in Figures 2.2 - 2.4).

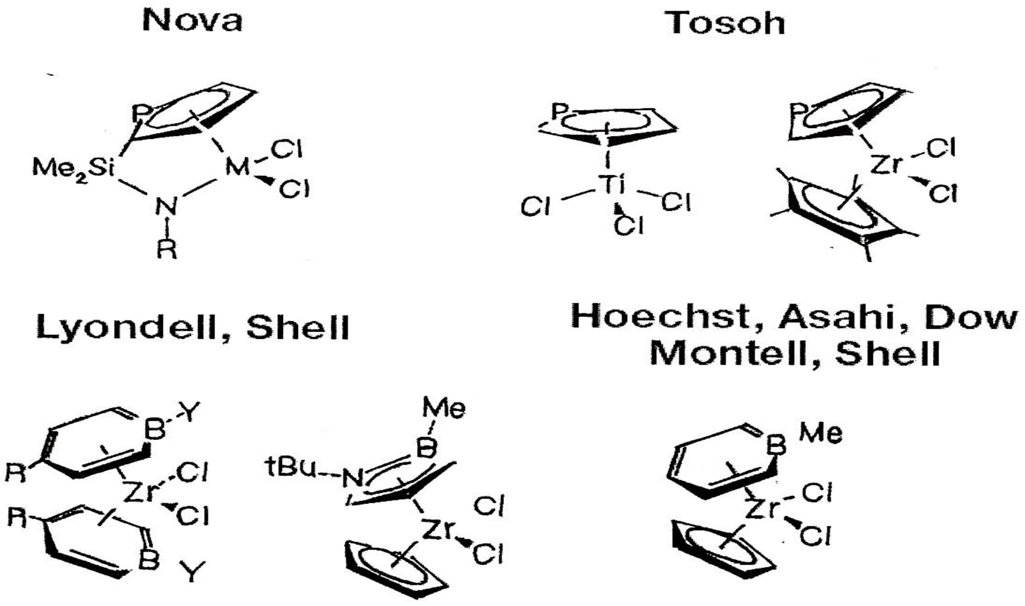


Figure 2.2. Non-metallocene ligand-based catalysts: Heteroatom cyclic complexes.

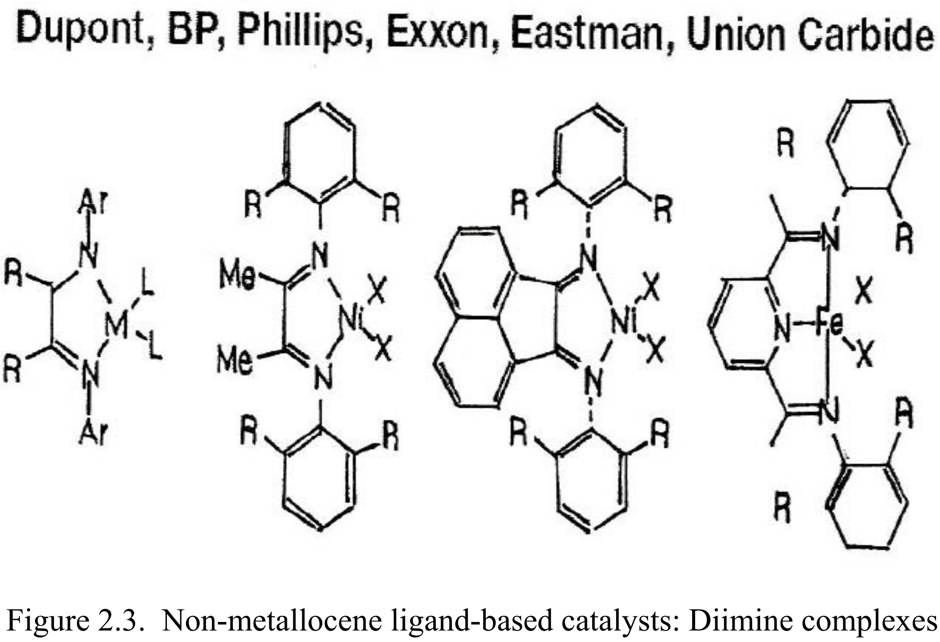


Figure 2.3. Non-metallocene ligand-based catalysts: Diimine complexes.

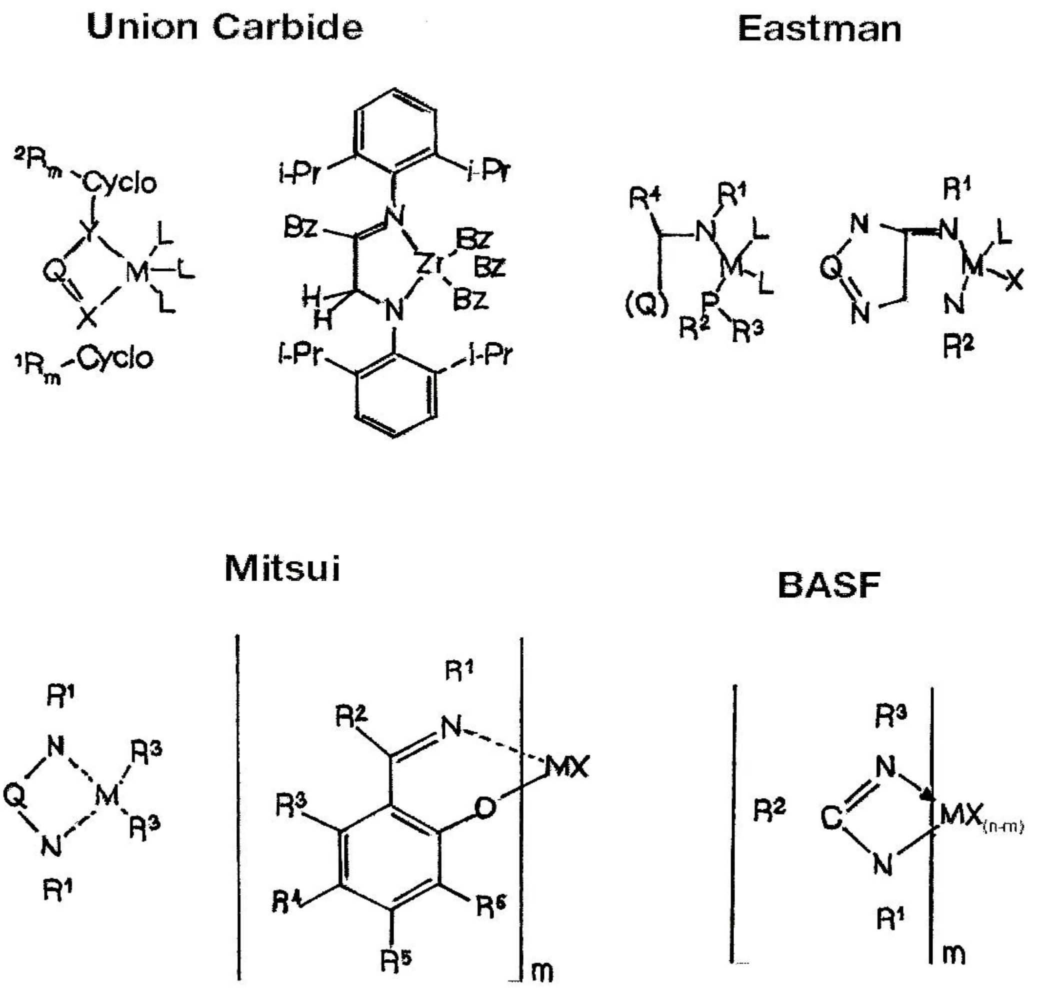


Figure 2.4. Non-metallocene ligand-based catalysts: Heteroatom chelates.

2.2.1 Ethylene polymerization process

2.2.1.1 The Phillips process

About the same time that Ziegler group was working on the polymerization of ethylene using transition metal organic complexes, researchers at the Phillips Petroleum company in the United States investigated a similar reaction catalyzed by various supported transition metal oxides. Experiment with ethylene as the feed stock resulted in the production of high molecular weight ethylene polymer. Their product proved to be similar to the high density polyethylene produced by Ziegler's low pressure, low temperature polymerization process. The Phillips reaction took place in a hot solvent at the modest pressure (relative to the low density polyethylene process) of 500 psi, using a supported chromium oxide as the catalyst. Subsequently the Phillips high density polyethylene was found to have a slightly higher density than Ziegler-Natta type of materials, indicating a greater degree of linearity.

2.2.1.2 The Standard oil process

Concurrent with the development of the Phillips process, Standard Oil of Indiana developed a similar ethylene polymerization process. The basis of this process was the catalysis of ethylene to high density polyethylene using a supported molybdenum oxide catalyst under relatively modest conditions of temperature and pressure. The product has a range of densities similar that available from the Phillips process.

2.2.1.3 Ziegler-Natta type catalyzed copolymerization

Ziegler-Natta catalysis is one of the two method used commercially to produced high density polyethylene, the other being metal oxide catalysis. Ziegler-Natta catalyst consists of a complex of a base metal from groups I-III used in combination with transition metals from groups IV-VIII. A classic complex example is the complex of triethyl aluminium ($AlEt_3$) with titanium tetrachloride ($TiCl_4$). Ziegler-Natta catalysts used in the solution polymerization are homogeneous catalyst, while those used in gas-phase reactors are supported on materials such as silica, magnesium dichloride. Products of Ziegler-Natta catalysts depend on the polymerization conditions, types of comonomer feed stock and nature of the catalysts. Other evidences among the new form of polyethylene with its negligible branching displayed many properties that were superior to those of the highly branched resins previously available. Among the significant improvements was a softening point elevated by approximately 30°C over those of product of the high pressure process. Other improvements lay in the fact that its stiffness and strength were also increased. With its higher degree of crystallinity and higher density it was named as high density polyethylene (HDPE), whereas the older type of polyethylene was known as low density polyethylene (LDPE).

2.3 Classification of polyethylene

Polyethylene is classified into several different categories based mostly on its mechanical properties. The mechanical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure, and the molar mass.

UHMWPE (ultra high molecular weight polyethylene)

This is polyethylene with a molar mass of usually between 3 and 6 million grams per mol. The high molar mass generates good packing of the chains into the crystal structure. This results in a very tough material. UHWPE is made through metallocene catalysis polymerization. It is used in high modulus fibers and in bulletproof vests.

HDPE (high density polyethylene)

This type of polyethylene has only little amount of short-chain branching and thus stronger intermolecular forces and tensile strength. The lack of branching is ensured by an appropriate choice of catalyst (e.g. Ziegler-Natta or metallocene catalysts) and reaction conditions. HDPE is used in plastic bags.

LDPE (low density polyethylene)

LDPE has many more branches ad branches on branches than HDPE, which means that the chains do pack into the crystal structure as well. It has therefore less strong intermolecular forces because the instantaneous-dipole induce-dipole attractions weaker. This results in a low tensile strength and increased ductility. LDPE is created by free radical polymerization.

LLDPE (linear low density polyethylene)

LLDPE is a substantially linear polymer, with significant numbers of short branches, commonly made by copolymerization of ethylene with longer olefins. It is made with Ziegler-Natta catalyst or metallocene catalysts. LLDPE is used primarily in flexible tubing and films.

2.4 Types of Ziegler-Natta catalyst

2.4.1 Homogeneous catalyst

Homogeneous Ziegler-Natta catalysts were examined in detail in the late 1950s by Breslow et al. for ethylene polymerization using bis(cyclopentadienyl)-titanium dichloride and organoaluminium chlorides. Zirconium metallocene combined with methyl aluminoxane co-catalyst can also polymerize α-olefins and it could be modified to prepare isotactic polypropylene.

2.4.2 Heterogeneous catalyst

In the past 10-15 years, a new technology has been developed based heterogeneous catalysts consisting of titanium chlorides supported on $MgCl_2$. These catalysts are much more effective, giving high rates, and high stereospecificity. Today, isotactic polypropylene is made probably > 80% with these new $MgCl_2$ based supported Z-N catalysts.

2.5 Types of support

Supported catalysts are used in industry to manufacture isotactic polypropylene. The supports studied are following: silica (SiO_2), alumina (Al_2O_3) and magnesium chloride ($MgCl_2$). Some other materials have been investigated such as zeolite, MgO, MgF_2, CaF_2 and AlF_3.

Silica (SiO_2)

Silica can be synthesized with a wide range of surface area, porosity and pore volume. Silica gel (HS) has a maximum number of eight Bronsted acidic OH groups per nm^2 (4 mmol OH/g) for silica with a surface area of approximately 300 m^2/g. Heat treatment of silica gel at 200°C gave a partially dehydroxylated silica having 2.3 mmol OH/g, half of which as geminal hydroxyl pairs and the other half as vicinal pairs. Above 600°C, a material referred to as dehydroxylated silica (DS) is obtained, which contains only 0.7 mmol OH/g.

Alumina (Al_2O_3)

Dehydroxylated alumina (DA) has ca 0.12 Bronsted acidic OH groups, ca 5.5 Lewis acidic Al^{3+} center and ca 5.5 Lewis basic oxide group per nm^2.

Magnesium dichloride ($MgCl_2$)

Two crystalline structures are known for $MgCl_2$, the commercial α-form and the less stable β-form. The α-form has a layer structure of $CdCl_2$ type and shows a cubic close-packed stacking (ABABC) of double chloride layers with interstitial Mg^{+2} ions in sixfold coordination. The β–form shows close packing like that of α-$TiCl_3$. There are two lateral cuts, coordination number 4 on the (110) cut and 5 on the (100) as shown in Figure 2.5.

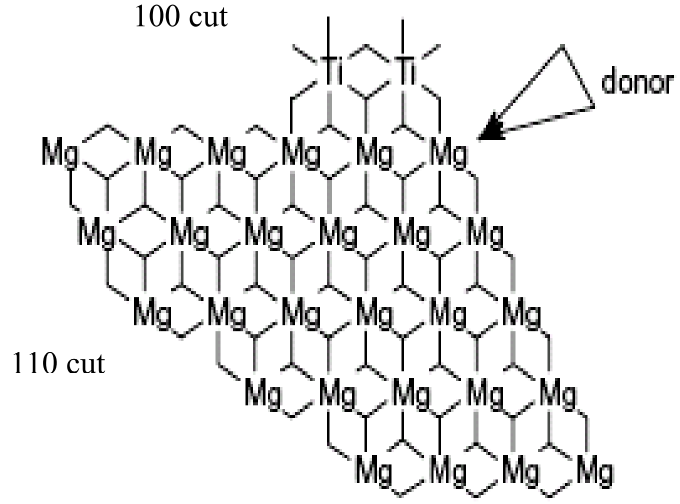


Figure 2.5. Model structure of $MgCl_2$ layers showing the (100) and (110) cuts and a position of a donor on a 4-coordinated Mg in the $MgCl_2$ crystal.

Surface properties of various supports are shown in Table 2.1

Table 2.1 Surface area and pore diameters of supports

Support	Surface area (m^2/g)	Pore diameters (nm)
Silica	50-800	2-200
Alumina	100-300	2-100
Magnesium chloride	10-250	-

2.6 Chemistry of Ti metal on $MgCl_2$ support

The structure of $TiCl_4/MgCl_2$ catalyst was proposed by the study of EXAFS. The experimental data are best described with a dimeric $TiCl_4$ adsorbed on an $MgCl_2$ (100) face. Each Ti atom has three Cl atoms at 2.1 Å in the first coordination sphere, one symmetric bridging chlorine atom at 3.0 Å, another asymmetric at 3.9 Å and finally one Mg atom at 3.6 Å and one Ti atom at 3.95 Å (as represented by site (4) in Figure 2.6). Such an asymmetric structure would explain the case of alkylation by alkylaluminium, because access to the Ti atom is favored.

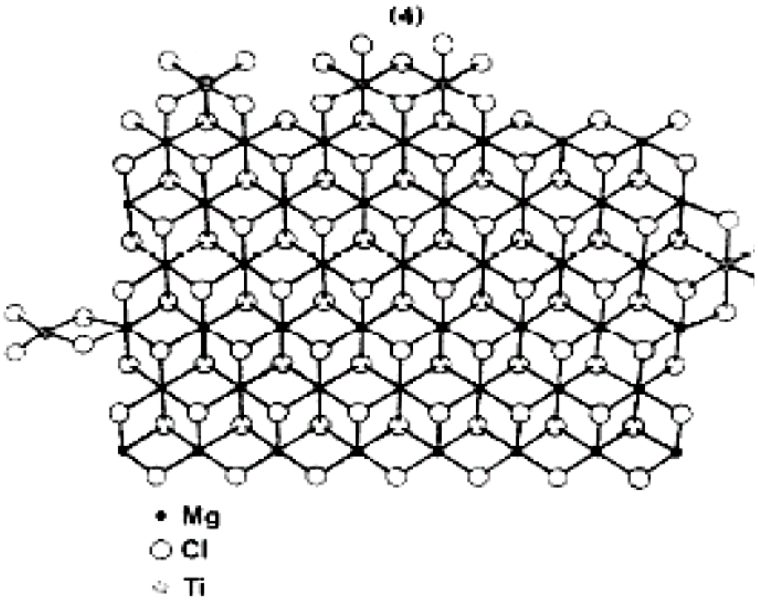


Figure 2.6. Structure of $TiCl_4$ on $MgCl_2$ surfaces.

2.6.1 Reaction of Lewis base with titanium complex

Lewis base is used to improve the stereospecific control. Lewis base must be added to both the catalyst and the cocatalyst. Properly chemical matching is necessary for catalyst system as indicated in Tables 2.2 and 2.3.

Table 2.2 Performance of the different catalyst generations

Generation	Composition	Productivity[a] (kg PP/g cat.)	Isotactic index (wt %)
1st	δ-$TiCl_3$ + 0.33$AlCl_3$+DEAC	0.8-1.2	90-94
2nd	δ-$TiCl_3$+DEAC	3-5 (10-15)	94-97
3rd	$TiCl_4$/ester/$MgCl_2$+TEAl/ester	5-10 (15-30)	90-95
4th	$TiCl_4$/diester/$MgCl_2$+TEAl/silane	10-25 (30-60)	90-99
5th	$TiCl_4$/diether/$MgCl_2$+TEAl	25-35 (70-120)	95-99
6th	Zirconocene + MAO	($5-9.10^3$) (on Zr)[b]	90-99[c]

[a] Polymerization: hexane slurry, 70°C, 0.7 MPa, 4 hrs, H_2 for MW control (value in brackets are from bulk polymerization for 2 hrs at 70°C, with H_2)

[b] one hour polymerization time

[c] mmmm% (by ^{13}C NMR)

Table 2.3 Performance of $MgCl_2$ supported catalyst with different Lewis bases

Catalyst	Cocatalyst	Maximum isotactic Index (wt %)	Remarks
$MgCl_2/TiCl_4$	$AlEt_3$	50	-
	$AlEt_3$/MPT	90	De/Al $\geq$ 0.3
$MgCl_2/TiCl_4$/EB	$AlEt_3$	60	Normal Al/Ti
		90	Very low Al/Ti
	$AlEt_3$/MPT	95	De/Al $\geq$ 0.3
$MgCl_2/TiCl_4$/DIBP	$AlEt_3$	70-80	All Al/Ti
	$AlEt_3$/DPMS	95-99	De/Al $\geq$ 0.02
$MgCl_2/TiCl_4$/DE	$AlEt_3$	95-99	Depending on De/Ti

EB = Ethylbenzoate;
MPT = Methyl-p-toluate;
DIBP=Diisobutylphthalate;
DPMS=Diphenyldimethoxysilane;
DE = 1,3-Diether

2.7 Mechanism of olefins polymerization

Mechanism proposed by Cossee and Arlman is the most acceptable one. The polymerization chain is growing via a cis-insertion of the olefin into a metal-carbon bond (migratory insertion mechanism, in which the metal-bound alkyl group migrates to the alkene) as in figure 2.7. In the Cossee mechanism (see Figure 2.7), a vacant coordination site is generated initially, followed by olefin complexation. Formal migration of the polymer chain, P, and formation of the metal-carbon bond occur concertedly through a four-center transition state. This recreates a vacant coordination site at the site originally occupied by the polymer chain and the process continues; the growing polymer chain terminus flips from site to site.

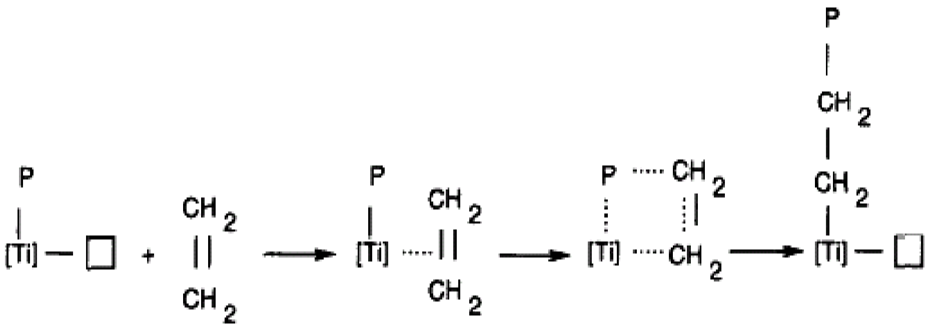


Figure 2.7. Cossee-Arlman mechanism.

2.8 Replication and polymer morphology

The polymer usually tends to duplicate, on a large scale, the physical characteristics (shape and texture) of the parent catalyst. This phenomenon usually called “replication”. A large body of experimental evidence demonstrates that the phenomena usually take place as follows:

1. As soon as the polymerization starts, the catalyst grain begins to disrupt into a huge number of small fragment. This process is very fast and proceeds to the crystallite dimensions or even smaller.

2. The catalyst fragment, though no longer in contact with each other, are kept together and uniformly dispersed in the polymer acting as a “cement.”

3. The fragments are spread outward as the particle grows but still remain uniformly distributed across the particle cross section. This implies that the polymer growth occurs around each fragment.

As far as the catalyst is concerned, a proper balance between reactivity and mechanical properties appear necessary, and this is possible only if the following requirements are met:

- High surface area;
- High porosity with a large number of cracks evenly distributed.
- High enough mechanical resistance to withstand handling, but low enough to allow breakage into microscopic particles during the polymerization;

- Homogeneous distribution of the active centers; and
- Free access of the monomer up to the innermost zones.

On the other hand, the polymerization conditions must be such as to avoid mass transfer limitation phenomena, which could result in an uneven polymerization rate across the particle.

2.9 Bimodal and multi-modal HDPE polymerization

In all the low pressure PE processes the polymer is formed through coordination polymerization. Three basic catalyst types used are: chromium oxide, Ziegler-Natta and single-site catalysts. The catalyst type together with the process defines the basic structure and properties of polyethylene produces. Apart from the MWD and comonomer distribution that a certain catalyst produces in polymerization in one reactor, two or more cascaded reactor with different polymerization conditions increase the freedom to tailor polymer properties by in-situ blending of two or more structurally different polyethylenes. Mostly, the bimodal process technology has been used to improve processibility, stiffness-impact balance, environmental stress crack resistance (ESCR) and high slow crack growth resistance (SCG), etc.

In bimodal and/or multimodal process, the catalyst is fed into the 1st reactor where the first polymer fraction which may be low MW or high MW is produced (see figure 2.8). After that the polymer is transferred into the 2nd reactor to produce the second polymer fraction. Depending on the process type used, between the reactors there may be a separation unit to remove unreacted monomer, hydrogen, etc. before the polymer is passed into the second reactor. In principle, the bimodal process operates under two different polymerization conditions. However, the weak point of Z-N catalyst is that the catalyst activity decreases irreversibly under polymerization condition of high hydrogen concentration. Consequently the polymer molecular weight fraction control is unbalanced. High catalyst amount must be fed into the 1st reactor to maintain the required fractions and the production rate. Moreover, the polymer contains high catalyst residues and high stabilizer levels need to be added to serve the service life of end-products. Consequently, highly balanced hydrogen response and activity of Ziegler-Natta catalysts are play important roles in those processes. In general, AB of catalyst was expressed by $AB = [\text{avg.CA} \times \log(MFI_2^*/MFI_2)]/|\Delta CA|$ where MFI_2^* = melt flow index at high H_2 pressure, MFI_2 = melt flow index at low H_2 pressure, CA = catalyst activity (g PE/g cat). The higher catalyst activity in low and high hydrogen pressure, the higher AB value was found.

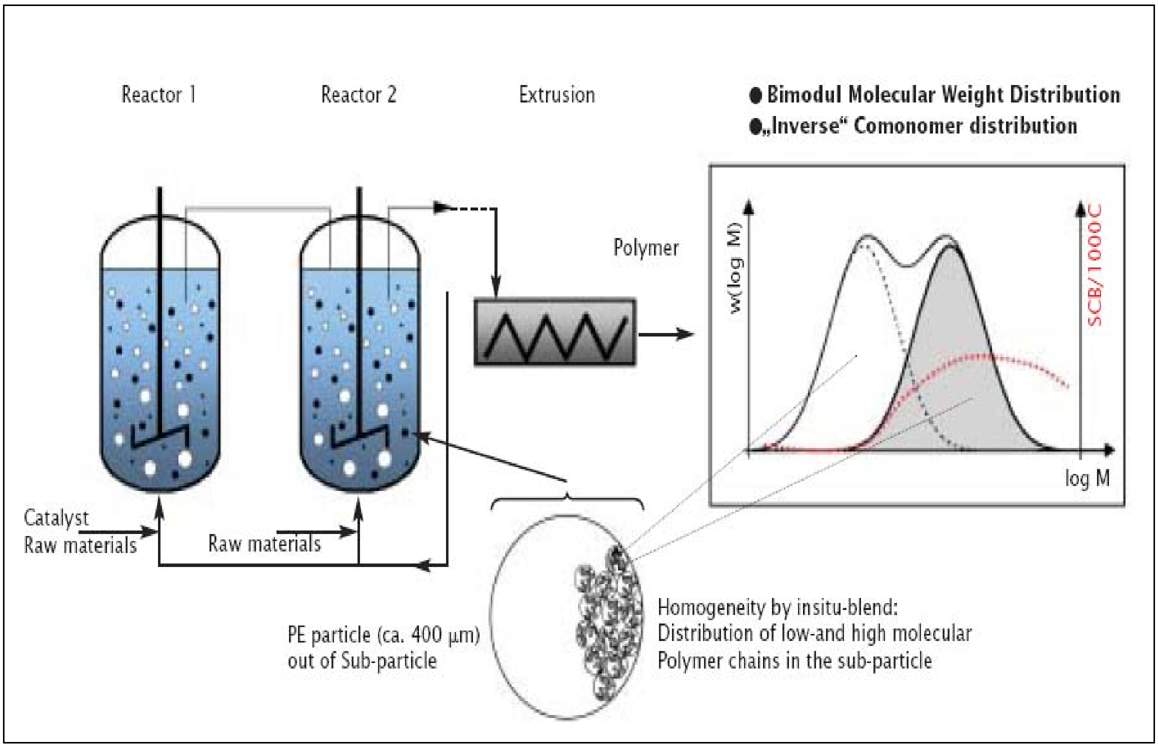


Figure 2.8. Bimodal molecular weight distribution production in Hostalen process.

CHAPTER III

LITERATURE

Many researchers pay enormous effort to improve catalyst efficiency and other performance of the traditional Ziegler-Natta catalyst using magnesium chloride support. A lot of work has been done to study effect of various parameters on the properties of catalysts and polymer as described below.

In 1975, MITSUI TOATSU CHEMICALS, INCORPORATED [3] disclosed a process for the polymerisation of ethylene. Ziegler-Natta catalyst was prepared by impregnation of titananum tetrachloride on anhydrous magnesium chloride, polysiloxane and organoaluminium compound via co-pulverizing using ball milling, column mill or jet in a range temperature of -30°C to 150°C. The catalyst gave high catalyst activity (17 Kg PE/g of cat.) and very high in ethylene copolymerization with 1-butene (up to 33 Kg/g of cat.). Molecular weight distribution was 6.5. However, specific surface area of catalyst is small, only 1.4 m^2/g and resultant polymers had low bulk density.

In 1995, Garoff et al. [4] prepared a procatalyst by mixing treated SiO_2 support with ethylaluminium dichloride (EADC) to obtain $Si–O−Al−Cl_2$ groups and free ethylaluminium dichloride as internal cocatalyst existed in SiO_2 support. Magnesium complex of butyloctyl magnesium and 2-ethyl-1hexanol was prepared and then deposited on SiO_2 support particles. The catalyst was suitable for gas phase polymerization.

In 1998, Hidryckx et al. [5] prepared supported catalyst by reacting organomagnesium with alkylaluminum compound in inert hydrocarbon at room temperature and with n-propyl alcohol to obtain di n-proproxy magnesium/tri n-proproxy aluminum complex. Tetrabutoxy titanium was added to obtain di n-proproxy magnesium/tri n-proproxy aluminum/tetrabutoxy titanium complex. After that solution of ethylaluminum dichloride (EADC) was added and stirred for 12 hours. It was found that the catalyst activity was enhanced (from 239 to 7950 kg PE/ g Ti. h) when Ti content in catalyst was reduced (Al/Ti/Mg from 55/2/10 to 55/0.03/10).

In 2002, Leinonen et al. [6] disclosed the process for preparing a catalyst with improved high temperature activity in propylene polymerization. The steps of preparation comprised of reacting a compound of butyloctyl magnesium with 1, 2-phthaloyl dichloride as electron donor in toluene, then adding solution of complex to titanium tetrachloride solution to produce an emulsion. The catalyst activity was improved 1.4 times when increasing the polymerization temperature from 70°C to 80°C. The catalyst stability was also improved. However, it showed broad particle size distribution.

In 2003, Jin et al. [7] prepared a catalyst for ethylene polymerization by mixing anhydrous magnesium with toluene, epoxy chloropropane, tributyl phosphate and ethanol. Titanium tetrachloride was dropwise added, and then the temperature was raised to 80°C. The solid catalyst contained 1.92 wt % Ti, 17.5 wt % Mg, 56.5 wt % Cl, 13.2 wt % tributyl phosphate. The specific area was 290 m^2/g. Activity of the catalyst was 80 kg PE/g cat.

In 2004, Thorman et al. [8] prepared a Ziegler-Natta catalyst for polymerization of propylene. Butylethyl magnesium (BEM) was reacted with an alcohol to form a magnesium alkoxide compound, followed by contacting with a phosphorous compound to form a magnesium alkoxide phosphorous mixture. This was subsequently reacted with titanium tetrachloride to form a predominantly magnesium chloride support. Then, internal donor, di-n-butylphthalate was mixed to form a catalyst slurry. The addition of titanium tetrachloride was repeated twice more. Catalyst activity was 36 kg PP/g cat. h. and xylene soluble value is less than 3.6 wt.%. Fine content (under 106 μm) was less than 1 wt%.

In 2005, Wolf et al. [9] prepared and characterized heterogeneous Ziegler-Natta catalysts for the production of HDPE. The catalyst was formed from titanium tetrachloride and magnesium ethoxylate. Activity of catalyst decreased as a function of annealing during catalyst synthesis. Annealing transforms site of the $Ti(OCH_2CH_3)_nCl_{4-n}$ chlorinate type into Ti-O-Ti, with ethyl chloride elimination.

In 2006, Douglas et al. [10] used aluminium oxide (particle diameter of less than 5 μm) as a seed to crystallize magnesium chloride from solution. This was used as a support for Ziegler-Natta catalyst. The catalysts particles were uniform and had large surface area.

There are some works reported on activity and high hydrogen response Ziegler-Natta catalyst for ethylene polymerization. Most of the catalysts synthesis derived from chemical reaction route or melting and recrystallization of $MgCl_2$. However, Ziegler-Natta catalyst prepared by the chemical route showed many advantageous such as high hydrogen response, large polymer particle, very low fine polymer content and high bulk density.

In 2001, Chen, et al. [11] disclosed a new synthesis method of a Ziegler-Natta catalyst using a multi-step process. The catalyst was synthesized form following steps:

A) Preparation of magnesium complex by reacting butylethyl magnesium (BEM) with 2-ethyl-1-hexanol and triethyl aluminium (TEA) was used as viscosity reducing agent.

B) Chlorination of magnesium complex with or without monochlorotitanium compound in the presence of diisoamyl ether (DIAE). Methyltrichlorosilane was used as particle controlling agent. Efficiency of catalyst was 64,000 g PE/g cat. with low fine fluff particle content. Average catalyst particle sizes were in the range of 10-19 µm. The catalyst showed good hydrogen response.

In 2005, Zhu et al. [12] disclosed a method of making the catalyst system/supports for the polymerization of ethylene. A support was made from a reaction of magnesium compound, an alkyl silicate, a monoester and organoaluminum compound. Then, it was treated with $TiCl_4$. The catalyst particle size was 11-16 µm. The average diameter of particles of both catalyst and resultant polyethylene were larger when the catalyst support was made with an alkyl silicate and monoester. Also, melt flow index of the resultant polyethylene was higher. Activity of catalyst was about 37-55 kg PE/g cat. Particle size of polymer was 490-500 µm. The catalyst had good stability during polymerization process. The content of fine particle was notably lower.

In 2005, Steven et al. [13] disclosed a Ziegler-Natta catalyst for tuning MWD of polyolefin. The catalyst was prepared with multi-step preparation including the steps of (a) reacting ethylbutyl magnesium with 2-ethyl hexanol in the presence of triethyl aluminium and diisoamyl ether to provide soluble intermediate A, (b) reacting soluble intermediate A with monochlorotitanium triisoproproxide to provide intermediate B, (c) first titanation intermediate B with mixture of tetrabutoxy magnesium and titanium tetrachloride to provide precatalyst, (d) second titanation and activation with triethyl aluminium (TEA) at 90°C. Molecular weight distribution (MWD) of polymer increased with increased treatment time.

In 2005, Knoeppel et al. [14] disclosed Ziegler-Natta catalyst for polyolefins. The catalyst was prepared with the steps of (a) reacting ethylbutyl magnesium with 2-ethyl-1-hexanol in the presence of triethyl aluminium and diisoamyl ether as viscosity reducing agent, (b) reacting solution from step (a) with monochloro titanium triisopropoxide to provide intermediate A, (c) titanation of intermediate A with $TiCl_4$ for several times and activated with triethyl aluminium. An increased amount of TEA significantly increased catalyst particle and fluff morphology.

In 2006, Chang et al. [15] described morphology of a $TiCl_4/MgCl_2$ Ziegler-Natta catalyst prepared by forming toluene-soluble complex of $MgCl_2$ with epichlorohydrin and tributyl phosphate. The organic component was removed from the complex using excess $TiCl_4$. Heating resulted in precipitation of spherical $MgCl_2$ particle of which Ti distribution was homogeneous.

In 1986, Busico et al. [16] proposed a model for the active sites on the magnesium chloride crystal surfaces. Titanium (III) atoms located on the (100) cuts of magnesium chloride produced isotactic polymer, whereas isolated titanium (III) atoms on the (100) and (110) cuts give atactic polymer. They also proposed that internal ethyl benzoate predominately adsorbs on more acidic site, the (110) face, to prevent titanium tetrachloride forming non-stereospecific site. The external ethyl benzoate prevents the extraction of internal ethyl benzoate as well as deactivates the non-stereospecific site. Internal ethyl benzoate and external ethyl benzoate were coordinated on the (100) surface of magnesium chloride to form the highly isospecific site which has only one vacant site. As a consequence, the formation of bi- or multinuclear titanium species, which easily transform to non-stereospecific sites by the migration of a bridged chloride ligand, is inhibited.

In 1983 and 1988, Kashiwa and Yoshitake [17] disclosed the effect of external ethyl benzoate on the polymerization activity and molecular weigh of polypropylene by using the $TiCl_4/MgCl_2$-$AlEt_3$ catalyst system. They reported that an appropriate external ethyl benzoate amount addition can kill the non-stereospecific sites and further increase in propagation rate constant on isotactic polymerization.

In 1983, Chien [18] reported magnesium chloride support Ziegler-Natta catalyst (called CH-type catalyst) when the catalyst was prepared from soluble magnesium compounds. In-situ dioctyl phthalate (DOP) was used as internal donor which was derived from the reaction of phthalic anhydride and 2-ethyl -1-hexanol during the catalyst preparation. $MgCl_2$ contains dioctyl phthalate (DOP) while hydrochloric acid will liberate during the titanation step.

Morphology of fluff polymer is very important in polymerization of fluidize bed process, gas phase process, also slurry process, and combined slurry with gas phase process. Those processes desired good morphology of both catalysts and polymers. Good morphology of catalysts and polymers can prevent reactor fouling, improve polymer fluff and medium separation, increase efficiency of drying process, and also increase transportation. Many research works have been done on magnesium chloride containing organosilane. They are described as follow:

In 1998, Anonio et al. [19] disclosed a Ziegler-Natta catalyst supported on magnesium chloride incorporated with some additives. A group of additives was selected from a mixture of a) an aluminium alkoxide compound and polydimethylsiloxane, b) an aluminosiloxane $[Al(O^iPr)_2OSiMe_3]_m$, c) the reaction product of an aluminium alkyl and calixarene, and d) the reaction product of an aluminium alkyl and cyclodrextrin. These additives can improve the activity of catalyst toward polymerization reaction. The catalysts were suitable for producing extrusion film, blow molding, extrusion pipe HDPE, etc.

In 2004, Yashiki et al. [20] disclosed a catalyst for ethylene polymerization. The catalyst was prepared by the step of dissolving magnesium chloride with 2-ethyl-1-hexanol at 130°C for a course of 3 hours results a homogeneous solution. Tetraethoxysilane was then added to homogeneous solution at 50°C and further reacted for 2 hours. A mixture from this reaction was transferred to other reaction vessel of titanium tetrachloride solution at 0°C over 1 hour. The catalyst mixture was heated to 110°C over 2 hours. The catalyst component was washed with hexane and decane at 110°C until any titanium liberated in mother liquor was not detected. Catalyst components composed of 6.5-7.5 wt % Ti, 15-16 wt % Mg, and 62 wt % Cl. The catalyst gave very high activity. Catalyst efficiency was about 45 -53 Kg PE/ g cat and contained very low fine fluff polymer.

In 2007, Lindroos et al. [21] reported about Ziegler-Natta catalyst supported on silica for slurry polymerization. Catalyst was prepared by reacting magnesium complex of butyloctyl magnesium with 2-ethyl hexanol and then transfer this complex to an emulsion of ethyl aluminium dichloride (EADC) in octadecafluorooctane (PFO) to obtain spherical $MgCl_2$ base supports. Then, magnesium chloride based support was titanized with titanium tetrachloride to obtain Ziegler-Natta catalyst. Solid catalyst was separated and washed. Finally, the catalyst was treated with THF for 2 h at 40-50°C. Molecular weight distribution of copolymerization of ethylene was reduced from 5.0 to 3.9 at the molar 1.1 THF/Ti ratio. Xylene soluble (XS, wt %) was reduced from 12.1 to 2.6 wt %, indicating low molecular weight component decreased by the modified catalyst.

CHAPTER IV

EXPERIMENTAL

4.1 Raw materials

All manipulations involving air and moisture sensitive compounds were always carried out under dry nitrogen.

Table 4.1 List of chemicals and their sources

Chemical list	Source
-$TiCl_4$	Commercial grade, Ti Oxide UK Limited, England
-Triethyl aluminium	Commercial grade, Chemtura, Germany
-Toluene	Sigma Aldrich
-20%Ethylbutyl magnesium in heptane	commercial grade, Chemtura
-Ethyl benzoate	Sigma Aldrich
-2-Ethyl-1-hexanol	Sigma Aldrich
-Heptane	PP plant (commercial grade, IRPC PCL, Thailand)
-Hexane	HD plant (commercial grade, IRPC PCL, Thailand)
-Ethylene gas	IRPC production plant (polymerization grade, IRPC PCL, Thailand)
-Hydrogen gas	IRPC production plant (polymerization grade, IRPC PCL, Thailand)
-Nitrogen gas	IRPC production plant (polymerization grade, IRPC PCL, Thailand)
-0.1M Cerium (IV) sulfate	Fluka
-Sulfuric acid	Fluka
-Diphenylamine	Fluka
-Trichlorobenzene	Fluka

4.2 Equipments and instruments:

1. 1,000 ml 4-neck round bottom flask
2. Heater and circulator oil bath
3. Motor and stirrer rod
4. 300 ml dropping funnel
5. Thermometer
6. Schlenk tube
7. 1.5 stainless steel reactor with motor stirrer
8. Melt flow indexer (Gottfert MPX 62.92) for the determination of melt flow index and melt flow ratio of polymers
9. Gel permeation chromatography (Model PL-GPC 220 from Polymer Lab) for the measurement of molecular weight and molecular weight distribution of polymers
10. Scanning electron microscopy (JSM 6301F; JEOL instrument operating at 1-3 kV) for the characterization of catalysts and polymers morphology
11. Cone & Plate rheometer (Physica MCR 301) for the measurement of complex viscosity
12. Gas chromatography (Model GC 5890) for the measurement of ethyl benzoate (EB) content in the catalysts
13. Sympatec HELOS-VARIO/KF (Laser Diffraction, HELOS Sensor R3) for the measurement of particle sizes and span of catalysts and polymers
14. PERKIN ELMER spectrometer (FTIR model 1760X) for the characterization of catalyst functional

4.3 Catalyst preparation

A) Preparation of magnesium complex

A mixture of 200 ml (175 mmol) of 20 wt% butyloctyl magnesium (BOMAG) in heptane and 200 ml toluene were introduced to a 1000 ml round bottom flask with 4 necks equipped with motor stirrer. Then, 625 mmol triethyl aluminium (TEA) was added. TEA/Mg molar ratios were varied from 0 - 1. Subsequently, 95.5 ml (87.5 mmol) 2-ethyl-1-hexanol (2-EHA) was slowly added to a reaction mixture at temperature of 20 - 40°C at stirring speed of 300 rpm to create 2-EHA/Mg molar ratio of 3.5. After that the reaction mixture was allowed to complete reaction for another 30 min.

B) Preparation of $MgCl_2$ based support

17.2 ml (175 mmol) $TiCl_4$ was dropped to magnesium complex from A (the Ti/Mg molar ratio of 1) at room temperature while stirring at 250 rpm. White solid $MgCl_2$ was formed after complete $TiCl_4$ adding. The $MgCl_2$ suspension was further stirred for 30 min. Then the agitator was switched off to allow settling of $MgCl_2$. The supernatant was siphoned off. $MgCl_2$ was washed with heptane twice. It was suspended in 200 ml heptane before use in the titanation step.

C) Titanation of $MgCl_2$

57.7 ml (565 mmol) $TiCl_4$ was slowly added to the $MgCl_2$ from B at 85°C while stirring at 250 rpm over a course of 3 h. Ti:Mg molar ratio used is fixed at 3:1. The mixture was stirred for another hour.

D) Aging step

This is a step to tune the molecular weight distribution of polymer. Time and temperature treatment or aging after the titanation step was applied.

Aging temperature was maintained at 85°C and aging times were about 0, 5, 10 and 15 h. For aging time fixed at 5 h, aging temperatures were varied from 80 to 100°C following the decantation to remove unreacted components and by-products.

E) Decantation step

After the aging step, the agitator was switched off to settle the catalyst particle and the supernatant was siphoned to eliminate the by-products. The catalysts particles were washed with 400 ml dried hexane for 5 times. During this step, temperature of suspended catalyst was controlled above 60°C to prevent the by-product such as low chloride content of $Ti(OR)_{4-x}Cl_x$ (where x = 1 or 2) precipitated with solid catalyst. Ti content in mother liquor was measured by titration technique. Content of Ti in mother liquor must less than 10 mmol/l.

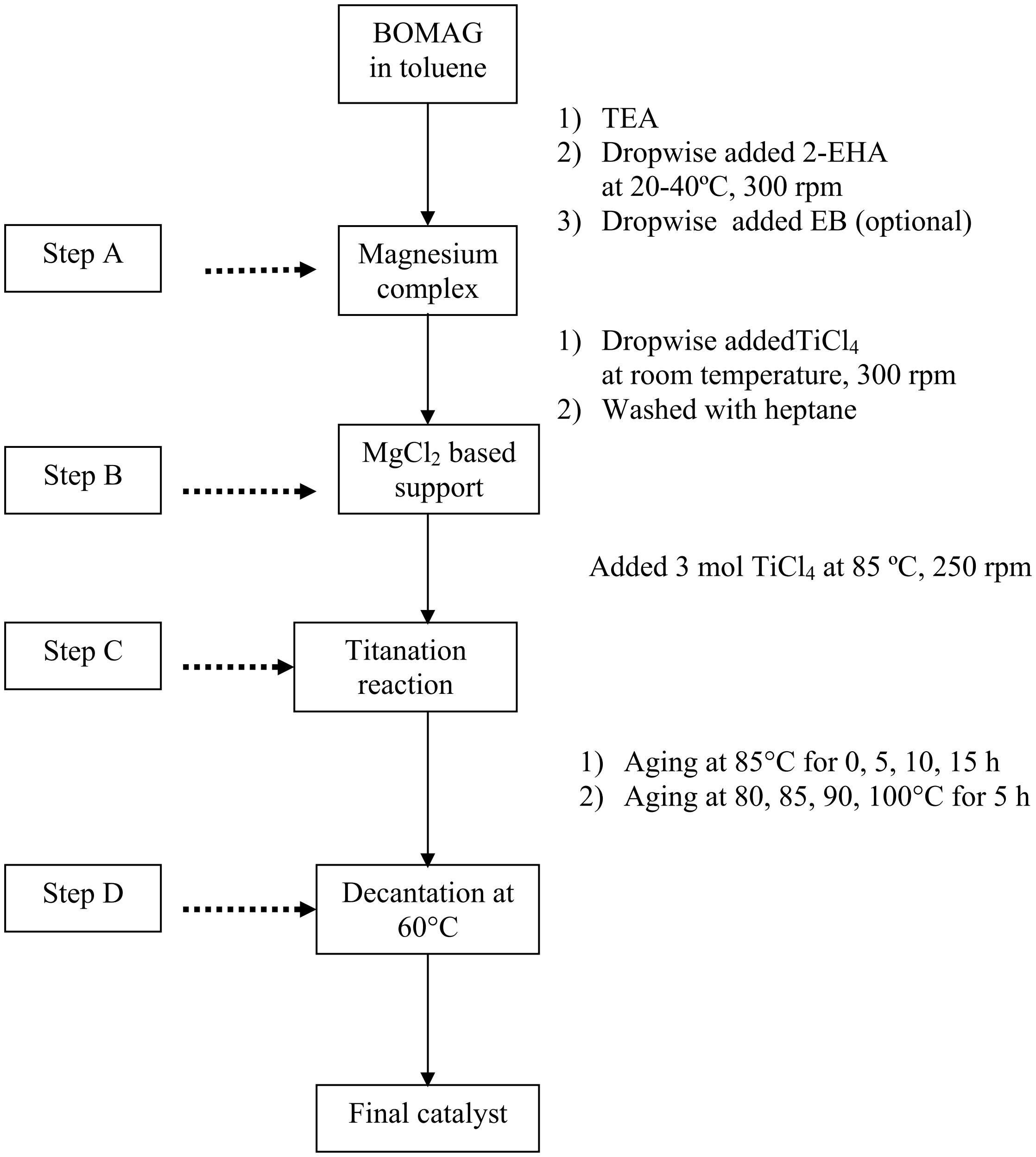


Figure 4.1. Catalyst preparation procedure of Ziegler-Natta catalyst.

Procedures and variable parameters related to Ziegler-Natta catalysts on magnesium chloride support prepared from magnesium complex were described as follows:

4.3.1 Effect of triethyl aluminium (TEA)/Mg molar ratios

Triethylaluminium (TEA) is used to reduce viscosity of magnesium complex. TEA/Mg molar ratio in this experiment was varied as in Table 4.2.

Table 4.2 TEA/Mg molar ratio used for magnesium complex preparation
(Constant parameters: 2-EHA/Mg ratio = 3.5, Ti/Mg ratio at step B = 1, Ti/Mg ratio at step C = 3, reaction temperature/time= 85°C/4 h)

TEA/Mg molar ratio
0
0.25
0.5
1

4.3.2 Effect of Ti/Mg molar ratios

The optimum Ti/Mg molar ratio from section 4.3.1 was selected to further study. Ti/Mg molar ratio used in the titanation step was indicated in Table 4.3.

Table 4.3 Ti/Mg molar ratio used for the preparation of Z-N catalyst at optimum TEA/Mg molar ratio of 0.5
(Constant parameters: 2-EHA/Mg ratio = 3.5, Ti/Mg molar ratio at step B = 1, reaction temperature/time = 85°C/4 h)

Ti/Mg molar ratios
2
3
4

4.3.3 Effect of EB/Mg molar ratios

The best catalyst activity from section 4.3.2 was selected to further study the effect of ethyl benzoate (EB)/Mg molar ratios on the property of Ziegler-Natta catalyst. Ethyl benzoate was introduced to magnesium complex and stirred for 5 min before $MgCl_2$ based support preparation. Amount of ethyl benzoate used was indicated in Table 4.4.

Table 4.4 EB/Mg molar ratio used for the preparation of Z-N catalyst at Ti/Mg ratio of 3 (Constant parameters: 2-EHA/Mg ratio = 3.5, TEA/Mg ratio = 0.5, Ti/Mg ratio at step B = 1, Ti/Mg ratio at step C = 3, reaction temperature/time = 85°C/4 h)

EB/Mg molar ratios
0
0.125
0.25
0.50

4.3.4 Effect of aging time

The best catalyst by means of catalyst activity and activity balance (AB) from section 4.3.3 was selected to further study the effect of aging time on the property of catalyst. The catalyst preparation was the same as that in section 4.3.3. Optionally, the catalyst component was aging at 85°C under various times prior to the decantation step to remove unreacted components. Time used in aging was indicated in Table 4.5.

Table 4.5 Aging times used after the titanation step
(Constant parameters: 2-EHA/Mg ratio = 3.5, TEA/Mg ratio = 0.5, Ti/Mg ratio at step B = 1, EB/Mg ratio = 0.125, Ti/Mg ratio at step C = 3, reaction temperature/time = 85°/4 h)

Time (h)
0
5
10
15

4.3.5 Effect of aging temperature

The catalyst component was aged at the temperature range of 80-100°C under aging time of 5 h. Aging temperature used was indicated in Table 4.6.

Table 4.6 Aging temperatures used after the titanation step
(Constant parameters: 2-EHA/Mg ratio = 3.5, TEA/Mg ratio = 0.5, Ti/Mg ratio at step B = 1, EB/Mg ratio = 0.125, Ti/Mg ratio at step C = 3, reaction temperature/time = 85°C/4 h, aging time = 5 h)

Temperature (°C)
80
85
90
100

4.4 Comparative catalysts

Comparative catalyst I

Comparative catalyst I is used in IRPC plant (Thailand). $MgCl_2$ was formed by reacting $Mg(OC_2H_5)_2$ with $TiCl_4$ at Ti/Mg molar ratio of 2.5 at 85°C. Then, it was titanated with excess $TiCl_4$ at 85°C for 5 h. Further treatment at 120°C for 18 h generates the catalyst intermediate. After which the catalyst was preactivated with triethyl aluminium (TEA) at 85°C for 2 h to convert Ti(IV) to be Ti(III) at level of 85%.

Comparative catalyst II

This catalyst is the commercial one supplied by BASF Company. The catalyst was prepared as reported by Zhu et al. [13]. The catalyst was prepared by steps of melting $MgCl_2$ with 2-ethyl 1-hexanol at 120°C. Tetraethylorthosilicate (TEOS) was added to improve catalyst morphology. Ethyl benzoate was used as internal donor. Then, this complex was quenched to -20°C and large amount of $TiCl_4$ was added to this solution. $MgCl_2$ was recrystallized and was repeated titanation with $TiCl_4$ at 90°C.

4.5 Characterization

4.5.1 Determination of titanium

The catalyst was hydrolyzed with 1.0 M H_2SO_4 and then it was reduced by shaking with Zn-amalgam for 10 min. After separation of Zn-amalgam, sample solution was titrated with 0.1 M cerium (IV) sulfate using diphenylamine as an indicator until end point, deep violet clear solution.

4.5.2 Quantitative analysis of magnesium and chloride content

Catalyst suspension (25 mL) was hydrolyzed by 250 mL of 3 M H_2SO_4. Organic medium was separated from sample solution. Volume of sample solution was made to 250 mL and pH was adjusted in range of 4-6. After filtering of titanium hydroxide precipitate, sample solution was diluted to 500 mL. It was separated into two parts. One was quantitatively analyzed for Mg content following ASTM D511-88. The other part was quantitatively analyzed for Cl content following ASTM D512-88.

4.5.3 Particle size and particle size distribution of catalysts and polymer particles

Average particle size and particle size distribution (PSD) of catalysts and polymers were measured using Sympatec HELOS-VARIO/KF (Laser Diffraction, HELOS Sensor R3 for size range of 0.5-175 μm, focal length = 100 mm). Suspended catalyst was filled into small volume unit which was connected to SUCELL suspension dispersion system under nitrogen gas. Concentration of injected catalysts was monitored via HELOS program.

4.5.4 FTIR-spectra of catalysts

FTIR-spectra of catalysts were recorded on PERKIN ELMER spectrometer (model 1760X). Catalyst samples were milled with KBr in nitrogen glove box and compressed to thin discs. The sample was placed in sample holder under nitrogen atmosphere. FTIR-spectra of catalysts were recorded at the wavelength of 400-4000 cm^{-1}.

4.5.5 Ethyl benzoate (EB) content

1.5 g dried Z-N catalyst was charged into 20 ml vial in 10 ml hexane. 10 ml H_2SO_4 was added and shake until mixture of catalysts was completely dissolved. A portion of clear hexane was transferred to another vial containing 10 ml H_2SO_4 and n-nonane as internal standard. Small amount of anhydrous Na_2SO_4 was introduced. Then 1 μl of the colorless liquid is injected into a pre-set up gas chromatography (GC).

GC Condition:

Detection system = Flame Ionization Detector (FID)
Precolumn = Glass insert with glass wool

Column:

Type = High performance capillary column (HP-1)
Length * diameter = 25 m * 0.320 mm
Phase ratio = 75

Film thickness = 1.05 µm

Carrier gas:

Type = N_2 gas
Flow rate = 1.5 (ml/min)
Split ratio = 100 : 1
Injector temperature = 250 °C
Detector temperature = 250 °C

Oven temperature:

Temperature program = At 90 °C, hold for 2.0 min, raise to 220 °C at the rate of 70 °C/min then hold for 0.5 min

4.5.6 Molecular weight and molecular weight distribution of polymers

Polymer sample was prepared at a concentration of 1.0-2.0 mg/ml in trichlorobenzene, and was transformed into sample preparation unit (PL-SP-260 Polymer Lab) and hold at 160°C for 3 h for complete dissolution. Finally, the solution was analyzed by GPC by following the condition below:

Sample Concentration = 1.0-2.0 mg/ml
Injection Volume = 200 µl
Temperature = 160°C
Solvent = Trichlorobenzene stabilized with 250 ppm butylated hydroxytotuol (BHT)
Column = 2 x PLgel mixed B (300 x 7.5 mm) with PLgel 10 µl guard (50 x 7.5 mm)
Flow rate = 1 ml/min
Detector = PL-GPC220 Differential Refractometer (DRI)
PL-BV 400 Capillary Bridge Viscometer

4.5.7 Complex viscosity

Polymer powder was premixed with 1 phr antioxidant in internal mixer of brabender at 190°C for 4 min. Then, it was melted and compression molded into 2 mm (thickness) sheet. The condition of plate preparation was given below.

Temperature = 170°C
Pre-heating = 6 min
1st compression = 50 kN/1min
2nd compression = 100 kN/1min
3rd compression = 175 kN/1min
De-molding = < 40°C

The sheet was cut into disc with a diameter of 25 mm and thickness of 2 mm. Parallel plate setting was used for measurements under atmosphere. Oscillatory measurements were performed at 220°C with a frequency sweep 0.01 to 100 Hz at 5% of strain and 1.75 mm of gap. When a specimen undergoes oscillatory stress with frequency, the response can be expressed in terms of complex viscosity.

4.5.8 Morphology of catalysts and polymers

The sample was quickly fixed on a glue-covered tape and then transferred to the chamber of gold sputtering and coated with vapor of gold for 30 min.

4.5.9 Melt flow index

- Melt flow index (MFI_2): measured according to ASTM D1238-99 (190°C, under 2.16 kg loading)
- Melt flow index (MFI_5): measured according to ASTM D1238-99 (190°C, under 5 kg loading)
- Melt flow ratio (MFR): the ratio of MFI_5/MFI_2

4.5.10 Bulk density of polymer

Bulk density of polymer was measured according to ASTM D1505-98

4.6 Polymerization

4.6.1 High molecular weight polyethylene condition

The polymerization reactions were carried out in a 2-liter reactor equipped with a mechanical stirrer. $Al(C_2H_5)_3$ was added to 1,000 ml dried hexane (stripped by N_2 for 10 min) and then filled into the reactor. Amount of $Al(C_2H_5)_3$ was fixed at the molar ratio of Al/Ti = 50. 0.025-0.05 mmol catalyst suspension was introduced into the reactor by pipette. After that the reactor content was purged with 3 times of 5 bars nitrogen gas following 3 times of 10 bars hydrogen gas. The reactor was heated up to 85°C and pressurized with 1 bar hydrogen gas and ethylene gas to constant total pressure of 8 bars over the reaction time of 2 h. The pressure was kept constant during polymerization by ethylene flow rate control. The polymerization was stopped after 2 h by shutting off ethylene valve and cooling to room temperature. The resulting polymer suspension was separated and dried at 80°C in drying oven for 2 h.

4.6.2 Low molecular weight polyethylene condition

The polymerization of ethylene was performed as described in section 4.6.1 except the amount of hydrogen fed into the reactor was 3 bars.

CHARPTER V

RESULTS AND DISCUSSION

In this study, Ziegler-Natta catalysts were prepared via multi-step procedure. Several parameters were studied. Magnesium chloride based support was prepared by reacting magnesium complex with titanium tetrachloride using triethyl aluminium (TEA) as viscosity reducing agent. TEA was added to diluted butyloctyl magnesium in heptane. TEA/Mg ratios used were varied from 0 to 1.0. Then, $MgCl_2$ based support was titanated with $TiCl_4$ at Ti/Mg molar ratio of 3 at 85°C over the reaction time of 4 h, shown in section 5.1. The effect of Ti/Mg molar ratio on catalyst properties and its performances were demonstrated in section 5.2. Optimized Ti/Mg molar ratio was chosen for next study. Later, the effect of ethyl benzoate (EB) as internal donor was used in activity balance improvement. Ethyl benzoate was injected into magnesium complex solution at room temperature before forming $MgCl_2$. EB/Mg molar ratios used were varied from 0 to 0.5. The effect of ethyl benzoate on the coordination of Ti on $MgCl_2$ based support and activity balance (AB) improvement were discussed in section 5.3. In addition, the effect of aging time on the catalyst was studied. The chosen catalyst from section 5.2 was used in further aging as a function of times at 85°C after the titanation. Catalyst properties and its performances in ethylene polymerization were studied as demonstrated in section 5.4. Furthermore, Aging temperature of the reactor was varied to 80, 85, 90, and 100°C after the titanation step. Properties of catalyst and its performances in ethylene polymerization were demonstrated in section 5.5.

Titanium (Ti), magnesium (Mg), and chloride (Cl) contents of the catalysts were analyzed. The existed ethyl benzoate incorporated in the catalysts complex was characterized by FTIR-spectroscopy. The content of ethyl benzoate of the catalyst was measured by using gas chromatography. Interaction of ethyl benzoate with magnesium and titanium was studied by Raman spectroscopy. Particle size and particle sized distribution of the catalyst were determined by particle sizer.

Activity of catalysts was investigated in ethylene polymerization under low and high hydrogen pressure. Melt flow index of polymers were studied as well as activity balance (AB) value. AB of catalyst was expressed by AB = $[\text{avg.CA}\times\log(\text{MFI}_2{}^*/\text{MFI}_2)]/|\Delta\text{CA}|$ where $\text{MFI}_2{}^*$ = melt flow index at H_2 pressure 3 bar, MFI_2 = melt flow index at H_2 pressure 1 bar, CA = catalyst activity (g PE/g cat).

The replication phenomenon of polymers from the catalysts was studied by using scanning electron microscopy (SEM). Molecular weight and molecular weight distribution of polyethylene was studied by gel permeation chromatography (GPC).

5.1 Effect of triethyl aluminium (TEA)/magnesium molar ratios

In this study, triethyl aluminium was used as dispersing agent. The effect of triethyl aluminiun on dispersability of $MgCl_2$ was studied with TEA/Mg molar ratio varied in the range of 0.25-1.00.

It was found that good dispersed $MgCl_2$ particles in aromatic hydrocarbon were formed only at TEA/Mg molar ratio of 0.50 during the course of $TiCl_4$ addition, similar to what reported by Hidryckx et al. [5]. At other ratios, the reaction mixtures exhibited gel-like structure or agglomeration. Further titanation made the catalyst mixture sticky. The catalyst could not be isolated and dried. Gel-like material is assumed to be partially magnesium chloride [11]. Reactions of catalyst preparation can be summarized below.

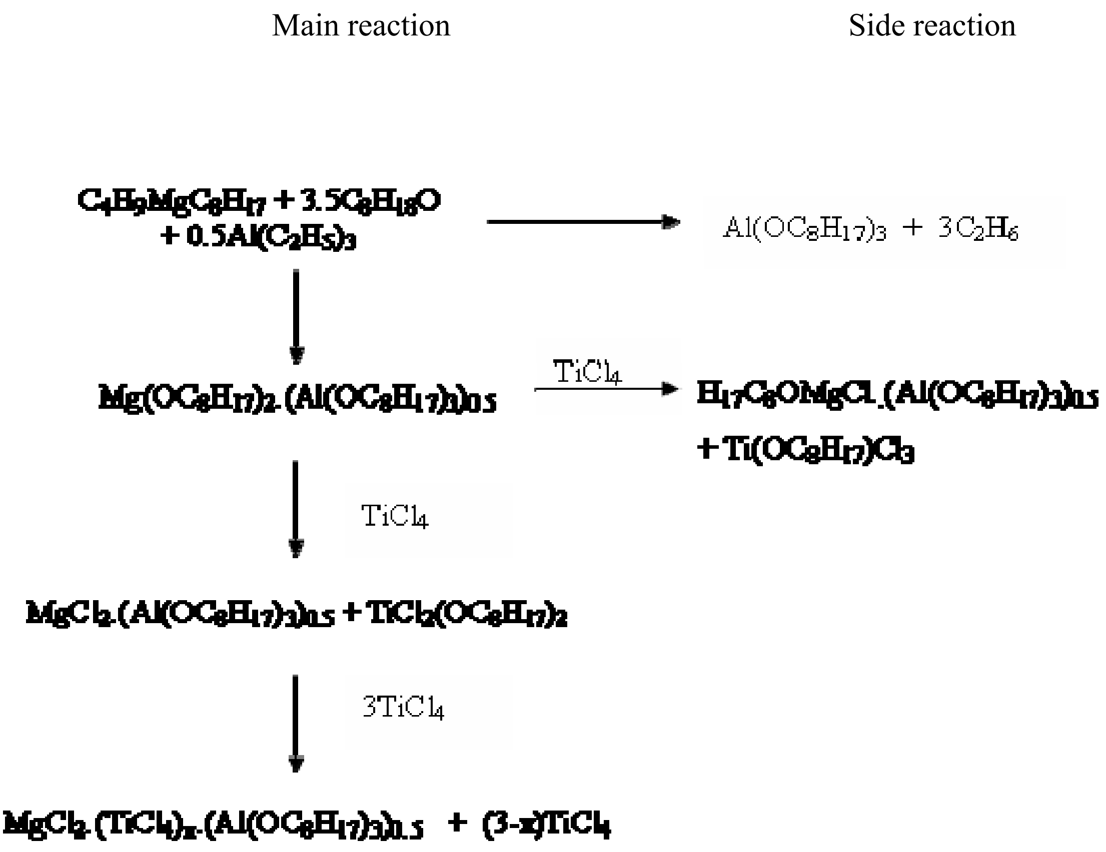


Figure 5.1. Schematic of main reactions and side reactions in catalyst synthesis

In main reactions, butyloctyl magnesium reacted with 2-ethyl-1-hexanol to be di-2-ethyl-1-hexanolate magnesium adduct $Mg(OC_8H_{17})_2.(Al(OC_8H_{17})_3)_{0.5}$ Then, this adduct was reacted with titanium tetrachloride ($TiCl_4$) to form magnesium chloride ($MgCl_2$) based support.

In side reactions, triethyl aluminium ($Al(C_2H_5)_3$) reacted with 2-ethyl-1-hexanol ($C_8H_{18}O$) to tris-2-ethyl-1-hexanolate aluminium and di-2-ethyl-1-hexanolate magnesium aluminium adduct $Mg(OC_8H_{17})_2.(Al(OC_8H_{17})_3)_{0.5}$ could also reacted with titanium tetrachloride to be 2-ethyl-1-hexanolate magnesium chloride aluminium adduct ($H_{17}C_8OMgCl..(Al(OC_8H_{17})_3)_{0.5}$).

The catalyst synthesized by using 0.5 TEA/Mg molar ratio contains 13.2 wt % Mg, 9 wt % Ti, and 51.2 wt % Cl. The average particle size and span of prepared catalyst were 7.2 µm and 2.4, respectively. This TEA/Mg molar ratio was chosen for further preparation of magnesium chloride based support.

The performance of Ziegler-Natta catalyst in ethylene polymerization was studied at 85°C by using triethyl aluminium as a cocatalyst. Hydrogen pressure at 1 bar and 3 bar were used to control molecular weight. Melt flow index of polymers and activity balance of catalysts were studied. The performance of catalyst produced at TEA/Mg ratio of 0.5 is shown in Table 5.1.

Table 5.1 Performances of Ziegler-Natta catalysts produced at TEA/Mg molar ratio of 0.5 under hydrogen pressures at 1 bar and 3 bars.

Item	Unit	Hydrogen pressure (bar)	
		1	3
Catalyst activity	g PE/g cat	20,990	14,294
- MFI $_{2.16\ \mathrm{kg}/190°\mathrm{C}}$	g/10min	1.7	18
- AB value	-	2.7	2.7
- APS of polymer	µm	107	92
- Fine content	vol. %	37	52
- BD	g/cc	0.41	0.41

Polymerization conditions: catalyst amount 0.02 mmol (Ti), TEA cocatalyst 1.0 mmol, ethylene monomer, total pressure 8 bar, temperature 85°C, time 2 h.

The results from Table 5.1 showed the activity of the catalyst (produced TEA/Mg molar ratio of 0.50) was 20,990 g PE/g cat at hydrogen pressure of 1 bar and 14,294 g PE/ g cat at hydrogen pressure of 3 bars.

The activity balance (AB value) of catalyst synthesized at TEA/Mg molar ratio of 0.5 was 2.7. In general, the AB of catalyst related to two factors. The first one is activity of the catalyst and the second one is the MFI of polyethylene under low and high hydrogen pressure in reactor. High catalyst activity in low and high hydrogen pressure in reactor leads to high AB value. Moreover, high hydrogen response catalyst gives polymers with high MFI, resulting in the higher AB value.

The average particle size (APS) of polymers was 92-107 µm with fine polymer contents (at size fraction below 100 µm) of 37 vol. / % and 52 vol. % under hydrogen pressure 1 bar and 3 bars respectively. The bulk density of polymer powder was 0.41 g/cc. This high bulk density is due to small polymer particles.

Generally, the properties and performances of Ziegler-Natta catalyst do not only depend on the preparation method but also on specific active site (Ti) fixed on the catalyst supports. Therefore, the effect of molar Ti/Mg ratios on the properties and performance of Ziegler-Natta catalysts needs to be studied**.**

5.2 Effect of Ti/Mg molar ratios

In this section, Ziegler-Natta catalysts prepared with various Ti/Mg molar ratios were investigated. Ti/Mg molar ratios were varied. The results are shown in Table 5.2.

Table 5.2 Catalyst properties at different Ti/Mg molar ratios

Ti/Mg molar ratio	Catalyst properties					
	Mg (wt %)	Ti (wt %)	Cl (wt %)	Particle size (μm)	Span	Appearance
2	15.2	5.4	57.8	10.9	2.2	Good dispersion
3	13.2	9.0	51.2	7.2	2.4	Good dispersion
4	18.3	11.6	52.3	8.5	2.9	Good dispersion

Table 5.2 indicates that the Mg content detected in catalysts was independent on Ti/Mg ratios. The Mg content in catalysts was in the range of 13-18 wt %. The chloride content decreased with an increasing of the Ti/Mg molar ratios. The Ti fixed on $MgCl_2$ based support increased from 5.4 wt % to 11.6 wt % with an increasing of the Ti/Mg molar ratios from 2 to 4. Fregonese et al. [22] reported that specific titanium fixed on magnesium chloride support has strong effect on the efficiency of catalyst. In principle, catalyst composition alone does not imply the nature and performance feature of the catalyst. However, among element contents, Ti fixed on catalyst seems to be the most important performance parameter.

The particle sizes of the produced catalysts at different the Ti/Mg molar ratios do not have a relationship with an increasing of the Ti/Mg molar ratios, which were about 7.2 – 10.9 μm. The span was found in the range of 2.2 – 2.9.

5.2.1 FTIR spectra

To understand the characteristic of Ziegler-Natta catalysts on $MgCl_2$ based support, the catalyst produced at Ti/Mg molar ratio of 3 was recorded by means of FTIR-spectroscopy. The FTIR-spectra of the $MgCl_2$ based support and the catalyst were recorded and presented in Figures 5.2 and 5.3, respectively.

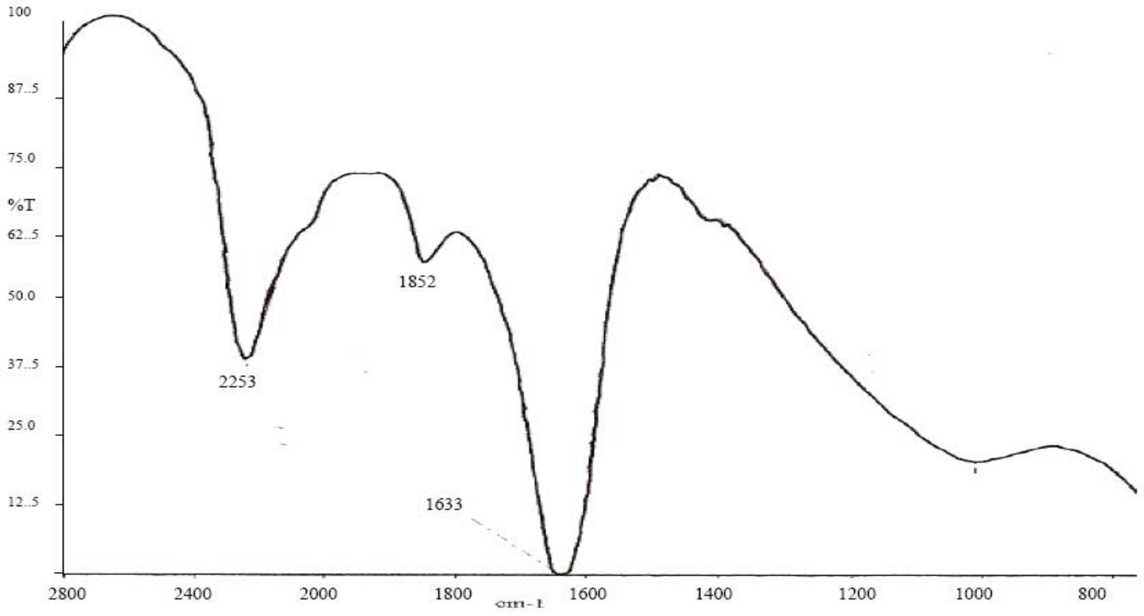


Figure 5.2. FTIR-spectrum of $MgCl_2$.

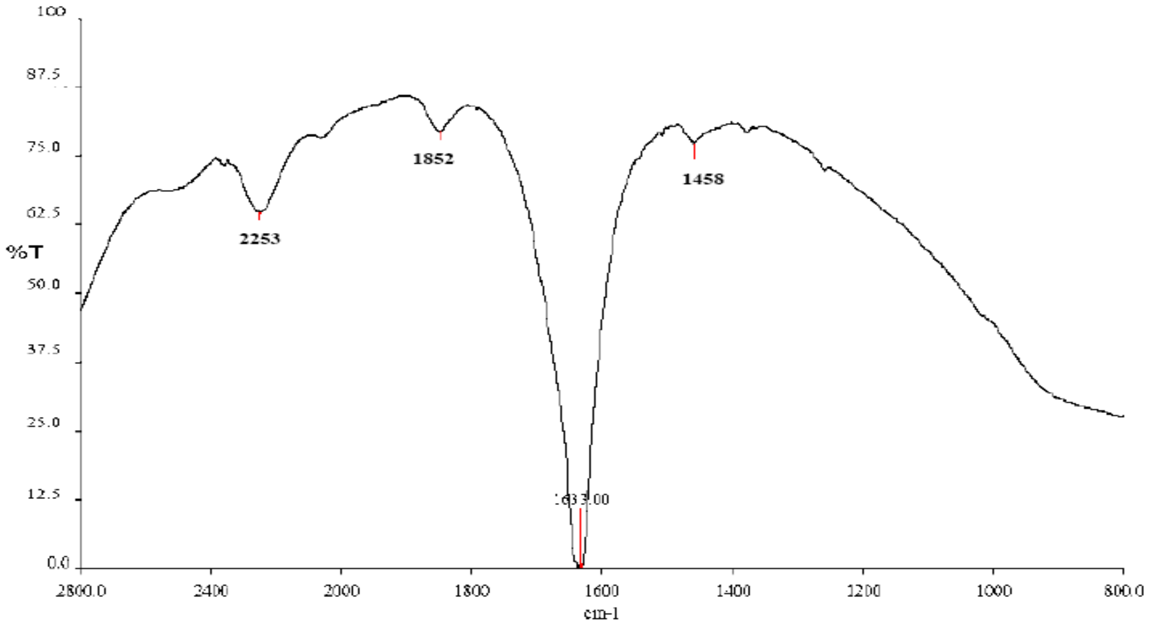


Figure 5.3. FTIR-spectrum of Z-N catalyst.

In Figures 5.2 and 5.3, the strong absorption peak of catalyst sample at 1633 cm^{-1} indicates the Mg─Cl stretching of free surface of $MgCl_2$ as displays in strong and broad absorption peak of Mg─Cl bond of $MgCl_2$ solid [23, 24]. Distinguished peaks at 1852 cm^{-1} and 2253 cm^{-1} stand for other vibrational modes of Mg-Cl whereas the peak at 1458 cm^{-1} is the CH_2/CH_3 deformation vibration of 2-ethyl-1-hexanol ($C_8H_{17}O$) adduct on the surface of $MgCl_2$.

5.2.2 Performances of catalysts

5.2.2.1 Activity of catalyst at hydrogen pressure of 1 bar and 3 bars

The activity of catalyst produced at different Ti/Mg molar ratios are demonstrated in Figure 5.4.

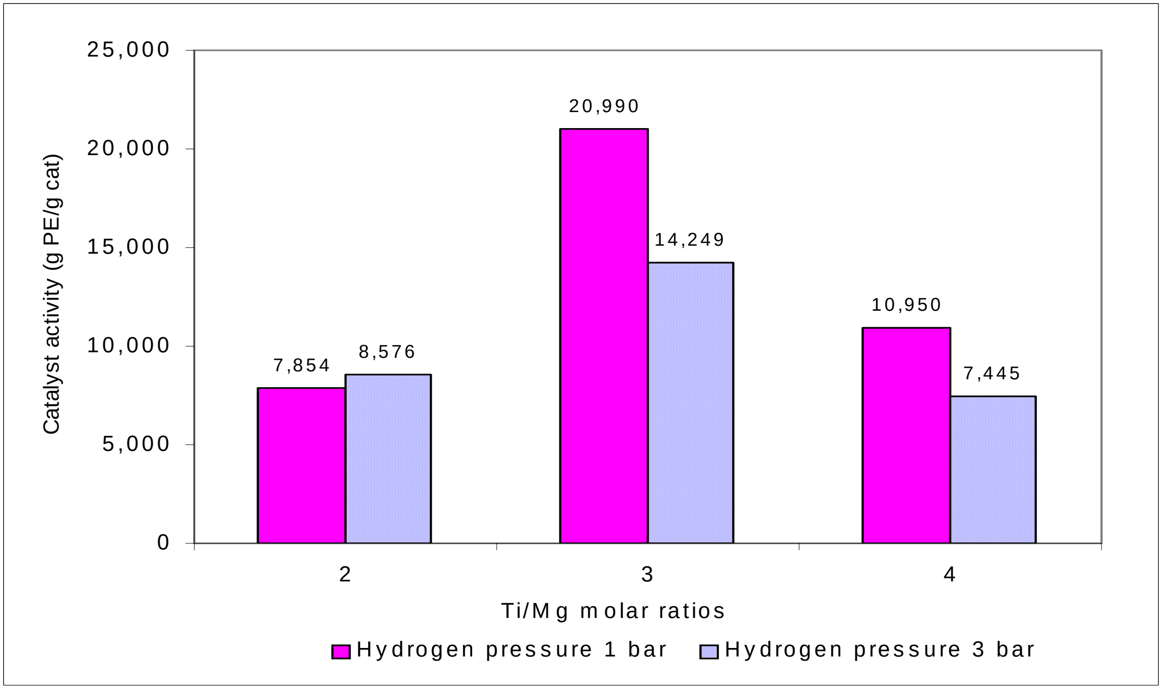


Figure 5.4. Activity of catalysts produced at different Ti/Mg molar ratios.

It was found that the catalyst activity increased dramatically from Ti/Mg molar ratio of 2 to Ti/Mg molar ratio of 3 but dropped at the molar ratio of 4. The catalyst produced with Ti/Mg molar ratio of 3 showed maximum polymer yield under both 1 and 3 bars hydrogen pressure.

The effect of variation of Ti/Mg molar ratios on hydrogen sensitivity of catalysts, activity balance (AB) and particle size of the obtained polymers was studied. The results are showed in Table 5.3.

Table 5.3 MFI_2, activity balance (AB) and particle size of polyethylene produced with Z-N catalysts at different Ti/Mg ratios under hydrogen pressure of 1 bar and 3 bars

Ti/Mg molar ratio	MFI_2 (g/10min)		AB value	APS		Span	
	1 bar H_2	3 bar H_2		1 bar H_2	3 bar H_2	1 bar H_2	3 bar H_2
2	1.6	6.8	10.4	115	115	0.8	0.9
3	1.7	18.0	2.7	107	92	1.0	1.2
4	0.2	1.9	2.4	100	100	0.8	1.2

The result in Table 5.3 indicated that MFI_2 of polyethylene of catalysts produced at Ti/Mg molar ratio of 2 and Ti/Mg molar ratio of 3 under hydrogen pressure 1 bar was low, especially at Ti/Mg molar ratio of 4 (MFI_2 = 0.2) but MFI_2 significantly increased at H_2 pressure of 3 bars. This indicated that the catalyst produced at Ti/Mg molar ratio of 4 had very low hydrogen sensitivity. One possible reason to explain why the catalyst produced at Ti/Mg molar ratio of 4 showed low MFI was that the active species of catalyst were more stable to chain termination by hydrogen than that of catalysts produced at Ti/Mg molar ratio of 2 and 3. It was found that the catalyst produced at Ti/Mg molar ratio of 3 gave a very high MFI (18.0 g/10min).

The activity balance value (AB) of the prepared catalyst decreased with increasing Ti/Mg molar ratios. The maximum AB was found at Ti/Mg molar ratio of 2. Higher Ti/Mg molar ratios resulted in decreasing AB values. Nevertheless, it was found that the activity of catalyst produced at Ti/Mg molar ratio of 4 was relatively lower than that of the catalyst produced at Ti/Mg molar ratio of 3. Consequently, the catalyst produced at Ti/Mg molar ratio of 3 was better than the catalyst produced at Ti/Mg molar ratio of 2 and it was chosen for the next study. The low activity balance (AB) for the catalysts produced at Ti/Mg ratio of 3 and 4 was due to high variation in activity at hydrogen pressure of 1 bar and 3 bars.

Particle sizes of polymers produced with Z-N catalyst at different Ti/Mg molar ratios of 2-4 were in the range of 100-115 µm and 92-115 µm when polymerization was carried out at hydrogen pressure of 1 bar and 3 bars, respectively.

From the above results, it pointed out that the catalyst synthesized from general components (based on $MgCl_2$, $TiCl_4$, and electron donor) would give high activity balance that means the catalyst has low variation in its activity at hydrogen pressure of 1 bar and 3 bars. Next study will be described the effect of ethyl benzoate as internal donor on the properties of catalyst.

5.3 Effect of ethyl benzoate/Mg molar ratios

The chosen catalyst system from section 5.2 was the one that prepared from TEA/Mg molar ratio of 0.5 and Ti/Mg molar ratio of 3. Therefore, the effect of ethyl benzoate on the performance of Z-N catalysts was studied for this system. The properties of the catalysts at different EB/Mg ratios were shown in Table 5.4.

Table 5.4 Properties of Ziegler-Natta catalysts produced at different EB/Mg molar ratios

EB/Mg molar ratio	Catalyst properties					
	Mg (wt %)	Ti (wt %)	Cl (wt %)	Particle size (μm)	Span	Appearance
0	13.2	9.0	51.2	7.2	2.5	Good dispersion
0.125	14.7	2.2	53.1	16.6	2.7	Good dispersion
0.25	16.7	1.2	54.8	13.3	2.0	Good dispersion
0.50	14.7	0.8	47.1	7.8	1.5	Good dispersion

The results from Table 5.4 showed that the particle size of the produced Z-N catalysts without ethyl benzoate was 7.2 μm. The average particle size of catalyst increased with the amount of ethyl benzoate but decreased at EB/Mg molar ratio of 0.50.

Ti and EB contents of the catalysts at different molar ratios were shown in Figure 5.6. In general, ethyl benzoate (EB) is typical basic internal donor (ID). Ethyl benzoate can act as morphology controlling agent. In this study, it was found that ethyl benzoate (EB) content was clearly related to the content of titanium on Z-N catalyst on $MgCl_2$ based supports. Ti and EB contents in the Z-N catalysts on $MgCl_2$ based support are shown in Figure 5.5.

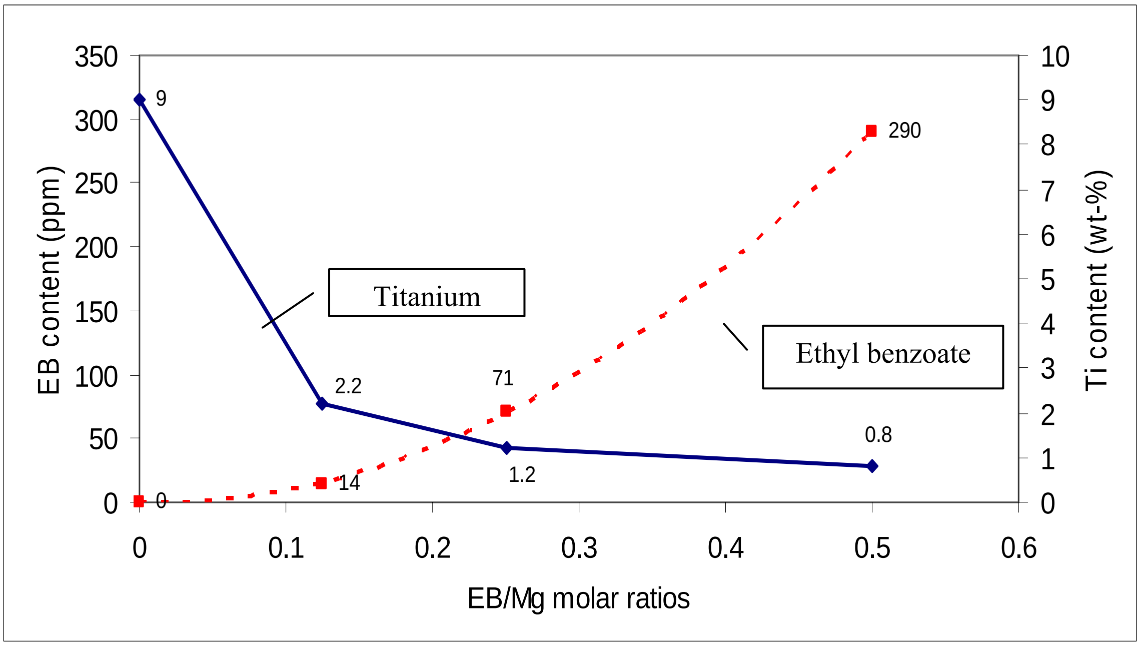


Figure 5.5. Ti and EB content of the catalysts at various EB/Mg molar ratios.

FTIR and Raman-spectroscopy were used to prove the existence of EB in the catalyst. FTIR-spectra of ethyl benzoate and catalyst (produced at 0.125 EB/Mg molar ratio) are shown in Figures 5.6 and 5.7. Raman-spectra of Z-N catalyst with and without ethyl benzoate are shown in Figure 5.8.

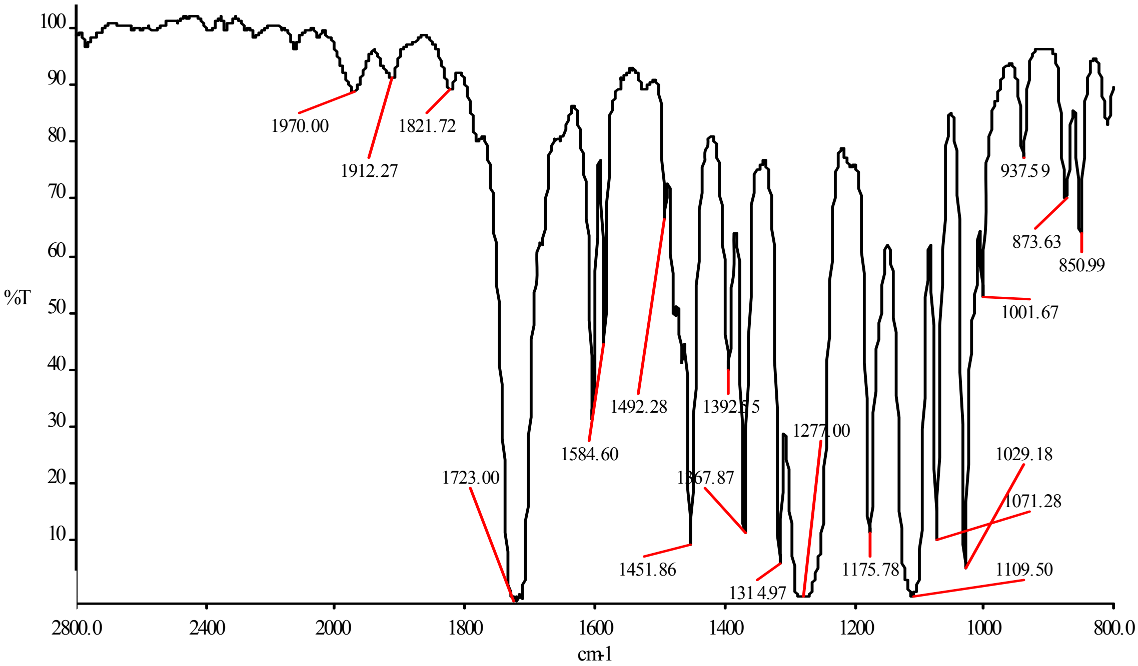


Figure 5.6. FTIR-spectrum of ethyl benzoate.

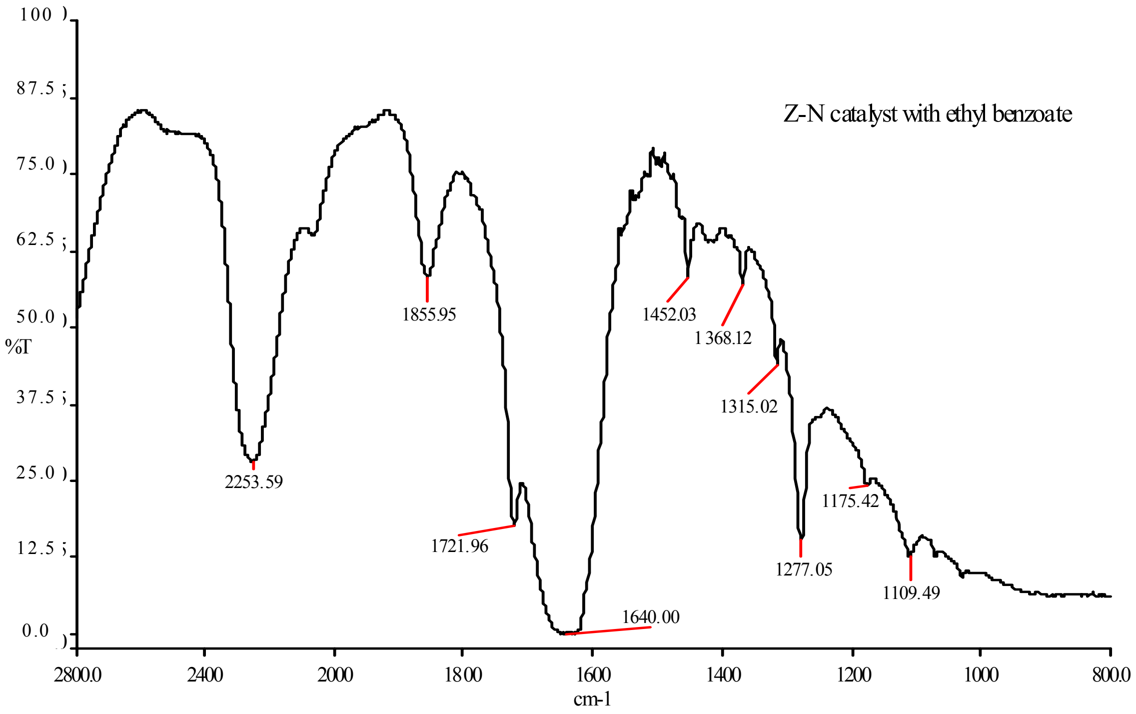


Figure 5.7. FTIR-spectrum of Ziegler-Natta catalyst containing ethyl benzoate.

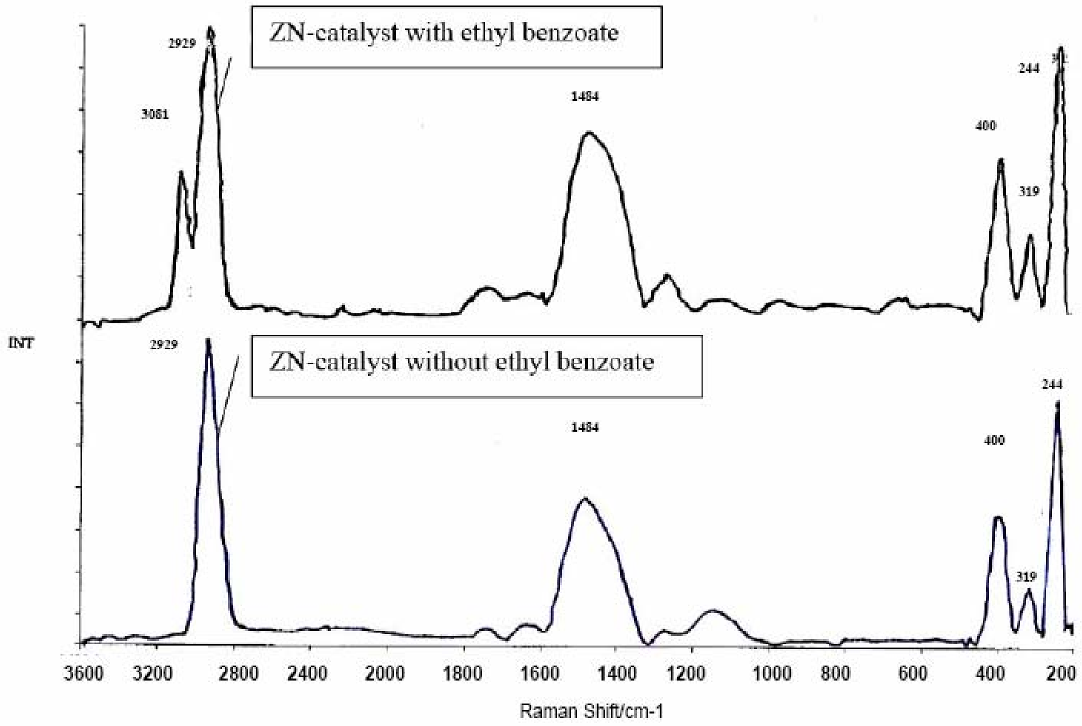


Figure 5.8 Raman-spectra of Z-N catalyst with and without ethyl benzoate.

In the IR spectrum, the signals of the Mg—Cl and ethyl benzoate as electron donor were mainly studied. From the results in Figures 5.6 and 5.7, it could be seen IR shift of the catalyst and ethyl benzoate. In Figure 5.7, There is the characteristic peak of carbonyl group (—C=O) at 1722 cm^{-1}, identical to C=O stretching of carbonyl group of ethyl benzoate displaying at 1723 cm^{-1} in Figure 5.6. Weak absorption peak at 1452 cm^{-1} is due to CH_2/CH_3 deformation. Absorption peaks at 1315 and 1368 cm^{-1} are assigned to be C—O—C asymmetric stretching. The absorption peak at 1277 cm^{-1} is assigned to be C—O—C symmetric stretching of ester conjugated to C=C aromatic ring as depicted in ethyl benzoate in Figure 5.7. The weak absorption peak at the range of 1109-1029 cm^{-1}in Figure 5.7 is due to O—C=O asymmetric stretching. Other peaks at 1640, 1856 and 2253 cm^{-1} are assigned to be Mg—Cl stretching.

Figure 5.8 shows the Raman vibration at the peak of 3081 cm^{-1}and it is assigned to C—H stretching of ethyl benzoate. The absorption peak at 2929 cm^{-1} is assigned to CH_2/CH_3 stretching whereas Ti—Cl, Mg—Cl, Ti–O, and Mg—O bonds are seen in the range of 240-400 cm^{-1} [28]. These results proved the existence of ethyl benzoate in the catalyst.

5.3.1 Performances of the produced catalysts

The effect of ethyl benzoate on the performances of Z-N catalysts was investigated. The amount of ethyl benzoate was varied from 0.125 to 0.5 mole based on one mole magnesium. The activity values of catalysts at different hydrogen pressure of 1 bar and 3 bars are shown in Figure 5.9.

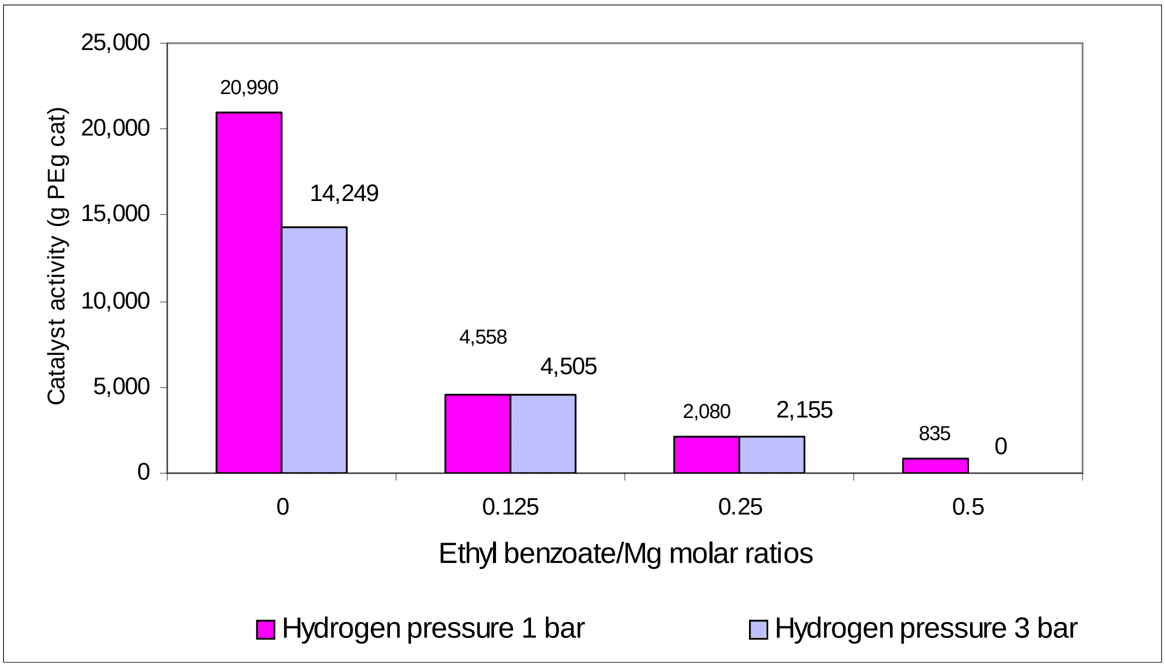


Figure 5.9. Activity value of catalysts produced at different EB/Mg molar ratios.

Figure 5.9 shows that the activity of catalysts decreased with increasing in EB/Mg molar ratio. The activities of catalysts were almost same at hydrogen pressure of 1 bar and 3 bars for EB/Mg ratios = 0.125 and 0.25. It might be explained that the catalysts exhibited high stability at high hydrogen pressure. The activity of catalyst (produced at EB/Mg ratio= 0.50) was zero at 3 bars hydrogen pressure. One explanation might be the extreme reduction of Ti fixed on $MgCl_2$ support in the presence of ethyl benzoate (Figure 5.5).

The effect of EB/Mg molar ratios on hydrogen response of catalysts was determined by melt flow indices (MFI) of polymers as shown in Table 5.5. The results showed that MFI of polymers polymerized at 1 bar hydrogen pressure was varied in the range of 0.9-2.0 g/10min while MFI of polymer polymerized at 3 bars hydrogen pressure was rapidly declined with EB/Mg molar ratios. This result indicated that high EB content in catalyst complex has negative effect on the performance of catalysts. It was found that the activity and hydrogen response of catalysts decreased with high EB content in catalyst complex. MFR of polymer polymerized at 1 bar hydrogen pressure was varied in the range of 2.7-3.1 while that of polymer polymerized at 3 bars hydrogen pressure was 2.1-3.1.

Table 5.5 MFI_2 and MFR of polyethylene under hydrogen pressure of 1 bar at different EB/Mg molar ratios

EB/Mg molar ratio	1 bar H_2 pressure		3 bar H_2 pressure	
	MFI_2 (g/10min)	MFR	MFI_2 (g/10min)	MFR
0	1.7	3.1	54.5	3.0
0.125	1.0	2.7	18.0	2.1
0.25	2.0	3.1	6.2	3.1
0.50	0.9	2.9	-	-

The effect of different EB/Mg molar ratios on activity balance (AB) value of the catalysts were studied and presented in Figure 5.10. It was found that the AB-value of Z-N catalysts (produced at EB/Mg molar ratios = 0.125) was much higher than those at other ratios. The AB–value of Z-N catalysts produced at EB/Mg molar ratio = 0.125 was 52.2.

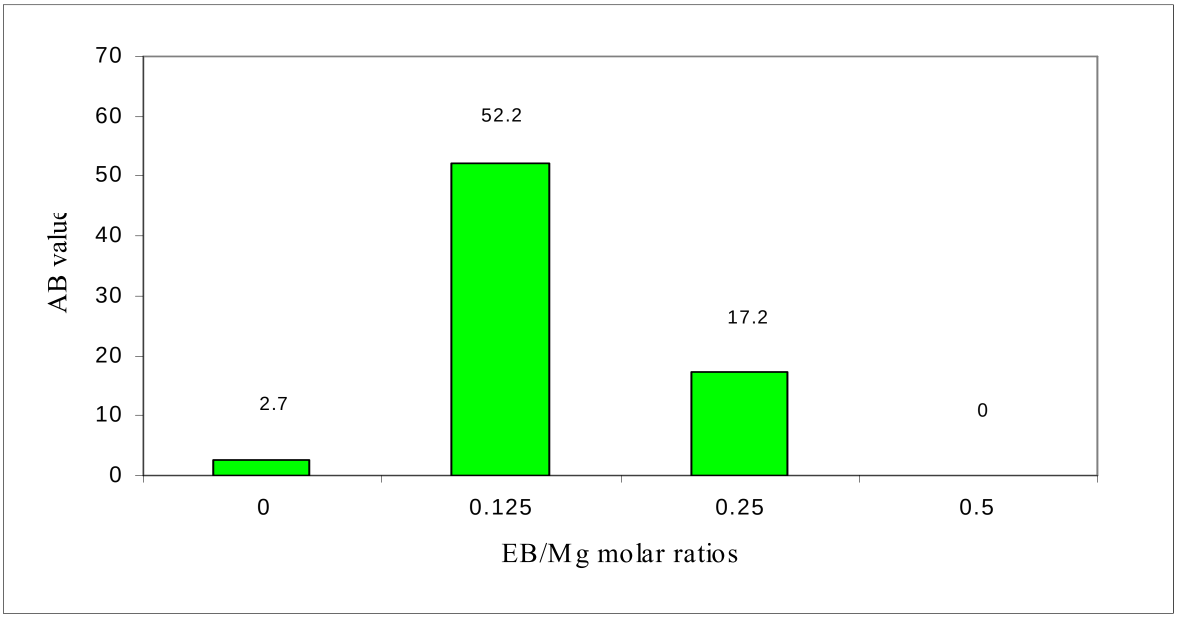


Figure 5.10. AB values of Z-N catalysts produced at different EB/Mg molar ratios.

In Figure 5.10, it can be concluded that the AB value of catalysts was much improved by ethyl benzoate because the catalyst activities were similar at 1 bar and 3 bars hydrogen pressure. The activity balance (AB) of catalysts increased from 2.7 to 52 with an increasing of EB/Mg molar ratio from 0 to 0.125. Then, the AB value of catalysts was significantly reduced at EB/Mg molar ratio ≥ 0.25.

The effect of EB/Mg molar ratios on particles sizes of polymers at different hydrogen pressures was shown in Table 5.6. It was found that the average particle size of polymers increased with increasing of EB/Mg molar ratios. Particle sizes of polymers increased from 107 μm to 126 μm at hydrogen pressure of 1 bar and increased from 92 μm to 150 μm at hydrogen pressure of 3 bars respectively. This indicated that EB could enhance mechanical stability of catalysts particles resulting in high fragmentation resistance of polymer particles. The span of particles was 0.9-1.3 indicating a narrow distribution.

Table 5.6 Particle sizes and spans of polymers produced with Z-N catalysts at different EB/Mg molar ratios under hydrogen pressure of 1 bar and 3 bars

EB/Mg molar ratio	1 bar H_2 pressure		3 bar H_2 pressure	
	APS	Span	APS	Span
0	107	1.0	92	1.3
0.125	112	1.1	110	1.1
0.25	126	0.9	150	1.1

It can be concluded that high AB catalyst could be synthesized at EB/Mg molar ratio of 0.125. However, it was observed that the activity of catalysts was significantly reduced with EB/Mg molar ratios, indicating that the active species of catalysts might not stable during the polymerization time or the coordination of Ti active species with ethyl benzoate became non specific active site. Then, the specific aging time is necessary for the reconstruction of the catalyst on $MgCl_2$ based support.

5.4 Effect of aging time

The results in the previous section evidenced that the activity balance of the catalyst can be improved by ethyl benzoate. The suitable EB/Mg molar ratio was 0.125. In this section, the effect of aging time on the properties of catalysts after the titanation will be described. The properties of the catalyst and its performances will also be discussed below.

5.4.1 Catalyst properties

The variable parameter in this study was aging time; 0, 5, 10, and 15 h while aging temperature was maintained at 85°C. Properties of catalysts were shown in Table 5.7.

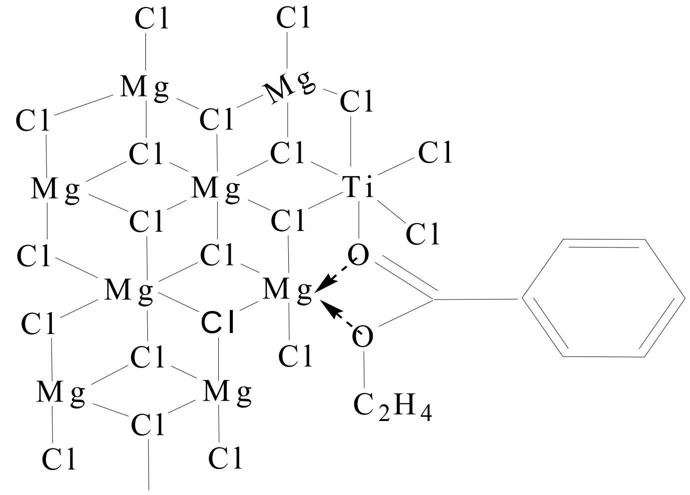
Table 5.7 Properties of the produced catalysts at various aging times
(Constant parameter: EB/Mg molar ratio = 0.125, Ti/Mg molar ratio = 3.0)

Time (h)	Catalyst properties					
	EB content (ppm)	Mg (wt %)	Ti (wt %)	Cl (wt %)	Particle size (μm)	Span
0	104	14.7	2.2	53.1	17	2.7
5	74	16.2	2.6	54.4	16	3.3
10	44	16.5	5.7	57.5	10	2.5
15	42	15.8	5.8	59.0	10	1.7

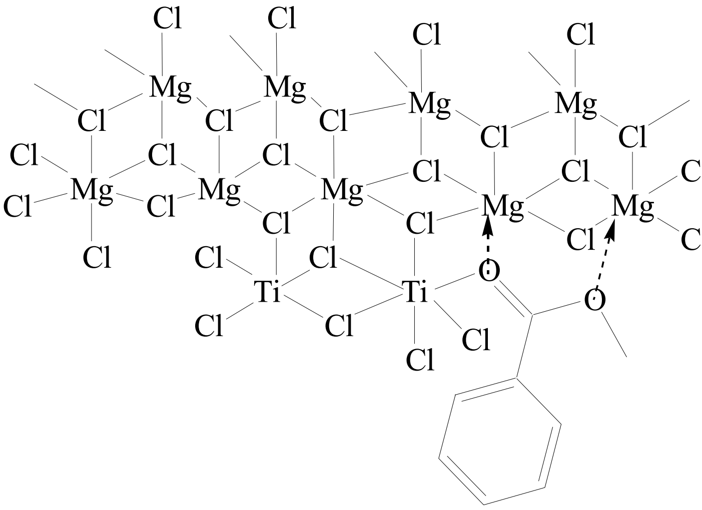
Table 5.7 shows that the EB contents in catalyst decreased with the aging time. However, the content of ethyl benzoate in the catalyst declined and constant at the aging time of 10-15 h. In addition, the content of EB was inversely proportional to the content of titanium in Z-N catalyst on $MgCl_2$ based supports. Ethyl benzoate on $MgCl_2$ surface might be replaced by Ti. The Ti content of catalysts was strongly increased from 2.2-2.6 to 5.7-5.8 wt % with increasing of the aging time from 0-5 h to 10-15 h. The results are corresponded to many literatures that the longer aging time, the higher Ti content presence in Z-N catalyst on $MgCl_2$ based supports [26, 27, 28].

The particle size of catalysts was slightly decreased with increasing the aging time, suitable for the production of HDPE in slurry process. The span value of catalyst particles was decreased with increasing the aging time.

To understand the specific active site of catalysts, the structure of titanium complex on $MgCl_2$ surface (100) and (110) cut were proposed by many authors. The possible structure of titanium complexes can be either monomeric or dimeric form, shown in Figure 5.11. It is believed that the active centers are located only at the edges or defective parts of $MgCl_2$ crystal. Both forms are believed to be responsible for isospecific active site and high active Z-N catalysts [28, 29, 30].



Monomeric structure on $MgCl_2$ surface (110) cut



Dimeric structure on $MgCl_2$ surface (100) cut

Figure 5.11. Proposed structures of $TiCl_4$ complexes on the (110) and (100) cut of $MgCl_2$ with ethyl benzoate as internal donor.

5.4.2 Performances of the produced catalysts

Performances of catalysts in terms of catalysts activities at hydrogen pressure of 1 bar and 3 bars were investigated. The melt flow index of polymers was measured. Subsequently, the activity balance of catalysts was evaluated. Performances of the catalyst produced at various aging times at 1 bar and 3 bars hydrogen pressure are shown in Figure 5.12.

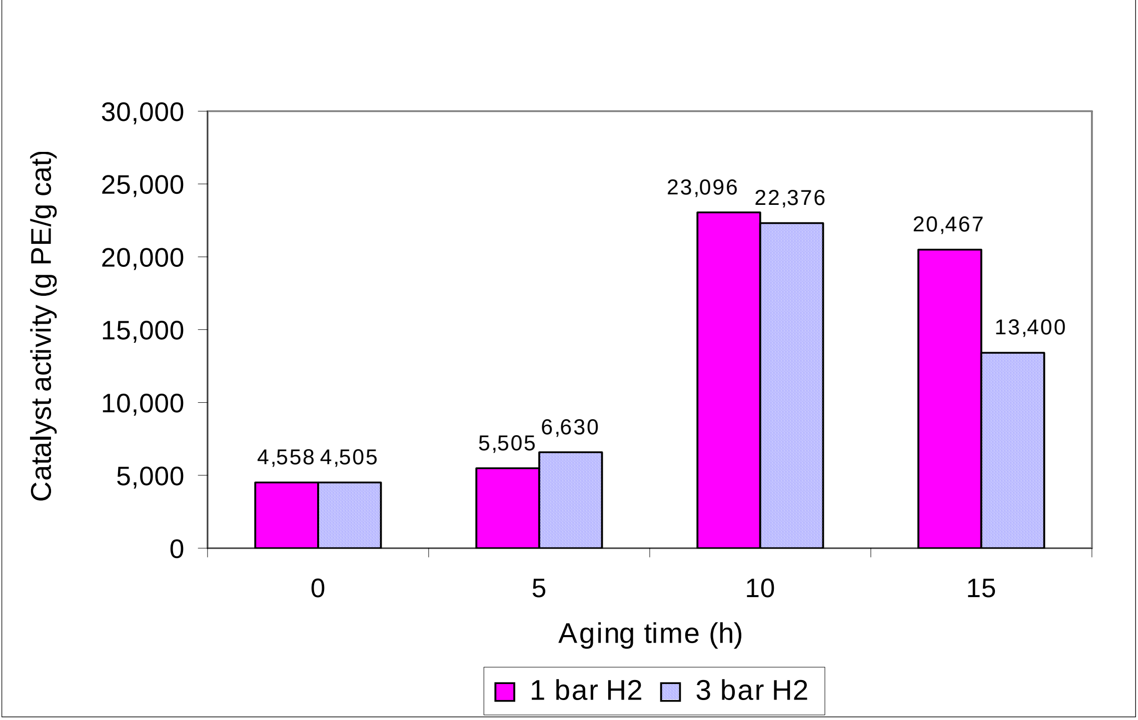


Figure 5.12. Activity values of catalysts produced at different aging times.

It was found that activity values of catalysts produced at different aging time at 1 bar and 3 bars hydrogen pressure increased with an increasing of the aging time. The maximum catalyst activity was obtained at the aging time of 10 h. This pointed out that specific aging time of 10 h created high catalytic active sites on $MgCl_2$ surface. Furthermore, the catalyst after aging at specific time of 10 h had high stability and high propagation rate of the polymerization. Catalyst activities under 1 bar and 3 bar hydrogen pressure increased to maximum (23,096 and 22,376 g PE/g cat.) at aging time of 10 h. It was noticed that catalyst activities of aged Z-N catalysts at 10 h under 1 bar and 3 bars hydrogen were comparable (23,096 vs 22,376 g PE/g cat.). The catalyst at aging time of 10 h gave high propagation rate throughout the polymerization. On the contrary, oxidation states of Ti might be reduced to Ti(III) and Ti(II) in the presence of cocatalyst during the polymerization process [31].

Melt flow indices of polyethylene produced at various aging times were shown in Table 5.8.

Table 5.8 MFI_2 and MFR of polyethylene under hydrogen pressure of 1 bar and 3 bars at different aging times

Aging time (h)	1 bar H_2 pressure		3 bar H_2 pressure	
	MFI_2 (g/10min)	MFR	MFI_2 (g/10min)	MFR
0	1.0	2.3	8.7	2.5
5	1.1	2.1	9.4	3.0
10	0.8	2.7	5.1	2.5
15	0.6	2.8	4.6	2.8

Table 5.8 showed that the MFI of polymers under 1 bar hydrogen pressure decreased with an increasing of the aging time. This indicated that hydrogen response of catalysts decreased when the catalysts were aged under long period of time. It could be explained that the nature of the active site might be changed. The structure of low hydrogen response catalyst probably contained Ti─O─Ti bond on $MgCl_2$ surface when long aging time was used [32]. MFR of high molecular weight polymer (1 bar H_2 pressure) was slightly increased with increasing aging time while MFR of low molecular weight polymer (3 bar H_2 pressure) was not significantly changed. The longer aging time, the catalyst contains various kinds of active sites. The MFI of polymers under 3 bars hydrogen pressure was significantly reduced from 9.4 g/10min at aging time of 5 h to 5.1-4.6 g/10min at aging time of 10 – 15 h.

Activity balance (AB) values of the catalysts produced at various aging times are shown in Figure 5.13. It was found that the AB decreased when the aging time was increased.

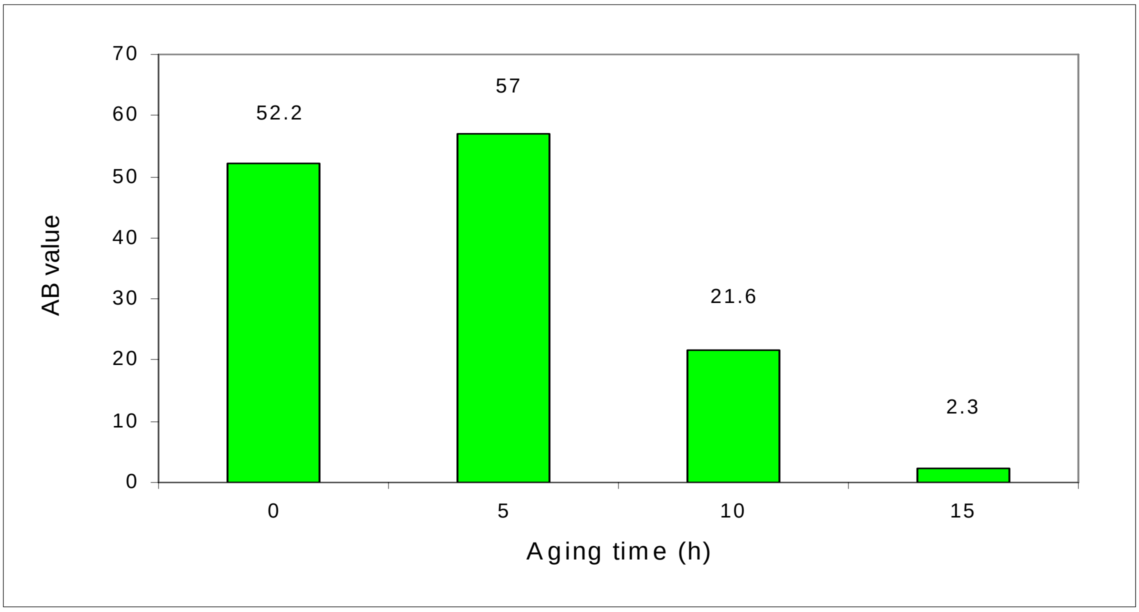


Figure 5.13. Activity balance (AB) values of Ziegler-Natta catalysts produced at different aging times.

The average particle sizes of catalysts and polymers at different aging times are shown in Table 5.9. The particle size of catalysts was significantly reduced from 16.7 μm at aging time of 0 h to 12.5 μm at aging time of 15 h. Sizes of polymers were increased with an increasing of the aging time from 106 μm to 152 μm and 117 μm to 152 μm under 1 bar and 3 bars hydrogen pressures, respectively. Since, the mechanical stability of catalyst particles increased with a increasing of the aging time, the polymer particles had high resistance to the fragmentation throughout the polymerization. This pointed out that the mechanical stability of catalysts is the most important factor. The reconstruction of $MgCl_2$ surface after the longer aging time used was believed to be improved the mechanical stability of the catalyst complex. Consequently, large polymer particles could be produced even the catalysts had small particle sizes.

Table 5.9 Average particle sizes of catalysts and polymers at different aging times

Aging time (h)	Particle size of catalyst (μm)	Particle size of polymer (1 bar H_2)	Particle size of polymer (3 bar H_2)
0	16.7	106	117
5	15.6	104	113
10	14.0	117	127
15	12.5	152	152

5.5 Effect of aging temperature

It is well-known that Z-N catalysts contain multiple the active species resulting in broad molecular weight distribution polyethylene. In general, the nature of Z-N catalyst with low hydrogen response is synthesized at high aging temperature under long aging time [25, 32]. Various aging temperatures (80-100°C) were studied. The effect of aging temperatures on properties of catalyst was studied when the aging time was maintained at 5 h. This aging time was chosen because it gave the catalyst having the highest AB. Properties of the catalyst and its performances at different aging temperatures are given in Table 5.10.

Table 5.10 Properties of the produced catalysts at different aging temperatures

Aging temperature (°C)	Catalyst properties				
	Mg (wt %)	Ti (wt %)	Cl (wt %)	Particle size (µm)	Span
80	11.4	2.6	53.2	9.0	2.8
85	16.2	2.6	54.4	16.0	3.3
90	15.5	10.5	44.8	9.9	1.9
100	16.6	10.0	45.1	7.3	1.2

The Ti content in the catalysts was low at aging temperature of 80-85°C, it was increased to 10.5 wt % at an aging temperature of 90°C. This indicated that the aging temperature strongly affected the Ti content fixed on $MgCl_2$ surface at temperature >85°C. The particle size of catalysts increased from 9.0 µm at 80°C to 16.0 µm at 85°C then it was dropped at temperature higher than 85°C. The Cl content in catalysts decreased to minimum (44.8 wt %) at temperature of 90°C. It was assumed that Cl was eliminated from the catalyst complex and new Ti−O−Ti bond was formed at high temperature corresponding to the literature [31].

5.5.1 Performances of the catalysts

The performances of catalysts under 1 bar hydrogen pressure was studied in ethylene polymerization under 1 bar and 3 bars hydrogen pressure. The activities of catalysts produced at different aging temperatures are shown in Figure 5.14.

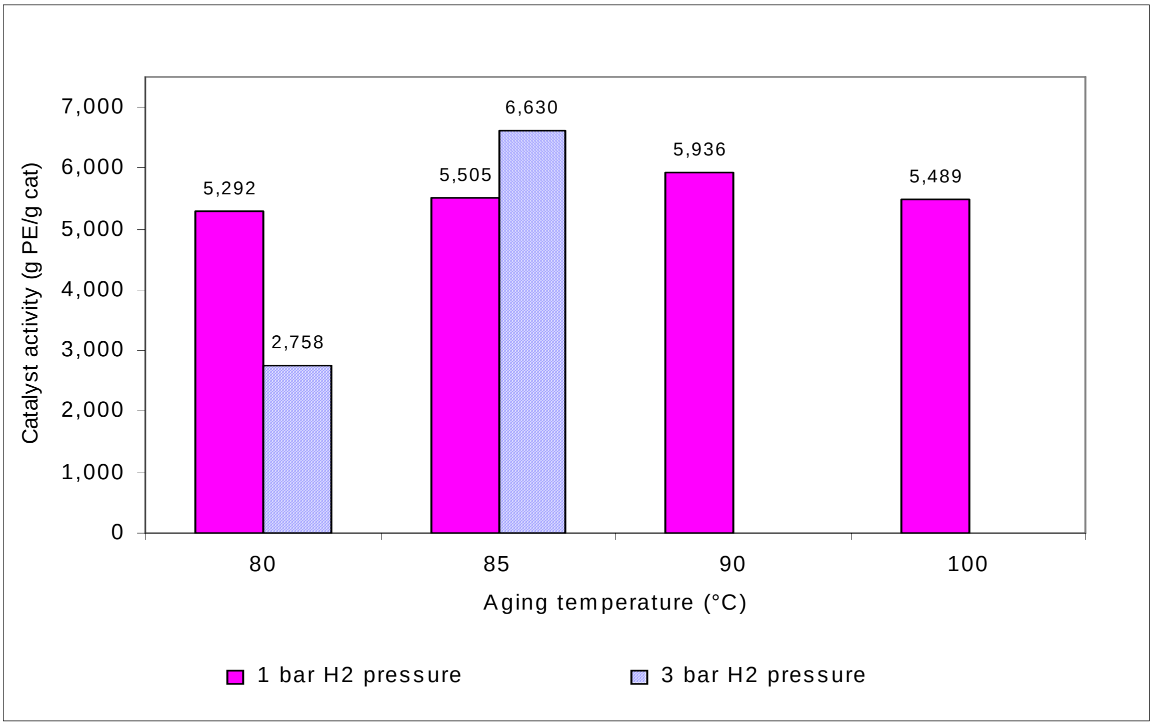


Figure 5.14. Activity values of catalysts produced at different aging temperatures.

Figure 5.14 shows that tendency of the activity of catalysts produced at different aging temperatures had slightly changed under 1 bar hydrogen pressure. Increased aging temperature did not improve catalyst activity. The activity of catalysts produced at aging temperature of 85°C was higher than that of catalysts produced at aging temperature of 80°C. This indicated that the suitable temperature of aging was 85°C. At aging temperature of 90-100°C, polymers were not obtained at 3 bars H_2 pressure, the active site might be destroyed by hydrogen.

The melt flow index value of polyethylene produced at various aging temperatures under 1 bar and 3 bars hydrogen pressure are shown in Table 5.11.

Table 5.11 MFI_2 of polyethylene under hydrogen pressure of 1 bar and 3 bars at different aging temperatures

Aging temperature (°C)	1 bar H_2 pressure		3 bar H_2 pressure	
	MFI_2 (g/10min)	MFR	MFI_2 (g/10min)	MFR
80	6.8	2.6	19.7	2.7
85	1.1	2.9	9.7	2.9
90	1.6	3.0	-	-
100	1.1	3.0	-	-

The MFI value of polyethylene produced by using ZN-catalysts at aging temperature of 80°C was higher than that of polyethylene produced by using ZN-catalysts at aging temperature higher than 80°C. This indicated that the catalyst produced at aging temperature of 80°C yielded the catalyst having high hydrogen response. The MFR value of polyethylene was slightly increased from 2.6 to 3.0 with an increasing of the aging time. The molecular weight distribution (MWD) of polyethylene produced by using catalyst at temperature of 90-100C was broader than that of polyethylene produced with catalyst at lower temperature.

Activity balances of Ziegler-Natta catalysts at different aging temperatures (80 and 85°C) are shown in Figure 5.15. It can be seen that the AB value of the aging temperature at 85°C was higher tan that of the aging temperature at 80°C.

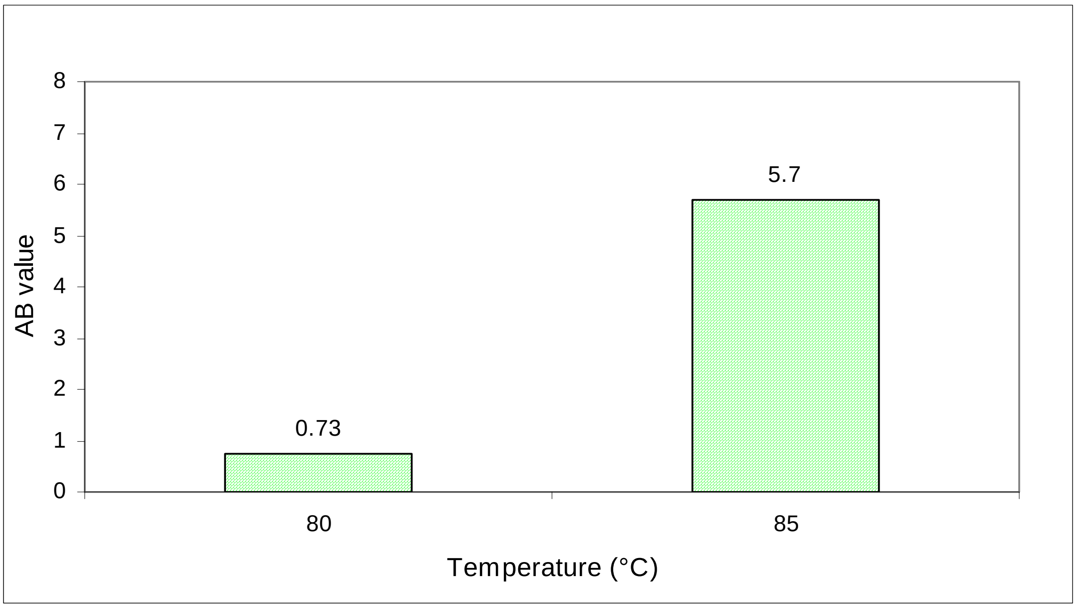


Figure 5.15. Activity balances of ZN-catalysts produced at different aging temperatures.

The average particle sizes of catalysts and polymers at different aging temperatures are shown in Table 5.12. The particle size of catalysts was independent on the aging temperature (see also Table 5.10).

Table 5.12 Average particle sizes of catalysts and polymers at different aging temperatures

Aging temperature (°C)	Particle size of catalyst (µm)	Particle size of polymer (1 bar H_2 pressure)	Particle size of polymer (3 bar H_2 pressure)
80	9.0	94	103
85	16.0	116	105

It could be concluded that the suitable aging temperature and aging time were 85°C and 10 h, respectively. The catalyst produced at such conditions exhibited high activity balance. In the last section will describe the comparative study of the properties of the invented catalysts and the comparative samples.

5.6 Properties of HDPE synthesized by using the produced catalysts and the comparative catalysts

The best catalyst obtained composed of $MgCl_2/3TiCl_4/0.125EB$ with 10 h aging time. The properties of polyethylene prepared from this invented catalyst such as catalyst activity, MFI, MFR, AB value, particle size, span of catalyst particles and SEM micrograph of polyethylene were compared with those of polyethylene prepared from the commercial catalysts.

Table 5.13 Properties of the invented catalyst and comparative Ex. I-II catalysts

Type of catalyst	Catalyst properties					
	EB content (ppm)	Mg (wt %)	Ti (wt %)	Cl (wt %)	Particle size (µm)	Span
The invention	44	16.5	5.7	57.5	9.9	2.5
Comp. Ex. I	0	19.4	5.0	64.3	9.1	1.4
Comp. Ex. II	68	15.8	7.3	58.3	10.0	1.5

The comparative catalyst I did not have ethyl benzoate (EB) while the comparative catalyst II had. The EB content in the invented catalyst was 44 ppm while of the comparative catalyst II was 68 ppm. The Mg content of the invented catalyst was relatively close to that of the comparative examples II whereas the comparative example I has higher Mg content (19.4 wt %). Ti content of the invented catalyst was about 5.7 wt % whereas the comparative example II had maximum Ti content (7.3 wt %). Cl content in the invented catalyst was relatively close to that of the comparative example II.

Particle size of the invented catalyst was not significantly different from those of comparative catalysts while the span of the invented catalyst was higher than that of comparative catalysts. The particle sizes of all catalysts are suitable for the HDPE slurry process.

The activity of the invented catalyst and comparative catalysts I-II were studied under the same polymerization conditions. The performances of the catalysts in ethylene polymerization at 1 bar and 3 bar hydrogen pressure are shown in Table 5.14-5.15.

Table 5.14 Performances of the invented catalyst and comparative examples I-II at hydrogen pressure 1 bar

Type of catalyst	Catalyst activity (g PE/g cat)	MFI_2 (g/10min)	MFI_5 (g/10min)	MFR (g/10min)	AB value	APS of PE (μm)	Span	Fine content (vol. %)
The invention	23,096	0.8	2.3	2.8	21.6	126	1.1	25
Comp. Ex. I	6,159	0.2	0.5	3.0	17.4	155	0.9	11
Comp. Ex. II	19,975	2.7	4.7	1.7	16.0	284	0.6	3

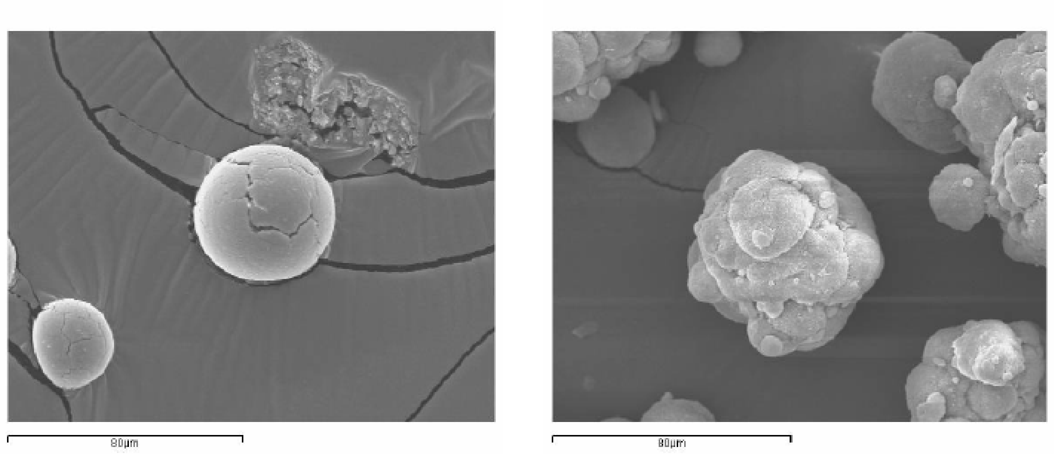
Table 5.15 Performances of the invented catalyst and comparative examples I-II at hydrogen pressure 3 bars

Type of catalyst	Catalyst activity (g PE/g cat)	MFI_2 (g/10min)	MFI_5 (g/10min)	MFR (g/10min)	APS of PE (μm)	Span	Fine content (vol. %)
The invention	22,376	5.1	12.8	2.5	115	1.2	31
Comp. Ex. I	5,720	3.0	9.5	3.1	142	1.0	18
Comp. Ex. II	18,682	31.8	95.0	3.0	226	0.9	3

Table 5.14-5.15 show that the activity of the invented catalyst was higher than that of the comparative examples I-II. MFI of polymers prepared from the invented catalyst was medium range compared with that of polymers of the comparative examples I and II under hydrogen pressure of 1 bar and 3 bars. The AB value of the invented catalyst was higher than that of comparative examples I and II. This indicated that the catalyst showed high stability throughout the polymerization time. Consequently, the invented catalyst system was more suitable for multimodal PE production by sequential polymerization in multi-reactor cascade. The invented catalyst had high accuracy in high molecular weight and low molecular weight fraction controlling for multi modal HDPE production in slurry process.

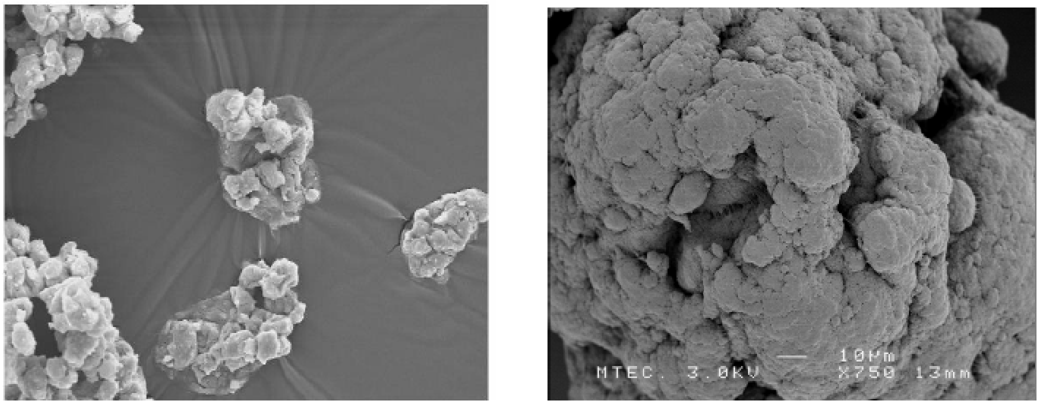
The invented catalyst gave polymers having average particle sizes somewhat smaller than that of the comparative examples. Small polymer particles in the polymerization reactor would cause a serious problem. Moreover, the catalyst did not cause of reactor fouling. They might reduce the drying efficiency and the lifetime of the dryer system. The bulk density of polymers obtained by using the invented catalyst was higher than that of the comparative ones.

SEM micrographs of the invented catalyst and derived polymers of the invented and comparative catalysts are depicted in Figure 5.16.



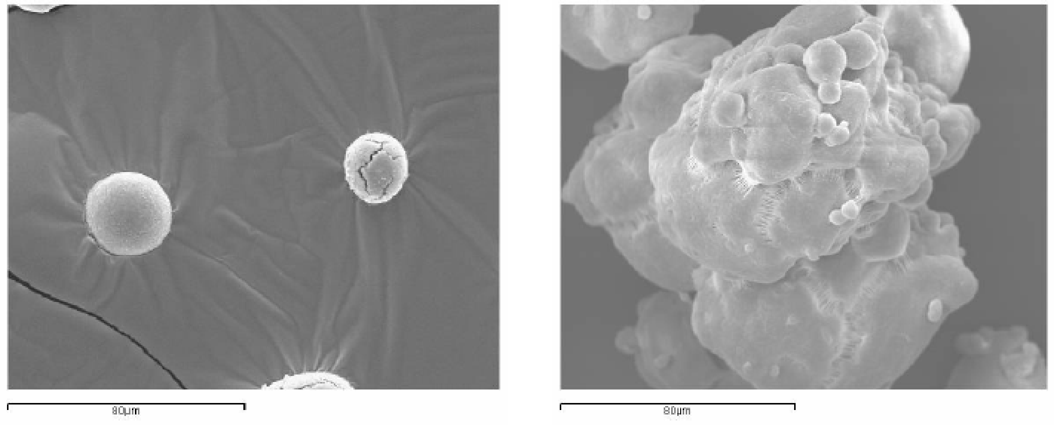
(A) The invented catalyst, 750X

(B) Polymer, 750X



(C) Comp. Ex. I catalyst, 750X

(D) Polymer, 750X



(E) Comp. Ex. II catalyst, 750X

(F) Polymer, 750X

Figure 5.16. SEM micrographs of the invented catalyst ($MgCl_2/3TiCl_4/0.125EB/10h$) (A), polymer obtained from the invented catalyst (B), Comp. Ex. I catalyst (in-situ $MgCl_2$ from $Mg(OEt)_2$) (C), polymer obtained from Comp Ex. I catalyst (D), Comp. Ex. II catalyst (melt quenching and re-crystallization) (E), polymer obtained from Comp. Ex. II catalyst (F) at magnification 750X.

As seen from Figure 5.16, SEM micrographs of polymers derived from different catalysts showed different surface properties. The surface of polymers derived from the invented catalyst was smooth. The polymers derived from comparative Ex. II shows small fibril linkage of each primary particle of macroparticles. A plausible mechanism is that the $MgCl_2$-supported catalyst is subjected to a gradual break-up from the surface to the interior of the particles. The polymerization rate at the surface of a catalyst particle is initially much higher than that in the interior, so a crust is formed quickly around the particle. But, as the catalyst break-up moves toward the center of the particle, the rate of the polymer growth inside the particle increases and eventually becomes higher than that on the particle surface. As a consequence, the polymer crust on the surface breaks to form some cold-drawn threads. Another possibility is that the fiber-like materials were formed by the amorphous or low molecular weight parts of the polymer [33]. Nevertheless, it could be explained that fibril linkage of each primary particle could prevent fragmentation of macroparticles during the particle growing.

The properties of polyethylene of the invented catalyst and comparative catalysts are shown in Table 5.16.

Table 5.16. Properties of polyethylene produced in this work and comparative catalysts at MFI_5 ranging of 1.5 – 2.3 g/10min

Type of catalyst	MFI_2 (g/10 min)	MFI_5 (g/10 min)	MFR	Density (g/cc)	Complex viscosity (at 0.00314 1/s)	Mn (g/mol)	Mw (g/mol)	MWD
Invention[a]	0.8	2.3	2.8	0.9591	9,460	30,000	192,000	6.4
Comp. Ex. I[b]	0.6	1.6	2.9	0.9590	18,900	35,000	235,000	6.7
Comp. Ex. II[c]	0.7	1.9	2.7	0.9595	12,500	32,700	213,000	6.5

[a] catalyst amount 0.02 mmol (Ti), TEA cocatalyst 1.0 mmol, ethylene monomer, H_2 pressure 1.0 bar, total pressure 8 bar, temperature 85°C, time 2.0 h.

[b] catalyst amount 0.02 mmol (Ti), TEA cocatalyst 1.0 mmol, ethylene monomer, H_2 pressure 1.5 bar, total pressure 8 bar, temperature 85°C, time 2.0 h.

[c] catalyst amount 0.02 mmol (Ti), TEA cocatalyst 1.0 mmol, ethylene monomer, H_2 pressure 0.5 bar, total pressure 8 bar, temperature 85°C, time 2.0 h.

As seen from Table 5.16, complex viscosity of polymer was related to MFI. Higher MFI polymer gave lower complex viscosity. The molecular weight distribution (MWD) of polymers produced by using the invented catalyst was 6.4, close to that of polymers obtained from the comparative catalysts. This *Mw/Mn* value suggested that polymers were produced by a multi active species. The density of polymers was 0.9591 g/cc, which was in the range of high density polyethylene (0.940-0.975 g/cc).

CHARPTER VI

CONCLUSIONS AND SUGGESTIONS

6.1 Conclusions

In this study, Z-N catalysts were prepared via multi steps. Several parameters affected on the catalysts properties: TEA/Mg molar ratio, EB/Mg molar ratio, Ti/Mg molar ratio, aging time, and aging temperature were studied. It was found that the best conditions to prepare a high performance Z-N catalysts were TEA/Mg molar ratio = 0.50, 2-ethyl-1-hexanol/Mg molar ratio = 3.5, Ti/Mg molar ratio = 3.0, EB/Mg molar ratio = 0.125, aging temperature = 85°C, aging time = 10 h, and agitator speed = 300 rpm. The best catalysts composed of Mg = 16.5 wt %, Ti = 5.7 wt %, Cl = 57.5 wt %, EB content = 44 ppm, and particle size = 9.9 μm. SEM micrographs of the catalysts show spherical. Activity values of the catalysts in ethylene polymerization at 1 bar and 3 bar hydrogen pressure were studied. It was found that activity values of the catalysts at 1 bar and 3 bar hydrogen pressure were 23,096 and 22,376 g PE/g cat, respectively. The catalyst exhibited high hydrogen response. The activity balance (AB) of the prepared catalyst was 21.6. Thus, the catalyst was suitable for multimodal HDPE in slurry process.

In addition, the results in this study can be summarized as the following:

1. The effect of TEA/Mg molar ratio: the increased TEA/Mg molar ratio strongly affected dispersion of the $MgCl_2$ based support in toluene. The suitable TEA/Mg molar ratio was 0.5.

2. The effect of Ti/Mg molar ratio: the Ti content in the catalyst increased as the Ti/Mg molar ratio increased. The suitable Ti/Mg molar ratio was 3.0.

3. The effect of EB/Mg molar ratio: the EB content in catalysts increased while Ti content in catalysts decreased with an increasing of EB/Mg molar ratio. The activity of catalysts decreased while the AB of catalysts increased with an increasing of EB/Mg molar ratio. The catalyst produced at the EB/Mg molar ratio of 0.125 gave the maximum AB of 52.2. This indicated that ethyl benzoate can

improve stability of polymer particles during polymerization. The suitable EB/Mg molar ratio was 0.125.

4. The effect of aging time: the increased aging time affected the Ti fixed on $MgCl_2$ based support. The activity of the catalyst increased with an increasing of the aging time. The suitable aging time was 10 h. The MFI of polymers slightly decreased with an increasing of the aging time. The AB values of the catalyst decreased with an increasing of aging time. However, the AB value of catalysts at the aging time of 10 h was 21.6 which was acceptable.

5. The effect of aging temperature: the increased aging temperature affected the Ti content in the catalyst. The suitable aging temperature was 85°C and the obtained AB was 5.7.

6. The catalyst prepared under the conditions of TEA/Mg = 05, Ti/Mg = 3.0, EB/Mg = 0.125, aging time = 10 h and aging temperature = 85°C gave good activity balance (AB). The Ti content in the invented catalyst was 5.7 wt % while that of the comparative I and II were 5.0 wt % and 7.3 wt %, respectively. The activity order of the catalysts was the invented catalyst > Comp. Ex. II > Comp. Ex. I. Hydrogen response order of the catalysts was Comp. Ex. II > the invented catalyst > Comp. Ex. I. The AB of the invented catalyst was higher than that of comparatives I and II, respectively.

7. From SEM micrographs, the morphologies of the invented catalyst and the Comp. Ex. II were spherical while those of Comp. Ex. I was irregular and non uniform. The invented catalyst and Comp. Ex. II provide good polymer morphology controlling. Polymer grains obtained from the invented catalyst were regular and spherical. This pointed out that the catalyst prepared from magnesium complex could overcome the risk of reactor fouling.

8. The molecular weight and molecular weight distribution (MWD) of polymers obtained from the invented catalyst were 192,000 and 6.4, respectively. MWD of polyethylene prepared from the invented catalyst was relatively close to that of polyethylene obtained from comparatives I ad II. Therefore, the invented catalysts could be used in the production scale without the process parameters adjusting.

The catalyst was suitable for multimodal polyethylene production in cascade polymerization of HDPE slurry process. The catalyst was suitable for the production of HDPE for film, high pressure PE pipe, blow molding, and injection molding applications.

6.2 Suggestion for further study

To reduce high fine polymers content (25-30 vol. %) obtained from the invented catalyst, the stability of catalysts and polymer particles during the polymerization should be improved. Organosilane as a binding agent such as dicyclopentyl dimethoxysilane (DPDMS) and cyclohexylmethyl dimethoxysilane (CHMDS) were suggested for the further study to improve mechanical stability of the catalysts and polymers.

APPENDICES

Table A1 Performances of Ziegler-Natta catalysts produced at different Ti/Mg ratios at hydrogen pressure of 1 bar

Item	Unit	Ti/Mg molar ratio		
		2	3	4
Catalyst activity	g PE/g cat	7,854	20,99	10,950
MFI_2	g/10min	1.6	1.7	0.2
AB value	-	10.4	2.7	2.4
APS of PE	µm	115	107	100
Span	-	0.8	1.0	0.8
Fine content	vol. %	19	37	32
BD	g/cc	0.34	0.41	0.4

Table A2 Performances of Ziegler-Natta catalysts produced at different Ti/Mg ratios at hydrogen pressure of 3 bars

Item	Unit	Ti/Mg molar ratio		
		2	3	4
Catalyst activity	g PE/g cat	8,576	14,294	7,445
MFI_2	g/10min	6.8	18.0	1.9
APS of PE	µm	115	92	100
Span	-	0.9	1.2	1.2
Fine content	vol. %	20	52	35
BD	g/cc	0.43	0.41	0.42

Table A3 Performances of Ziegler-Natta catalysts produced at different EB/Mg ratios at hydrogen pressure of 1 bar

Item	Unit	EB/Mg molar ratio			
		0	0.125	0.25	0.50
Catalyst activity	g PE/g cat	20,990	4,558	2,080	835
MFI_2	g/10min	1.7	1.0	2.0	0.9
MFI_5	g/10min	5.3	2.7	9.9	2.6
MFR	-	3.1	2.7	3.1	2.9
AB value	-	2.7	52.2	17.2	-
APS of PE	µm	107	112	126	-
Span	-	1.0	1.1	0.9	-
Fine content	vol. %	37	31	20	-
BD	g/cc	0.41	0.41	0.36	-

Table A4 Performances of Ziegler-Natta catalysts produced at different EB/Mg ratios at hydrogen pressure 3 bars

Item	Unit	EB/Mg molar ratio		
		0	0.125	0.25
Catalyst activity	g PE/g cat	14,294	4,505	2,080
MFI_2	g/10min	54.5	8.7	2.0
MFI_5	g/10min	164	18	6.2
MFR	-	3.0	2.1	3.1
APS of PE	µm	92	110	150
Span	-	1.3	1.1	1.1
Fine content	vol. %	52	34	16
BD	g/cc	0.41	0.38	0.37

Table A5 Performances of catalysts at different aging times at 1 bar hydrogen pressure

Item	Unit	Time (h)			
		0	5	10	15
Catalyst activity	g PE/g cat	4,558	5,505	23,096	20,467
MFI_2	g/10min	1.0	1.1	0.8	0.6
MFI_5	g/10min	2.2	2.2	2.3	1.6
MFR	-	2.3	2.1	2.8	2.7
AB value	-	52.2	57	21.6	2.3
APS	µm	112	116	126	153
Span	-	1.1	1.1	1.1	1.1
Fine content	vol. %	32	30	25	18
BD	g/cc	0.41	0.40	0.42	0.43

Table A6 Performances of catalysts at different aging times at 3 bar hydrogen pressure

Item	Unit	Time (h)			
		0	5	10	15
Catalyst activity	g PE/g cat	4,505	6,630	22,376	13,400
MFI_2	g/10min	8.7	9.4	5.1	4.6
MFI_5	g/10min	21.9	28.4	12.8	12.8
MFR	-	2.5	3.0	2.5	2.8
APS	µm	110	105	115	154
Span	-	1.1	2.1	1.2	1.1
Fine content	vol. %	34	43	31	19
BD	g/cc	0.38	0.42	0.41	0.42

Table A7 Performances of catalysts at different aging temperatures at 1 bar hydrogen pressure

Item	Unit	Temperature (°C)			
		80	85	90	100
Catalyst activity	g PE/g cat	5,292	5,505	5,936	5,489
MFI_2	g/10min	6.8	1.1	1.6	1.1
MFI_5	g/10min	17.7	3.2	4.8	3.3
MFR	-	2.6	2.9	3.0	3.0
AB	-	0.73	5.7	-	-
APS of polyethene	µm	94	116	140	-
Span	-	0.9	1.4	1.2	-
Fine content	vol. %	42	30	39	-
BD	g/cc	0.41	0.40	0.33	-

Table A8 Performances of catalysts at different aging temperatures at 3 bars hydrogen pressure

Item	Unit	Temperature (°C)	
		80	85
Catalyst activity	g PE/g cat	2,758	6,630
MFI_2	g/10min	19.7	9.7
MFI_5	g/10min	53	28
MFR	-	2.7	2.9
APS of PE	µm	103	105
Span	-	1.4	2.1
Fine content	vol. %	45	43
BD	g/cc	0.40	0.42

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