ผลของไฮโดรเจนที่มีต่อตัวเร่งปฏิกิริยาแบบซีเกลอร์-นัตตาที่เตรียมโดยวิธีต่างกันสำหรับปฏิกิริยาเอทิลีนพอลิเมอร์ไรเซชัน

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EFFECT OF HYDROGEN ON ZIEGLER - NATTA CATALYSTS PREPARED BY DIFFERENT METHODS FOR ETHYLENE POLYMERIZATION

Miss Thanyathon Niyomthai

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By	Miss Thanyathon Niyomthai
Field of Study	Chemical Engineering
Thesis Advisor	Professor Piyasan Praserthdam, Dr.Ing.
Thesis Co-Advisor	ProfessorVincenzo Busico, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

....Dean of the Faculty of Engineering
(Associate Professor Supot Teachavorasinskun, D.Eng.)

THESIS COMMITTEE

....Chairman
(Professor Suttichai Assabumrungrat, Ph.D.)

....Thesis Advisor
(Professor Piyasan Praserthdam, Dr.Ing.)

....Thesis Co-Advisor
(ProfessorVincenzo Busico, Ph.D.)

....Examiner
(Professor Bunjerd Jongsomjit, Ph.D.)

....Examiner
(Associate Professor Anongnat Somwangthanaroj, Ph.D.)

....External Examiner
(Wanna Phiwkliang, Ph.D.)

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งานวิจัยนี้เน้นผลของไฮโดรเจนในระบบตัวเร่งปฏิกิริยาซีเกลอร์-แนตตาสำหรับปฏิกิริยาเอทิลีนพอลิเมอไรเซชัน โดยงานวิจัยนี้แบ่งการศึกษาออกเป็น 4 ส่วน ในส่วนแรกเป็นการศึกษาเปรียบเทียบตัวเร่งปฏิกิริยาซีเกลอร์-แนตตา 2 ชนิด [$TiCl_4/MgCl_2/THF$ (ZN-THF) และ $TiCl_4/MgCl_2$•6EtOH (ZN-EtOH)] ผลที่ได้พบว่า ZN-EtOH มีการกระจายตัวของไซต์ที่ว่องไวดีกว่า ZN-THF เป็นผลให้ ZN-EtOH สามารถยับยั้งผลของไฮโดรเจนและแสดงค่าความว่องไวสูงกว่า ZN-THF เนื่องจากการตอบสนองต่อไฮโดรเจนที่สูงกว่าของ ZN-THF งานวิจัยส่วนที่สองและสามจึงได้นำตัวเร่งปฏิกิริยา ZN-THF นี้มาศึกษาต่อโดยปรับปรุงด้วยกรดลิวอิสเพื่อพัฒนาการเร่งปฏิกิริยาโดยเลือกใช้อะลูมิเนียม (III) คลอไรด์และไอร์ออน (II) คลอไรด์ จากผลการทดลองพบว่าไอร์ออน (II) คลอไรด์แสดงประสิทธิภาพสูงในการกำจัดเตตระไฮโดรฟูแรนที่เหลือในโครงสร้างแมกนีเซียม (II) คลอไรด์และให้การตอบสนองต่อไฮโดรเจนดีกว่าอะลูมิเนียม (III) คลอไรด์ สำหรับงานวิจัยส่วนที่สามศึกษาซิงค์ (II) คลอไรด์ ซิงค์ (II) คลอไรด์ผสมอะลูมิเนียม (III) คลอไรด์และซิงค์ (II) คลอไรด์ผสมไอร์ออน (II) คลอไรด์ในระบบ ZN-THF ผลที่ได้พบว่าซิงค์ (II) คลอไรด์เป็นพิษต่อตัวเร่งปฏิกิริยาเป็นผลทำให้ค่าความว่องไวลดลง การเติมกรดลิวอิสตัวที่สองสามารถเพิ่มค่าความว่องไวได้ แต่อย่างไรก็ตามค่าความว่องไวยังคงต่ำกว่าตัวเร่งปฏิกิริยาที่ไม่เติมซิงค์ (II) คลอไรด์เล็กน้อย สำหรับงานวิจัยส่วนสุดท้ายศึกษาผลของแอลคอกซีไซเลนในฐานะตัวจ่ายอิเล็กตรอนต่อประสิทธิภาพของตัวเร่งปฏิกิริยาเชิงพาณิชย์ 2 ชนิด คือ $TiCl_4/MgCl_2$•nEtOH และ $TiCl_4$/phthalate type/$MgCl_2$ ผลที่ได้พบว่าไซโคลเฮกซิลเมทิลไดเมทอกซีไซเลนสามารถลดค่าความว่องไวได้มากกว่าไดเมทิลไดเมทอกซีไซเลนและให้การตอบสนองไวต่อไฮโดรเจนที่สูงกว่า

ภาควิชา วิศวกรรมเคมี
สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2559

ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

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THANYATHON NIYOMTHAI: EFFECT OF HYDROGEN ON ZIEGLER - NATTA CATALYSTS PREPARED BY DIFFERENT METHODS FOR ETHYLENE POLYMERIZATION. ADVISOR: PROF. PIYASAN PRASERTHDAM, Dr.Ing., CO-ADVISOR: PROF.VINCENZO BUSICO, Ph.D., 126 pp.

This study focuses on effect of hydrogen on Ziegler-Natta (ZN) catalyst system for ethylene polymerization. The study was divided into four parts. Regarding to the first part, two types of ZN catalysts, $TiCl_4/MgCl_2/THF$ (ZN-THF) and $TiCl_4/MgCl_2 \bullet 6EtOH$ (ZN-EtOH) catalysts, were compared. The results showed that ZN-EtOH had better active center distribution than that of ZN-THF. As a result, ZN-EtOH could retard the effect of hydrogen and showed higher activity than ZN-THF. According to higher hydrogen response of ZN-THF, ZN-THF system was selected to study in the second and the third parts with Lewis acid modification in order to improve the catalytic performance. $AlCl_3$ and $FeCl_2$ were employed in the second part. $FeCl_2$ showed higher efficiency to remove the remaining THF in $MgCl_2$ structure and provided better hydrogen response than $AlCl_3$. For the third part, $ZnCl_2$, mixed $ZnCl_2$ with $AlCl_3$ and mixed $ZnCl_2$ with $FeCl_2$ were studied in ZN-THF system. The results showed that $ZnCl_2$ acted as a poison to catalyst resulting to the reduction of activity. The addition of the second Lewis acid could improve the activity; however, activity was still slightly lower than undoped $ZnCl_2$ catalyst. For the last part, effect of alkoxysilanes as external donor on 2 types of the commercial catalysts, $TiCl_4/MgCl_2 \bullet nEtOH$ and $TiCl_4$/phthalate type/$MgCl_2$, was investigated. Cyclohexylmethyldimethoxysilane could decrease activity more than dimethoxydimethylsilane did and provide higher hydrogen sensitivity as well.

Department:	Chemical Engineering	Student's Signature	....
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CHAPTER I

INTRODUCTION

At present, plastic is probably the most important material to be used to make almost everything. This is due to the facts of its low in production cost, easy to both synthetize and mold into any kind of shapes, and good mechanical and chemical properties. Among many types of plastic, one of the most common polyolefin is polyethylene (PE) which is the largest plastic commodity consumed nowadays. Due to its versatility and durability, it is chosen as a main polymer to create an extensive range of products. To synthetize such useful polymer, Ziegler-Natta catalysts (ZN)[1,2] and metallocene catalysts[3,4] are generally employed. However, ZN catalysts remain the first choice for being industrial catalysts because of their lower cost and broader molecular weight distribution (MWD) than metallocene catalysts.

One thing that industries usually concern is how to control the MWD of obtained polymers because it could significantly affect the final mechanical and processing properties of the polymer[5-8]. Polymer having short chains provides good processability, while having high molecular weight fraction provides good mechanical properties. Therefore, polymers having both short and long chains are required to produce polymers with a broad MWD[9]. However, narrow or board MWD depends on what desired application to polymer is used for.

As it is widely noticed, hydrogen is the commercial key agent usually used to control molecular weight of polymer. Therefore, hydrogen was used in a large volume for olefin polymerization. The presence of hydrogen in the polymerization medium also influences the catalytic activity, but it depends on the nature of catalyst, cocatalyst, monomer, donor systems as well as polymerization conditions[5,10-13]. That is why effect of hydrogen on activity is complicated to forecast. This is because it depends on several factors. For example, the activity of $TiCl_3/MgCl_2$ and supported metallocene catalysts decreases obviously in ethylene polymerization. On the contrary, the activity showed the different results in propylene polymerization[11]. This shows that hydrogen effect relies on monomer types. Furthermore, it has been perceived that active center distribution also has a strong effect on MWD of polymer. It means that the surface structure of $MgCl_2$ affects on MWD, which influences the physical and mechanical properties, and processability of polymer[2,14]. Up to this point, it can be said that the controlling of polymer properties can be done by the modification of $MgCl_2$ and the addition of hydrogen. The addition of Lewis acid and bases with $MgCl_2$ support is one of the most effective ways to modify the catalyst surface structure including active center distribution as well. As a consequence, it is interesting to study about how active sites dispersed in ZN catalysts. In the current study, we try to use hydrogen to describe roughly about active center distribution. Thus, a small amount of hydrogen until its large volume was added into the system to investigate the response of hydrogen in every concentration for ethylene polymerization.

1.1 Motivations

1. Due to the fact that the determination about active center distribution is complicated and ill-defined. Thus, hydrogen was used to describe how active sites dispersed in ZN catalysts.
2. The modification of $MgCl_2$ support with the addition of the 2nd metal chloride is less studied.
3. Effect of alkoxysilanes on catalytic activity in ethylene polymerization is less investigated.

1.2 Objectives

The objectives of this research are to study effect of hydrogen on ZN catalytic system in ethylene polymerization based on activity and properties of polyethylene. ZN catalysts prepared by different methods including ZN catalysts modified with different Lewis acids and bases (alkoxysilanes) were studied. From now on hydrogen response in this study means effect of hydrogen on surface active sites.

1.3 Scope

All parts of this study focus on effect of hydrogen on catalytic activity with ZN system in ethylene homo-polymerization.

1. The study covers only the effect of two types of ZN catalysts, which are $TiCl_4/MgCl_2/THF$ (ZN-THF) and $TiCl_4/MgCl_2{\bullet}6EtOH$ (ZN-EtOH) catalysts, prepared by different methods on catalytic activity for ethylene polymerization with hydrogen addition.
2. Single Lewis acid was used at a time to study its effect on catalytic activity in the presence of hydrogen for ethylene polymerization. $TiCl_4/MgCl_2/THF$ catalysts were modified with single Lewis acid such as $AlCl_3$ and $FeCl_2$.

3. Change in catalytic activity and thermal properties of PE from mixed $ZnCl_2$ Lewis acids ($ZnCl_2$ with $AlCl_3$ and $ZnCl_2$ with $FeCl_2$) with $TiCl_4/MgCl_2$/THF catalysts in the presence of hydrogen and vice versa was observed.
4. Effect of alkoxysilanes as external donor on activity via two types of commercial ZN catalysts [$TiCl_4/MgCl_2$•nEtOH (Cat-A) and $TiCl_4$/phthalate type/$MgCl_2$ (Cat-B)] was investigated in ethylene polymerization with additional hydrogen. Cyclohexylmethyldimethoxysilane (CHMDMS) and dimethoxydimethylsilane (DMDMS) were employed as external donor.

This study is mainly divided into five parts. Chapter 1 is to introduce the rational and overall concept of ZN catalysts and the objective of this work. Next, Chapter 2 is deal with background theory, $MgCl_2$ structure, mechanism of ethylene polymerization and literature review related to ZN catalysts modified with Lewis acids and Lewis bases and their chemistry. After that, Chapter 3 is to describe the experimental steps such as the laboratory procedure for the catalyst preparations, ethylene polymerization and the characterization methods. The result and discussion found of this work are presented in Chapter 4. The last chapter is the conclusions and recommendations.

1.4 Research Methodology

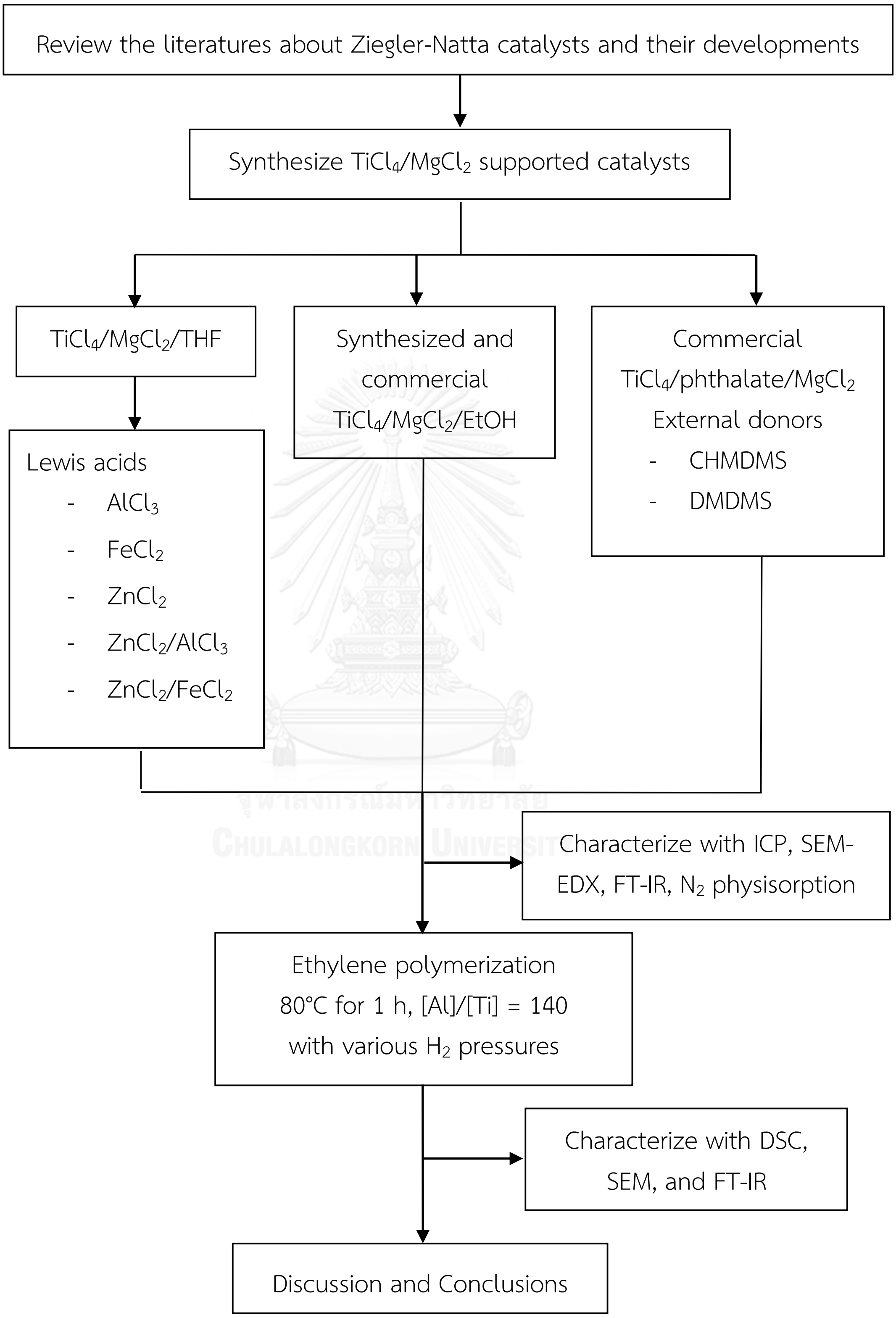

Figure 1.1 Flow diagram of this research methodology

CHAPTER II

THEORY AND LITERATURE REVIEWS

Titanium-based Ziegler–Natta catalytic systems have evolved and have been widely utilized in olefin polymerization over several decades. Up to the present time, these heterogeneous Ziegler-Natta catalysts are still major choices for the polyolefin production due to their versatility and low in cost[15,16]. The catalyst performance and the final properties of synthetized polyolefin are depended on several factors: catalyst preparation method, metal active sites, support, co-catalyst and polymerization temperature[2,17,18]. There are many literatures reported that the molecular weight (MW), molecular weight distribution (MWD), melting temperature and percent of crystallinity of synthetic polymers are strongly relied on polymerization parameters like ethylene pressure, hydrogen pressure, polymerization temperature, and polymerization time[2,5,19-23].

To get better understanding about related chemistry and roles of the heterogeneous Ziegler-Natta system, more details are explained as follow:

2.1 Structure of $MgCl_2$

Support selection is one of the important factors affecting the catalyst productivity. Magnesium chloride ($MgCl_2$) is commonly chosen as a support for

Ziegler-Natta catalysts because it has similar crystal structure to that of $TiCl_3$ and acts as the active catalyst material. $MgCl_2$-supported catalysts have the advantages of higher activity, higher stereospecificity and controlled morphology[24]. Spaleck *et al.* revealed that $MgCl_2$ is a one of ZN active site due to the fact that Mg and Ti have similar atomic size and shape. Moreover, δ-$MgCl_2$ has a similar crystalline structure to that of δ-$TiCl_3$ and the nearly identical ionic radii and lattice distances resulting the increase in propagation rate constant (k_p) as well as the number of active sites [C*][25]. This leads to higher productivity.

In principle, $MgCl_2$ has two crystalline forms: the common α-form and the less stable β-form[24]. The α-form shows as a distorted cubic closed packing (CCP) of Cl atoms (e.g. …ABC ABC ABC…). In contrast, the β-form of $MgCl_2$ develops to be hexagonal close packing (HCP) of Cl atoms (e.g. …AB AB AB…). $MgCl_2$ in both α-form and β-form exhibit layered structures with two outer Cl atoms sandwiching a single plane of Mg atoms, as depicted in **Figure 2.1**[24]. The transformation of $MgCl_2$ to active catalyst or δ-$MgCl_2$ which exhibits a disordered structure arising from the translation and rotation of the structural Cl-Mg-Cl layers with respect to one another that destroy the crystal order in the stacking direction[24-26]. Hence, the X-ray spectrum displays a gradual disappearance of the (104) reflection and its replacement by a broad “halo” centered at *d* = 2.65 Å. As displayed in the **Figure 2.2,** the disordered δ-$MgCl_2$ structure showed broad bands centered at 2θ = 15, 32 and 50.5°[27].

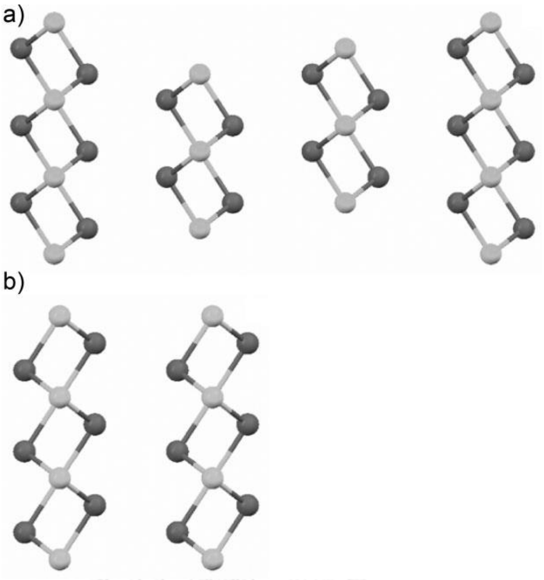

Figure 2.1 $MgCl_2$ matrix in (a) α-form having cubic closed packing and (b) β-form having hexagonal closed packing of Cl–Mg–Cl triple layers. Dark gray and light gray spheres mean to the chlorine and magnesium ions, respectively[24].

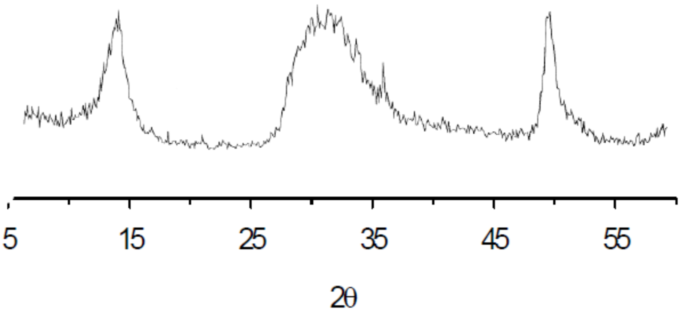

Figure 2.2 X-ray powder spectrum of δ-$MgCl_2$[27]

2.2 Catalysts preparation method

For industrial aspects, it is extremely important to find the simple method for catalyst synthesis to achieve a lower cost. Tetrahydrofuran (THF) and alcohol are a kind of Lewis base usually used to react with solid $MgCl_2$ due to low in cost and easy to prepare.

Morphology of catalyst particle is one of the main factors that industries concern as well, because it affects in industrial processes like reactor loading and reactor fouling. Thus, two main catalysts (used THF or alcohol as solvent), which are industrially viable, have been conducted to fulfill the requirements. A short description is given below.

2.2.1 $TiCl_4/MgCl_2/THF$ catalyst

$TiCl_4/MgCl_2/THF$ catalytic systems are often utilized to prepare ZN catalysts because of their benefits such as good hydrogen response ability, low cost and suitable for copolymers[28]. THF, which is ether, is kind of Lewis base usually used to react with solid $MgCl_2$. A treatment with $TiCl_4$ providing active catalysts is followed.

Sobota (2004) revealed that THF is the most mature as a selectivity control agent in ethylene polymerization[29].

By dissolving $MgCl_2$ and $TiCl_3$ together in THF, a complication system is formed *in situ*:

$3.14MgCl_2 + TiCl_4 + THF(Sol.) \longrightarrow (TiCl_4)(MgCl_2)_{3.14}(THF)_x$ (2.1)

$3.14MgCl_2 + TiCl_3{\cdot}1/3AlCl_3 + THF(Sol.) \longrightarrow TiCl_3)(AlCl_3)_{1/3}(MgCl_2)_{3.14}(THF)_y$ (2.2)

$3.14MgCl_2 + TiCl_3 + THF(Sol.) \longrightarrow (TiCl_3)(MgCl_2)_{3.14}(THF)_z$ (2.3)

Where Sol. = Solvent

The complexes in Equation (2.1)-(2.3) may be different in solution or solid state. This difference will directly affect the properties of catalyst. In solution state, x, y, and z are all relatively big because THF will occupy all the coordination sites of Ti, Mg, and Al together with Cl. In solid state, the percentage of THF is closely related to x, y, and z. However, the remaining THF in the final catalyst resulting in the decreasing in catalytic activity because the excess THF may poison the catalyst active sites[18]. Therefore, the removal of THF is very crucial for catalyst preparation.

However, co-catalyst can coordinate with THF causing some THF to be removed from the Ti center and provide higher catalytic activity[30]. The reaction of $TiCl_4(TiCl_3)/MgCl_2/THF$ catalyst with co-catalyst (Co-cat) such as methylaluminoxane (MAO), alkylaluminum compound, etc. are described below:

$(TiCl_4)(MgCl_2)_{3.14}(THF)_x + n\text{Co-cat} \longrightarrow (TiCl_4)(MgCl_2)_{3.14}(THF)_{x-n} + nTHF{\cdot}\text{Co-cat}$ (2.4)

$$(TiCl_3)(AlCl_3)_{1/3}\ (MgCl_2)_{3.14}\ (THF)_y + n\text{Co-cat}$$

$$\longrightarrow (TiCl_3)(AlCl_3)_{1/3}\ (MgCl_2)_{3.14}(THF)_{y-n} + n\text{THF}\cdot\text{Co-cat} \qquad (2.5)$$

$$(TiCl_3)(MgCl_2)_{3.14}(THF)_z + n\text{Co-cat} \longrightarrow (TiCl_3)(MgCl_2)_{3.14}(THF)_{z-n} + n\text{THF}\cdot\text{Co-cat} \qquad (2.6)$$

According to Equations (2.4)-(2.6), pre-reduction of the catalyst with co-catalyst has at least two influences. First, it reduces Ti(IV) to Ti(III) then the catalyst has a very uniform activity to suit the fluidized bed and increase the stabilization of production which favor the granular morphology of the synthetic polymer. Second, THF occupies the coordination sites of Ti to make Ti as an inactive center. However, some THF was removed by complexation with co-catalyst as mentioned previously, hence this leads the catalyst to have higher activity[30].

2.2.2 $TiCl_4/MgCl_2$•nEtOH catalyst

The new catalyst preparation via alcohol adduct-based solution ($MgCl_2 \cdot nROH$ adduct) was found afterwards. This method provides good catalyst morphology and higher catalytic activity than $TiCl_4/MgCl_2/THF$ catalyst system[31-35].

The basic components for preparing the catalyst are the soluble of $MgCl_2$ with EtOH and its impregnation with $TiCl_4$.

The reaction of $MgCl_2 \cdot x$EtOH complex and internal donor are described in the following equations (2.9)-(2.12).

$$MgCl_2 \cdot EtOH + TiCl_4 \longrightarrow MgCl_2 + EtOTiCl_3 + HCl \tag{2.7}$$

$$MgCl_2 + MgCl_2 \longrightarrow MgCl_2\ (solid) \tag{2.8}$$

$$MgCl_2 \cdot EtOH + ID \longrightarrow MgCl_2 \cdot EtOH \cdot ID \tag{2.9}$$

$$MgCl_2 \cdot EtOH \cdot ID + TiCl_4 \longrightarrow MgCl_2 \cdot EtOTiCl_3 \cdot ID + HCl \tag{2.10}$$

$$MgCl_2 \cdot EtOTiCl_3 \cdot ID + TiCl_4 \longrightarrow MgCl_2 + MgCl_2 \cdot ID + TiCl_4 \cdot ID + TiCl_4 \cdot EtOTiCl_3 \tag{2.11}$$

$$MgCl_2 \cdot ID + TiCl_4 \longrightarrow MgCl_2 \cdot TiCl_4 \cdot ID \tag{2.12}$$

$$MgCl_2(solid) + TiCl_4 \longrightarrow MgCl_2\ (solid) \cdot TiCl_4 \tag{2.13}$$

Due to the residual alcohol and titanium alkoxides in the support act as catalytic poisons, Chirinos *et al.* applied to use silicon tetrachloride ($SiCl_4$) to react with $MgCl_2 \bullet n ROH$ adduct to form $MgCl_2$-$SiCl_{4-n}(OR)_n$ that alkoxysilane are formed from the alcohols used as solvents. Then, $TiCl_4$ is supported on the alcohol-free recrystallized $MgCl_2$-$SiCl_{4-n}(OR)_n$. After completed alcohol elimination, the formed alkoxysilanes remain grafted in the solid catalysts and act as an electron donor in the catalytic polymerization[36-42]. Nowadays, there are various methods to remove alcohol from the $MgCl_2 \bullet n ROH$ adduct such as thermal or chemical treatment. In part of chemical treatment, titanium tetrachloride ($TiCl_4$), triethylaluminium (TEA), dichlorodimethylsilane (DCDMS) and chlorotrimethylsilane are employed as a dealcohol agent[43,44].

2.3 Effects of Lewis bases and their chemistry

Tetrahydrofuran and alcohol, which are typically used as solvent in catalyst synthesis, are one kind of Lewis bases. Lewis bases or electron donors can be classified by their function into 2 types: Internal donor, adding during catalyst preparation, and external donor, adding during polymerization, to compensate the lost internal donor during catalyst activation (alkylation and reduction reactions with co-catalyst). If external donor is not added to the catalyst, the deactivation could reach its highest value, presumably because the non-specific sites deactivate faster than the specific sites. External donor can increase the population of specific sites at the consumption of the non-specific sites, which are more regioirregular[45]. Therefore, it can be said that the performance of the catalyst system depends on the amount of the internal/external donor exchange[46].

Much effort has been expended so far in finding better combinations between internal and external donor. Electron donor can be divided into 4 classes: alkoxysilanes, aromatic esters, amines and dialkyl propane ethers[46]. It is generally accepted that all types of external donor easily form complex with co-catalyst which is stable with silane compound. This is due to the fact that a silane donor contains at least one secondary or tertiary carbon linked directly to the silicon atom. This bulky hydrocarbon group is believed to protect the silane against the removal from the catalyst surface via complexation with alkyl aluminum.

However, Busico *et al.* revealed that electron donors may block or poison most of the less stereospecific active sites on the catalyst and turn them into isotatctic site. Thus, it can be said that electron donor is one type of poisons. As a consequence, if an excessive amount of donors are presented, they may cause the effective poisoning on active centers via direct binding to Ti atom which then affect the molecular weight of polymer. The selectivity of deactivation of external donor is controlled by the sterical size of hydrocarbon part instead of being controlled by electronegativity of oxygen in that molecule[47].

There are many studies about $MgCl_2$ crystal structure, Giannini *et al.* disclosed that Mg atoms coordinated by four Cl atoms on (110) and five Cl atoms on (100) lateral cut. Singh *et al.* reported that the presence of well-defined $MgCl_2$ crystallites prefers to form (100) or (104) plane with less Lewis acidity and more Lewis acidity in (110) lateral cuts. Thus, the (104) and (110) lateral cuts (**Figure 2.3**) are the surfaces where internal donors, titanium chloride species, and external donors bind to coordinatively unsaturated Mg^{2+} ions. Furthermore, they noted that $TiCl_4$ may not form complexes with $MgCl_2$ on (104) lateral cuts, owing to weak Lewis-basic sites, while forms stable complexes with Mg^{2+} ions at (110) lateral cuts. Thus, (110) lateral cuts become critical for active-site formation, and the core for stereospecific polymerization[24]. This is in agreement with Parada *et al.* They reported that the (110) face has more Lewis acidity than the (100) face. Therefore, internal donor would be easily removed from the (100) face. Then, $TiCl_4$ should bind on the face more easily, though it might be inhibited somewhat from fixing to the (110) face[38].

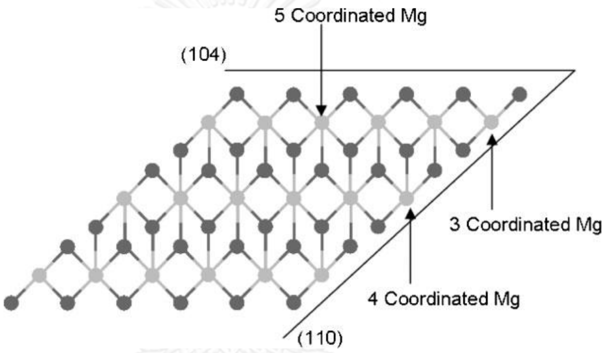

Figure 2.3 Model of $MgCl_2$ layer showing the (104) and (110) cuts; dark and light gray spheres correspond to the chlorine and magnesium ions, reapectively[24].

Andoni *et al.* reported preferential growth of $MgCl_2$ crystal along the (110) direction in the presence of 1,3-diethers, while the growth occurred along both the (110) and (104) directions in the presence of phthalates[48]. According to several studies using DFT calculations, it can be concluded that phthalates could be adsorbed at both the (104) and (110) planes of $MgCl_2$ with bridging or chelating forms; while 1,3-diethers or alkoxysilanes could be adsorbed only at the (110) plane with chelating forms because the distance between their two oxygens was shorter than those of phthalates[49,50].

Sacchi *et al*. proposed a general conclusion on the behavior of the internal (ID) and external donors (ED) including the interaction among the catalyst components with the following reaction model[51]:

$\text{Cat}{\bullet}\text{ID} + \text{AlEt}_3 \leftrightarrow \text{Cat-[ ]} + \text{AlEt}_3{\bullet}\text{ID}$ (2.18)

$\text{ED} + \text{AlEt}_3 \leftrightarrow \text{AlEt}_3{\bullet}\text{ED}$ (2.19)

$\text{Cat-[ ]} + \text{ED} \leftrightarrow \text{Cat}{\bullet}\text{ED}$ (2.20)

$\text{Cat-[ ]} + \text{AlEt}_3{\bullet}\text{ED} \leftrightarrow \text{Cat}{\bullet}\text{AlEt}_3{\bullet}\text{ED}$ (2.21)

$\text{Cat-[ ]} + \text{AlEt}_3{\bullet}\text{ED} \leftrightarrow \text{Cat}{\bullet}\text{ED} + \text{AlEt}_3$ (2.22)

Where Cat-[ ] is a catalyst free site, ID is an internal donor, and ED is an external donor.

Equilibrium (2.18) is always present, even in the absence of the external donor. The produced catalyst-free site could be either stereospecific or aspecific site. Equilibrium (2.19) is always present also, which is external donor and AlEt_3 could form an acid-base complex. However, the free external donor acts as a catalyst poison. This leads to avoidance of the interactions between the catalyst and the free donor (equilibrium 2.20). Therefore, the formation of the complex between AlEt_3 and external donors is important in order to reduce the concentration of the free donor. Up to this point, those of the donor-alkylaluminum complex are only considered. Theoretically, the donor-alkylaluminum complex could react with the catalyst free site in two different ways. The first way is the complex would be coordinated with the catalyst surface as showed in equation (2.21). Another way is the donor-alkylaluminum complex releases the donor, which is absorbed in the free form (equilibrium 2.22). However, Sacchi *et al.* stated that equilibrium (2.22) is more probable due to the fact that the role of co-catalyst is only to activate catalyst to form active site but it does not participate directly with the structure of active site. Therefore, equilibrium (2.21) is neglected[51].

The presence of Lewis bases in the system might cause the activity reduction. Parada *et al.* reported that the added Lewis bases may block $TiCl_4$ fixation to $MgCl_2$ crystallite resulting in the reduction of titanium content.[38] Zhang *et al.* also investigated the effect of internal and external donor on MW and MWD of ultra-high molecular weight of polyethylene (UHMWPE) with the $MgCl_2$-supported catalyst[52]. They used di-n-butyl-phthalate, di-sec-butyl-succinate and 1,3-diether as internal donor. Phenyltriethoxysilane (PTES), propyl-ipropyldimethoxysilane (PiPDMS) and di-n-propyldimethoxysilane (DnPDMS) were employed as external donor. They found that catalyst without internal donor gives the highest catalyst activity while catalysts containing internal donor showed lower activity in the following order: none > succinate > phthalate > diether. The decreasing of activity causes internal donor to have the poisoning effect on the non-stereospecific active sites, while the structure of external donor has less effect on catalyst activity, MW and MWD of UHMWPE. Moreover, MWD obtained by catalyst containing internal donor is broader than that obtained without internal donor. The viscosity-average molecular weight (Mv) and MWD of UHMWPE also decrease in the following order: succinate > phthalate > diether > none[52].

More results are available for the effect of the silane structure in phthalate/alkoxysilanes systems. According to Song *et al.,* Proto *et al.* and Sacchi *et al.*, the performance of silanes is depended on the number and size of the alkoxy group as well as the bulkiness of the moiety attached to Si (most often a hydrocarbyl radical). Two, or at most three, small alkoxy groups (methoxy or ethoxy) are required for high performance[49,53,54].

Regarding to MWD, Seppälä *et al.* reported that no correlation between MWD and the silane structure. Their result is consistent with Zhang *et al*[52]. At the same time, MW is generally reported to increase with the steric hindrance of silanes[55].

Buajaroen also proved that external donors have a significant effect on the catalytic activity not only improvement, but it can also deactivation which depends on the nature of each functional groups. Carbon numbers in the molecular structure was fixed. Thus, n-octanol, dibutyl ketone, heptyl acetate (ester) and dibutyl ether were represented for each functional group. The results showed that the catalyst activities were in the following order: di-ether > none > ester > alcohol > ketone. This was because di-ether can make δ-$TiCl_3$ which is considered to be more active. When having the same carbon numbers, molecular structures of alcohol carbon affected on activity as well. In this work, t-butanol and n-butanol were selected. From catalytic test, it can be reported that more bulky structure produced less deactivation effects than linear structure because the stability of the molecular structure increased with the steric hindrance of alcohol [56]. In addition, they noted that external donors can decrease the catalytic activity and molecular weight of polyethylene. In contrast, when di-ether acted as an external donor, it can increase the catalytic activity and enhance the MW of polyethylene[57].

Besides, electron donors have impacts on hydrogen response, the stereo- and regiochemistry of polypropylene and the morphology of the synthetic polymer. This is because Lewis bases influence the initial crystallites size of $MgCl_2$ and/or affect on the distribution of $TiCl_4$ in the final catalytic system[51]. For example, Song *et al.* compared between the characteristics of diether- and phthalate-based ZN catalysts in propylene and ethylene copolymerization. They found that the diether-based catalyst provided higher ethylene incorporation and lower hydrogen feed rate than those of the phthalate-based catalyst. This indicated that hydrogen response of the diether-based catalyst is better. Moreover, diether-based catalyst shows a narrower MWD of the polypropylene and copolymers than that with the phthalate-based catalyst. However, in terms of microstructure the melting or crystallization behaviors, the diether-based catalyst may produce copolymers having diverse polymer chains. From ^{13}C-NMR results, it seems that the diether-based catalyst leads to the obtained copolymers having a blockier ethylene sequence[58].

2.4 Effects of Lewis acids and their chemistry

In $TiCl_4/MgCl_2/THF$ catalytic system, activity can be improved by the elimination of THF in the structure of catalyst. Cocatalyst is one type of the effective Lewis acids, which can eliminate some THF in the catalyst by complexation, but it is a hazardous compound and has high cost. Hence, in order to improve the catalyst performance and reduce the amounts of cocatalyst used in catalyst treatment step, the Lewis acid halides are a promising alternative way to achieve high performance of catalyst system.

Several Lewis acid halides were investigated based on catalyst activity test and properties of synthetic polymer like MW, MWD and thermal property.

Chang *et al.* investigated about the THF elimination from $TiCl_4/MgCl_2$/THF catalytic system by increasing amount of diethylaluminium chloride (DEAC). The XRD results show that the peak patterns of anhydrous $MgCl_2$ (ME) and $TiCl_3$(AA) (T3M) precursors were different from other precursors. It means that anhydrous $MgCl_2$ and $TiCl_3$(AA) is structurally transformed via the interactions with THF. $TiCl_3$(AA)/3$MgCl_2$/THF (T3ME) catalyst exhibits the mixture of XRD pattern of ME and T3E as showed in **Figure 2.4**. The characteristic peaks of ME were presented at 2θ = 9.75°, 20.38°, and 32.38°. **Figure 2.4B** provides the XRD information about the structural change when these T3ME, T3MED2, T3MED4, T3MED8, and T3MED12 catalysts interacted with DEAC. The results indicated that THF could be washed out by the interaction with DEAC and results as structural changes. Besides, the characteristics of $MgCl_2$/THF (ME) structure is maintained in T3MED2 and T3MED4 but lost in T3MED8 and T3MED12 indicating that a small amount of DEAC does not break the ME structure but the larger amount does in contrast[59].

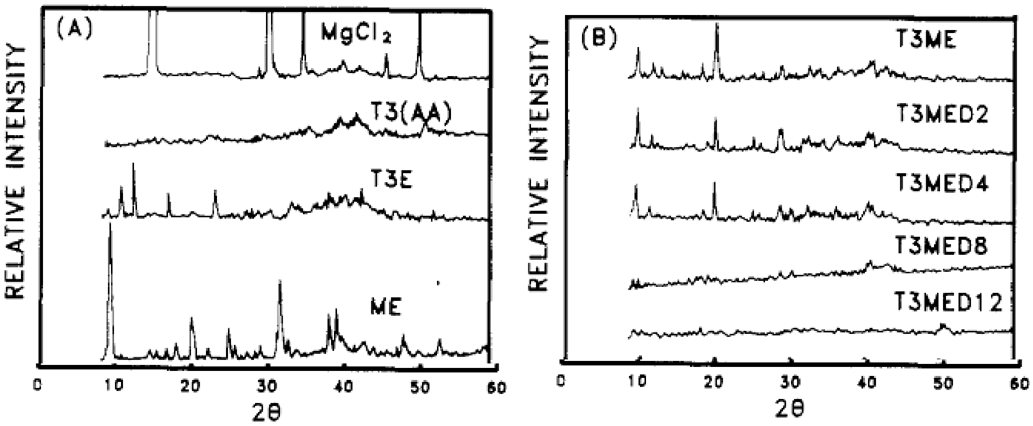

Figure 2.4 XRD patterns of (A) anhydrous $MgCl_2$, $TiCl_3$(AA) (T3(AA)), $TiCl_3$(AA)/THF (T3E), and $MgCl_2$/THF (ME) and (B) $TiCl_3$(AA)/3$MgCl_2$/THF (T3ME and T3MEDX, X = 2, 4, 8, 12) catalytic system[59]

Effects of DEAC on $TiCl_3$/2.5$MgCl_2$(0.5$MgEt_2$)/THF catalyst was performed by Chu *et al.*[60](1994) Their findings is accordant with Chang *et al.*[59] as described above. They used FT-IR and XRD measurements to examine the influence of DEAC addition on the catalyst structure. **Table 2.1** and **Figure 2.5** represent the FT-IR spectra of different kinds of complexes. The FT-IR analysis was used to identify the interaction of $MgCl_2$ with $TiCl_4$ or $TiCl_3$ in the presence of THF. Pure THF has the symmetrical and the asymmetrical C-O-C stretching bands at 912 cm^{-1} and 1071 cm^{-1}, respectively. For the synthesize of T3ME catalyst, $TiCl_3$(AA) was used to generate a complex with $MgCl_2$ in THF which causes change in acidity of $MgCl_2$ compounds. The Al-Mg-THF (AME) complex was formed through the reaction between $MgCl_2$ and $AlCl_3$ contained in the $TiCl_3$(AA) compound. The formation of AME complex is related to the capability of the aluminum compound which removes a halide anion from $MgCl_2$[61]. Mg of $MgEt_2$ is more basic than that of $MgCl_2$. Thus, when DEAC is added in the R catalyst, the C-O-C peaks are shifted to the lower frequencies. In the part of R12, the disappeared characteristic peaks might be due to the reduction of titanium (III) to titanium (II)[62]. This reduction of titanium (III) alters the acidity of titanium and eliminates the complex structure. The observation of the R catalysts through XRD patterns revealed in **Figure 2.6**. The similar findings between Chu *et al.* and Chang *et al. is* the characteristics peaks of the ME structure have been maintained in R, R2, R4, and R8 but lost in R12. It means that a small amount of DEAC could not break the ME structure but the larger amounts of DEAC could break the ME structure[59,60].

Table 2.1 FT-IR bands of different types of complexes[60]

Catalyst Abbreviation	Components	Characteristic absorbance (cm^{-1})	
THF		1071	912
T4ME	$TiCl_4/3MgCl_2/THF$	1027	876
ME	$MgCl_2/THF$	1036	891
T3E	$TiCl_3(AA)/THF$	1010	854
	Mixture of ME and T3E	1036/1010	891/854
T3ME	$TiCl_3(AA)/3MgCl_2/THF$	1027	876
R	$TiCl_3/2.5MgCl_2(0.5MgEt)/THF$	1035	885
R2	$TiCl_3/2.5MgCl_2(0.5MgEt)/THF(0.2)$	1032	880
R4	$TiCl_3/2.5MgCl_2(0.5MgEt)/THF(0.4)$	1028	878

Catalyst Abbreviation	Components	Characteristic absorbance (cm^{-1})	
R8	$TiCl_3/2.5MgCl_2(0.5MgEt)/THF(0.8)$	1027	876
R12	$TiCl_3/2.5MgCl_2(0.5MgEt)/THF(1.2)$	1022/997	876

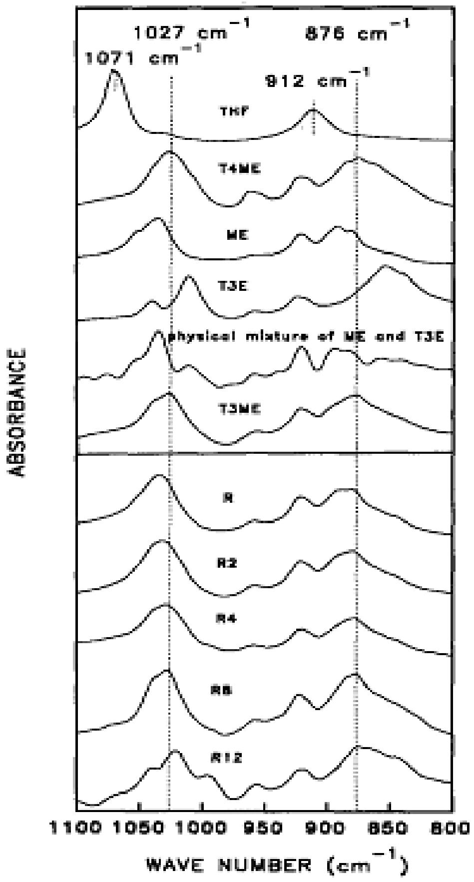

Figure 2.5 FT-IR spectra of tetrahydrofuran (THF), T4ME, ME, T3E, the physical mixture of ME and T3E, R, R2, R4, R8, and R12 respectively[60]

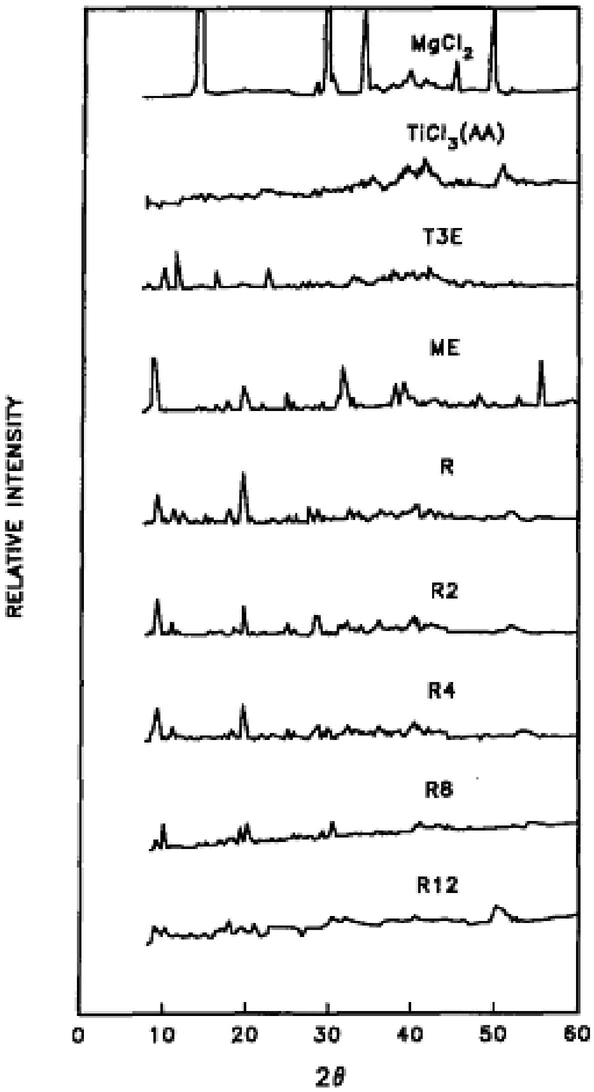

Figure 2.6 XRD patterns of $MgCl_2$, $TiCl_3$(AA), T3E, ME, R, R2, R4, R8, and R12 respectively[60]

$AlCl_3$-doped $MgCl_2$ support catalysts were studied in ethylene polymerization by Chen *et al*[2]. They found that when $AlCl_3$ was added, activity was slightly higher than undoped catalyst due to modification of $MgCl_2$ by $AlCl_3$. The doped $AlCl_3$ can increase surface area of the support or enhancement of the disorder of $MgCl_2$

crystallites. This helps to fix more $TiCl_4$ on the $MgCl_2$ support. However, the amount of loaded $AlCl_3$ has a limit. When $AlCl_3$ was in excess amount, Ti content of catalyst reduced leading to activity reduction. The MWD of polyethylene obtained with $AlCl_3$-doped catalysts is boarder that that of free $AlCl_3$ catalyst. This is due to the formation of new types of active sites by doping $AlCl_3$. Chen *et al.'*s report is concordant with Jiang *et al.'*s report, which studied about effects of doping LiCl into $MgCl_2$-supported catalysts in propylene polymerization[2,63].

Effect of $MnCl_2$ doping on the $MgCl_2$ support was investigated by Garoff and Leinonen[64]. No significant change in ability of $MgCl_2$ support to anchor Ti in the crystal structure could be detected. Polymerization tests showed that 10 mol% Mn doped material can pronounce the activity which was of the order of 100%. Nonetheless, when going to higher Mn concentration (around 30 mol% Mn doped), a linear drop in activity was observed. Thus, the optimum Mn loading was accomplished. $MnCl_2$ doped catalyst provided broader MWD and higher MW than unmodified catalyst at 10 mol % Mn. While, MW decreased with higher Mn doped concentration.

On the other hand, Jiang *et al.* disclosed that the NaCl doped catalysts provided lower catalytic activity and higher isospecificity in propylene polymerization in every NaCl loadings. This was because NaCl is not an effective support for anchoring $TiCl_4$. NaCl can be considered as kind of inert filler in the catalyst, and only $MgCl_2$ act as the active support for the Ti species. Besides activity tests, Lewis acids also have an influence on thermal properties of catalyst[65]. Fan *et al.* revealed that adding about 16% of NaCl in the $MgCl_2 \cdot 2.5EtOH$ adduct, by ball milling or simple mixing, can evidently increase the thermal stability of the catalyst adduct. XRD and electron diffraction measurements proved that Na_2MgCl_4 and $NaMgCl_3$, which were two types of mixed crystals, were found in a ball - milled mixture. In addition, they further analyzed the samples by TG and DSC analysis to obtain the indirect evidences supporting the presence of the mixed crystals in the ball-milled mixture[66].

$TiCl_4/MgCl_2/PCl_3$ catalysts were prepared via impregnation and ball milling method and then tested in ethylene-propylene copolymerization[1]. The results showed that Ti content in the catalyst decreased with the addition of PCl_3. That indicated the incorporation of PCl_3 in the catalyst crystal lattice. The reduction of Ti incorporation is probably due to the decrease of free-chloride crystal vacancies in the $MgCl_2$ surface, which caused by the complexation of PCl_3. However, the addition of PCl_3 can greatly increase $MgCl_2$ surface area. The magnitude of surface areas, relative to $MgCl_2$-PCl_3 supports, were the same of those obtained in supports prepared using ethyl benzoate as internal donor. This result indicated that the complexation behavior of both compounds on $MgCl_2$ must be similar. Therefore, PCl_3 was considered as an internal donor poisoning some catalytic active sites. As a consequence, the amount of active sites decreased leading to decrease in catalyst productivity and copolymer polydispersion when PCl_3 was introduced.

In part of $ZnCl_2$ aspects, Fregonese and Bresadola selected $ZnCl_2$ as doping salt because its XRD pattern resembles that of $MgCl_2$. This means that $ZnCl_2$ reasonably provided homogeneous mixtures on a molecular level with $MgCl_2$ support. From the XRD patterns, doped $MgCl_2$ support displayed the broad bands at 2θ = 15°, 32° and 50.5°, which corresponded to those exhibited by the disordered δ-$MgCl_2$ structure as presented in **Figure 2.7**. However, when compared with δ-$MgCl_2$, the broad peak at 2θ = 32° of Zn doped $MgCl_2$ was modified. This phenomenon might be ascribed both to the presence of alkyl metal derivatives and to structures in which magnesium is partially replaced by zinc, which is due to the fact that their ionic radii are very similar (Zn^{2+} = 0.88 Å; Mg^{2+} = 0.86 Å). Due to modification of $MgCl_2$ by doping $ZnCl_2$, the structural defects of supporting material were formed making the catalyst active sites more active. Nevertheless, no significant change in MWD was observed because the doped and undoped catalysts had basically the same types of active sites[27].

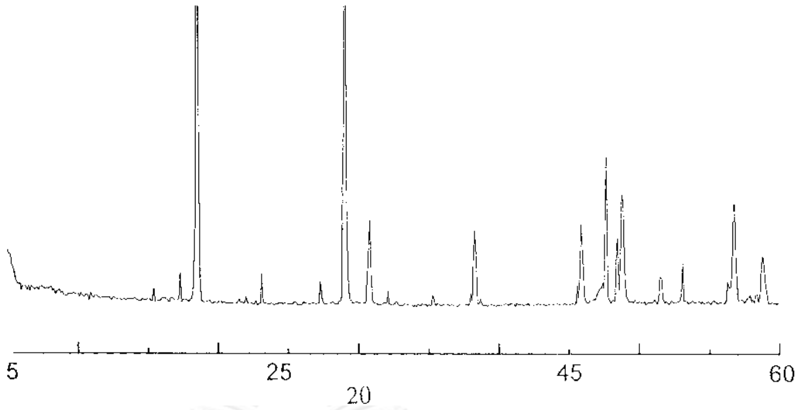

Figure 2.7 Powder XRD pattern of $ZnCl_2$[27]

Phiwkliang *et al.* further investigated about effect of mixed $ZnCl_2$ with $SiCl_4$-doped $TiCl_4/MgCl_2/THF$ catalysts for ethylene polymerization. They found that mixed Lewis acids doped catalyst exhibited the highest activity. The single Lewis acid doped catalysts provided higher activity than undoped catalyst as well due to higher Ti content and lower THF content in catalyst. Lewis acid can remove some THF in the catalyst structure improving catalyst productivity as reported in **Table 2.2**. As reported in XRD measurement in **Figure 2.8**, anhydrous $MgCl_2$ showed the strongest reflections at 2θ = 15.1°, 30.3°, 35° and 50.5°. The characteristic peaks of $MgCl_2/THF$ complex performed at 2θ = 10.4°, 20.2° and 32.3°. The $TiCl_4/MgCl_2/THF$ complex was found the peaks at 2θ = 11.5° and 18.3°. In addition, all catalysts exhibited the characteristic peaks of the $TiCl_4/THF$ complex around 2θ = 11.1° and 13.2° and the

$TiCl_3$/THF complex showed the XRD peak at 2θ = 16.7°. However, the characteristic peak of Lewis acids was not observed because $ZnCl_2$ and $SiCl_4$ completely dispersed in $TiCl_4/MgCl_2$/THF structure. Moreover, Lewis acid compounds probably destroy the crystalline structure of $MgCl_2$/THF complex, attributing to the reduction or disappearance of the intensity of XRD peaks at 2θ = 10.4°, 20.2° and 32.3°[67].

Table 2.2 The composition of catalyst and their catalytic activity[67]

Catalyst	**Composition**	**Ti[a] (wt%)**	**THF[b] (wt%)**	**Activity[c] (kg PE/molTi·h)**	**Activity ratio**
Cat-A	$TiCl_4/MgCl_2$/THF	7.86	32.7	406	1.00
Cat-B	$TiCl_4/ZnCl_2/MgCl_2$/THF	10.28	30.6	518	1.28
Cat-C	$TiCl_4/SiCl_4/MgCl_2$/THF	10.72	26.5	530	1.31
Cat-D	$TiCl_4/ZnCl_2/SiCl_4/MgCl_2$/THF	12.70	21.6	1053	2.59

[a] determined by EDX

[b] determined by GC

[c] Ethylene polymerization conditions: catalyst = 10 mg, [Al]/[Ti] = 100, n-hexane = 30 mL, [ethylene] = 0.018 mol, T = 80°C.

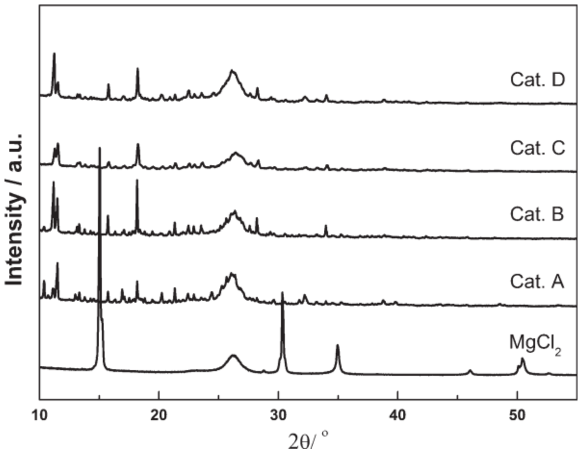

Figure 2.8 X-ray diffraction patterns of α-$MgCl_2$ and all catalysts[67]

2.5 Cocatalyst

ZN catalysts are generally activated by cocatalyst (alkylaluminum compound) in order to improve catalyst activity by changing the Ti oxidation state. The different characteristics of ZN catalysts rely on the Ti oxidation state during polymerization. As already known, Ti^{3+} species are active species for both ethylene and propylene polymerization while Ti^{2+} is active species for ethylene polymerization[68,69]. However, the catalytic activity and its stereospecificity rely on the molecular structure of cocatalyst. More bulky substituent extends diffusion limitations resulting in a decrease in the rate of activation of catalyst precursor. Thus, triethylaluminium (TEA) is reported as an effective cocatalyst in olefin polymerization because it provides the highest activity[70].

The actual mechanistic process is very complex and not well defined; however, basic steps of $TiCl_4$ and cocatalyst are given below:

- Alkylation reactions:

$$TiCl_4 + AlEt_3 \rightarrow EtTiCl_3 + AlEt_2Cl \quad (2.23)$$

$$TiCl_4 + AlEt_2Cl \rightarrow EtTiCl_3 + AlEtCl_2 \quad (2.24)$$

$$TiCl_4 + AlEtCl_2 \rightarrow EtTiCl_3 + AlCl_3 \quad (2.25)$$

- Reduction reactions:

$$EtTiCl_3 \rightarrow TiCl_3 + Et\text{-} \quad (2.26)$$

$$2Et \rightarrow C_2H_6 + C_2H_4 \quad (2.27)$$

According to these equations, it can be said that the different catalytic mixtures will be formed when the components $AlEt_3$ (or $AlEt_2Cl$) and $TiCl_4$ are mixed and used under different conditions. The nature of the catalyst changes with polymerization time. Not only cocatalyst affects on catalyst productivity, but also the molar ratio of Al/Ti, pre-contacting time of catalyst and polymerization condition, etc[71]. Until now, several researchers try to modify the catalyst in order to achieve the desire performance and product.

2.6 Ethylene polymerization

For PE production such as high density polyethylene (HDPE), it can be produced by Ziegler-Natta catalysts via a complex between transition metal and co-catalyst being key materials.

A conventional example for this catalytic system is $TiCl_4$ and TEA as shown a mechanism in **Figure 2.9- 2.13**[72]. The interaction complex between catalyst and co-catalyst, especially in $MgCl_2$ supported catalyst, leads to a variation of the transition oxidation state[73]. The co-catalyst must have one of alkyl group to incorporate into the transition metal, for example, one chlorine ion of $TiCl_4$ was displaced and substituted by ethyl group of co-catalyst. The initiation step is illustrated in **Figure 2.9**[74].

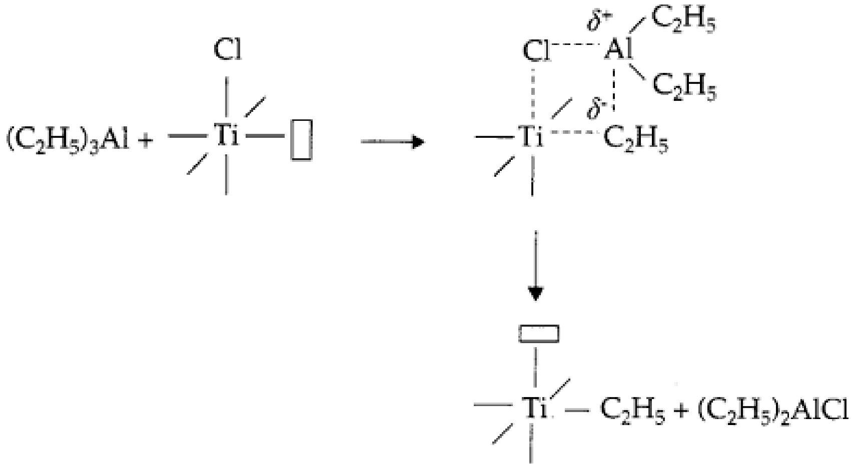

Figure 2.9 Formation of active sites by insertion of alkyl aluminum compound at titanium centers[22]

After Ti-C_2H_5 bond has been formed, ethylene molecule will coordinate at the vacant site of active centers by π-complex and insert into Ti-C bond. Then, the vacant site opened again and ready coordinated with the next molecule of ethylene. This step is called "chain propagation" step. The polyethylene chain is growing at the surface of catalyst as exhibited in **Figure 2.10**[22].

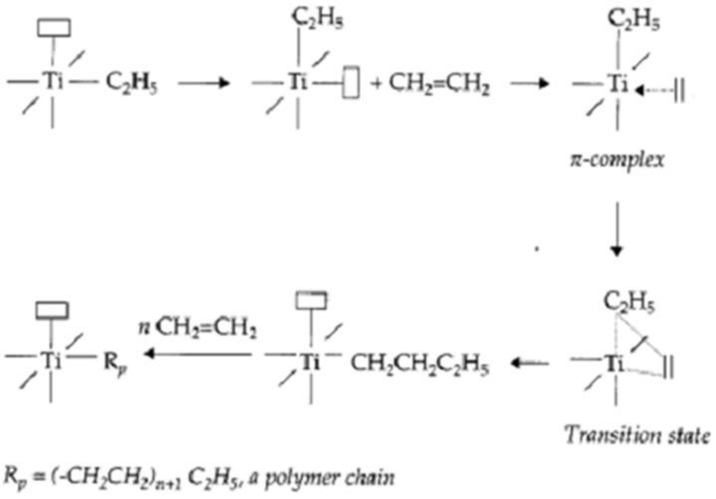

Figure 2.10 The chain propagation step of ethylene at the catalyst surface[22]

Owing to Ti-C_2H_5 σ-bonds is quite unstable, another mechanism as "bimetallic model" has been proposed. This model has explained that the polymerization mechanism of monomer similar to the Cossee-Arlman model: the monomer can also insert into Ti-C_2H_5 bond whereas difference on the participation of aluminum-alkyl to titanium-alkyl, presented in **Figure 2.11**. The coordination of aluminum-alkyl is believed to stabilize the Ti-C_2H_5 active centers[22].

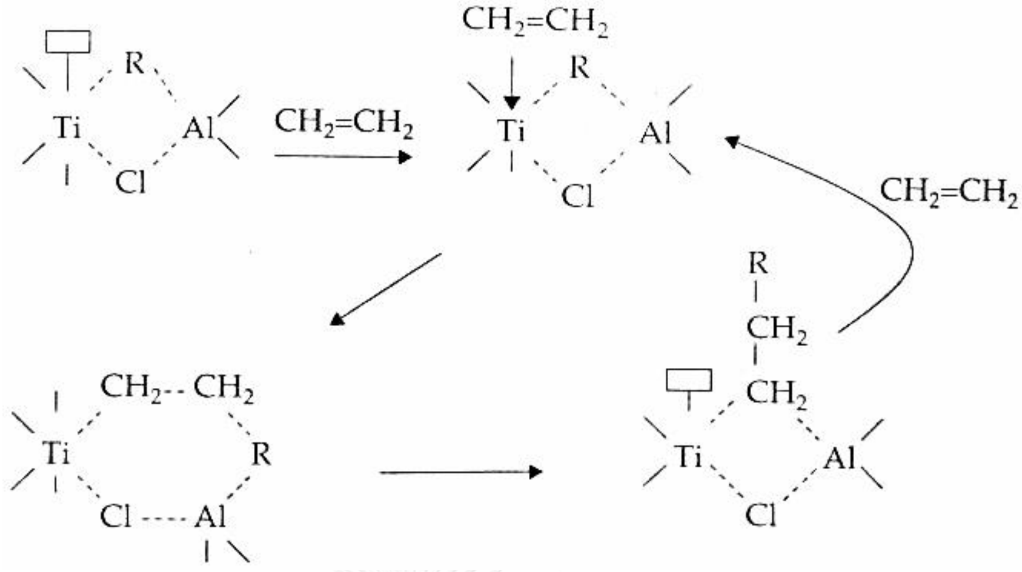

Figure 2. 11 The bimetallic model for ethylene polymerization[22]

In the termination step, it can be divided into two causes: termination by hydrogen, and β-elimination mechanisms. In case of termination by hydrogen, hydrogen may coordinate to the titanium atom and make more titanium-hydride. Then, the polymer chain will remove from active centers leading to a lower propagation rate[12]. However, in the latter case, hydrogen from β-position of polymer chain is transferred to titanium or monomer causing termination of the polymer chain propagation.

Titanium center still remains active when termination step and chain transfer reaction are done by the effect of hydrogen or monomer. The next ethylene molecule can be inserted into the titanium centers and further proceed the chain propagation. The mechanism of hydrogen and β-elimination at the active centers are shown **Figure 2.12** and **Figure 2.13**, respectively[22].

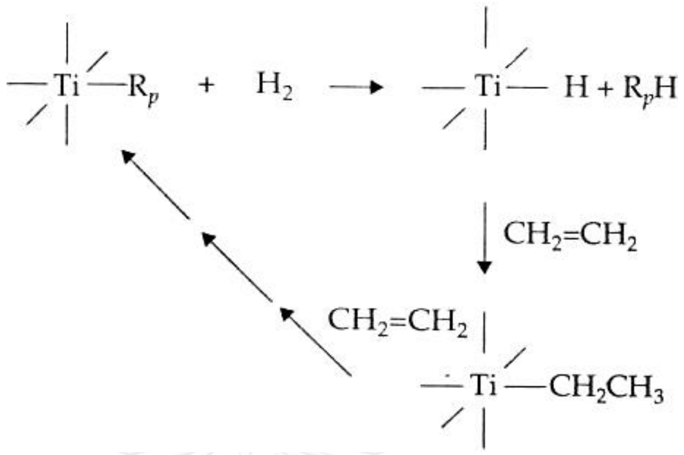

Figure 2.12 Chain termination mechanisms by hydrogen[22]

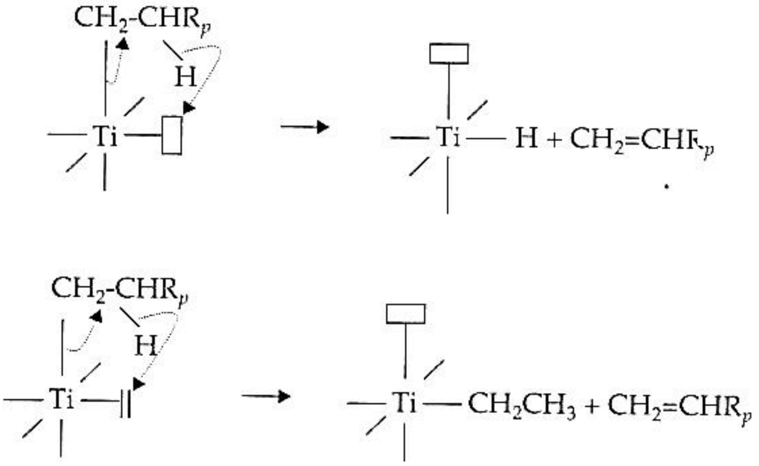

Figure 2.13 Chain termination mechanisms by β-elimination[22]

CHAPTER III
EXPERIMENT

3.1 Chemicals

The chemicals used in this study can be specified as following detail:

1. Ethylene polymerization grade (C_2H_4), ultra high purity hydrogen, nitrogen and argon (99.99%) were purchased from Linde Co., Ltd. and used as received.
2. Commercial Ziegler-Natta catalysts ($TiCl_4/MgCl_2$), anhydrous magnesium chloride ($MgCl_2$) as support, triethylaluminum (TEA) solution of 209 mmol/l in hexane as cocatalyst, diethylaluminum chloride (DEAC) and commercial grade of n-hexane as medium solvent were supplied from Thai Polyethylene Co., Ltd. and used without further purification.
3. Tetrahydrofuran (THF) and dimethoxydimethylsilane (DMDMS) as external donors were purchased from Sigma-Aldrich Inc.
4. Cyclohexylmethyldimethoxysilane (CHMDMS) as external donors was purchased from Alfa Aesar Inc
5. Anhydrous aluminium trichloride ($AlCl_3$), iron dichloride ($FeCl_2$) and zinc dichloride ($ZnCl_2$) were purchased from Sigma-Aldrich Inc.

6. Titanium tetrachloride ($TiCl_4$) was purchased from Merck Ltd. and used as received.
7. Ethanol (C_2H_5OH or EtOH) was dehydrated with molecular sieves 3Å.

To avoid air, moisture and other impurities, all chemicals and operation steps were performed under nitrogen atmospheres using a standard glove box and Schlenk techniques.

3.2 Catalyst preparation method

3.2.1 $TiCl_4/MgCl_2$/THF catalysts

A mixture of 2 g of anhydrous $MgCl_2$ and 150 ml of tetrahydrofuran was stirred using magnetic stirrer in the 500 ml three-necked round bottom flask. Then, 2 ml of $TiCl_4$ was injected dropwise. The reaction was heated up to 70 °C and held for 3 h. Then, the washing steps were carried out for 7 times with n-hexane prior to obtain the unmodified catalyst (None-THF).

The $TiCl_4/AlCl_3/MgCl_2$/THF, the $TiCl_4/FeCl_2/MgCl_2$/THF and the $TiCl_4/ZnCl_2/MgCl_2$/THF were denoted as Al-THF, Fe-THF and Zn-THF, respectively. Lewis acid was directly added to $MgCl_2$ in THF solution. All modified catalysts were synthesized by the same procedure as used for the preparation of the unmodified catalyst (None-THF) excepting for adding anhydrous $AlCl_3$ for Al-THF, $FeCl_2$ for Fe-THF, and $ZnCl_2$ for Zn-THF, with 0.07 mol/mol of Lewis acid/$MgCl_2$.

In case of the mixed Lewis acids addition, the $TiCl_4/ZnCl_2/AlCl_3/MgCl_2$/THF and the $TiCl_4/ZnCl_2/FeCl_2/MgCl_2$/THF were denoted as ZnAl-THF and ZnFe-THF, respectively. The addition of anhydrous $ZnCl_2$ with $AlCl_3$ for ZnAl-THF and $ZnCl_2$ with $FeCl_2$ for ZnFe-THF was employed with the ratio of each Lewis acid/$MgCl_2$ of 0.035 mol/mol.

3.2.2 $TiCl_4/MgCl_2$•nEtOH catalyst[75]

A mixture of 2 g of anhydrous $MgCl_2$ and n-hexane was added into the 500 ml three-necked round bottom flask. Under controlled temperature at 20 °C, the amount of 7 ml of C_2H_5OH was dropped and stirred for 2 h. After that, 7.2 ml of DEAC was also dropped into the mixture and stirred for another 2 h. About 4 ml of $TiCl_4$ was injected dropwise and heated up to 80 °C within 2 h and kept the mixture at this temperature for 2 h. Then, the washing was conducted with n-hexane for 7 times to obtain the final catalyst.

3.2.3 Commercial $MgCl_2$-supported Ziegler-Natta catalysts

As mentioned above, all of the commercial $MgCl_2$-supported Ziegler-Natta catalysts were supplied by Thai Polyethylene Co., Ltd. $TiCl_4/MgCl_2$•nEtOH catalyst

(Commercial Cat-A) was prepared according Mitsui Petrochemical Industries Ltd.[75], while $TiCl_4$/internal donor/$MgCl_2$ (Commercial Cat-B) contained a phthalate type as internal donor.

3.3 Ethylene polymerization

3.3.1 Effect of H_2/C_2H_4 molar ratio

Ethylene polymerization was performed in a 2 L autoclave reactor. The reactor was evacuated and purged by nitrogen gas many times. After that, 1 L of n-hexane and a designated amount of triethylaluminum ([Al]/[Ti] = 140) and external donor (if any, [Al]/[Si] = 10) were added under stirring into the reactor. Then, catalyst slurry was added into the autoclave. Next, 1 bar of nitrogen was filled and followed by the desired amount of hydrogen. The H_2/C_2H_4 molar ratio was varied in the range of 0-0.60. Then, ethylene was continuously supplied to start the polymerization and maintained the total pressure of 8 bars during the polymerization time of 1 h at 80 °C. The obtained polymer was dried at room temperature overnight.

3.3.2 Effect of polymerization time

Ethylene polymerization was conducted in the same procedures as the polymerization in the topic of effect of H_2/C_2H_4 molar ratio. However, the H_2/C_2H_4

molar ratio was fixed at 0.60 and polymerization time was varied in the range of 5-90 min (5, 15, 30, 60, 75 and 90 min).

3.4 Characterization techniques

3.4.1 Catalyst and support

3.4.1.1 Inductively Couple Plasma (ICP)

Inductively couple plasma optical emission spectrometer (ICP-OES optima 2100 DV from Perkin Elmer) was used to determine element content in bulk. To prepare the catalyst sample, the sample was digested with 5 ml of hydrochloric acid, and then the solution was diluted with DI water.

3.4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier transforms infrared spectroscopy was applied with Nicolet 6700 FT-IR spectrometer with transmittance mode to identify the interaction between catalyst and $MgCl_2$ support. The catalyst powder was prepared as a thin film on NaCl disk and kept under argon atmosphere. The measurement in transmittance values was analyzed under nitrogen atmosphere in the range of scanning between 400 to 4000 cm^{-1} for scanning of 400 times.

3.4.1.3 X-ray Diffraction (XRD)

XRD was performed to identify phases and crystallinity of the samples using Bruker of D8 Advance. The catalyst sample was placed on holder and sealed with mylar film under argon atmosphere. The spectrum was scanned at a rate of 0.3 second/step and step size of 0.02 in the 2θ range = 10-80 degrees.

3.4.1.4 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

Morphologies of catalyst and its elemental distribution were investigated under nitrogen atmosphere using SEM and EDX, respectively. The SEM of Hitachi mode S-3400N was applied, while the EDX was performed using Link Isis series 300 program.

3.4.1.5 Surface Area Measurement

The specific surface area of catalyst was measured by N_2 physisorption method (single point). The solid catalyst was prepared in a tube and sealed with paraffin film to prevent air and moisture. The adsorption was performed at -196 °C with liquid N_2. The desorption peak area signal was used to calculate as follow:

$$\text{Surface area} = \text{Peak area } (m^2) \,/\, \text{Weight of catalyst sample } (g)$$

3.4.2 Polymer

3.4.2.1 Differential Scanning Calorimetry (DSC)

The melting temperature (T_m) and percentage of crystallinity ($\%\chi_c$) of polyethylene were determined by DSC-TGA with TA Instruments SDT Q600 V8.1 Build 99. The measurement was performed at a heating rate of 10 °C/min in the temperature range of 30-600 °C. The crystallinity of polymers was calculated by the following equation:

$$\%\chi_c = [\Delta H/(\Delta H^\circ)]\times 100$$

where ΔH is heat of fusion of polyethylene sample.

ΔH° is the heat of fusion of linear polyethylene equals to 290 J/g.[67]

3.4.2.2 Gel Permeation Chromatography (GPC)

Molecular weight and molecular weight distribution of synthetic polymers were determined using a high temperature GPC (Waters 150 °C) equipped with a viscometric detector. The measurement was performed at 160°C and 1, 2, 4-trichlorobenzene was used as a solvent.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Influence of hydrogen on catalytic properties of Ziegler-Natta catalysts prepared by different methods in ethylene polymerization

4.1.1 Characteristic of catalysts

The chemical compositions of all catalysts in bulk were determined by ICP as presented in **Table 4.1**. It shows that ZN-THF and ZN-EtOH contain 4.07 wt% and 7.91 wt% of Ti, respectively. However, the ratios of Ti/Mg of ZN-THF and ZN-EtOH were similar (ca. 0.3).

Table 4.1 The components of the prepared catalysts

Catalysts	**Components**	**Elemental contents (wt%)**[a]			**Ti/Mg (mol/mol)**
		Ti	**Mg**	**Al**	
ZN-THF	$TiCl_4/MgCl_2/THF$	4.07	6.87	-	0.30
ZN-EtOH	$TiCl_4/MgCl_2{\bullet}6EtOH$	7.91	13.68	1.13	0.29

[a] Determined by ICP

EDX analysis was applied to identify roughly the active sites contents on the catalyst surface as shown in **Table 4.2**. It can be seen that ZN-EtOH has higher surface Ti/Mg ratio than ZN-THF. It indicates that ZN-EtOH has higher active sites than ZN-THF, which reacts with cocatalyst and initiates more polymerization. Furthermore, the results also show the significant difference in surface area which ZN-EtOH has much higher surface area than ZN-THF. EDX analysis and surface area measurement suggest that the ZN-EtOH could have better Ti dispersion on the catalyst surface than the ZN-THF. The Ti/Mg ratio on surface of catalyst and the specific surface area are important factors for polymerization. As mentioned, the specific surface area has a strong effect to polymerization reaction[76,77].

Table 4.2 The elemental compositions on the surface of catalysts and its surface area

Catalysts	Elemental contents (wt%)[a]			Ti/Mg	Surface
	Ti	Mg	Al	(mol/mol)	area[b] (m^2/g)
ZN-THF	27.59	72.41	-	0.19	5
ZN-EtOH	29.81	59.59	10.60	0.25	206

[a] Determined by EDX

[b] Measured by N_2 physissorption

IR spectra of all catalysts in the range of 3900-500 cm^{-1} are represented in **Figure 4.1**. There are many articles reported that the complex of $TiCl_4/MgCl_2$ with THF showed IR bands in the range of 1100–700 cm^{-1}, indicating the most sensitive to

THF complexes with a metal center[78,79]. In general, pure THF has the symmetrical and an asymmetrical C-O-C stretching bands around 913 cm^{-1} and 1071 cm^{-1}, respectively[79-81]. However, ZN-THF exhibits these two peaks, which are the symmetrical and the asymmetrical C-O-C stretching bands of THF around 883 cm^{-1} and 1033 cm^{-1}, respectively. They were shifted to the lower wavenumber and splitted into several components, suggesting that THF forms the bimetallic complex with a metal center, such as Ti-Mg-THF complex[28,60]. Furthermore, it was observed that IR spectrum in the range of 3000 – 3600 cm^{-1} for ZN-THF indicating a neutral alkoxy Ti species via the ring-opening of THF. This IR spectrum of ZN-THF is in good agreement with the report by Grau *et al*[82]. They reported that the nature of Ti species is modified by the interaction with $MgCl_2$ and THF give a transient cationic Ti mononuclear species, which finally leads to a neutral alkoxy Ti species via the ring-opening of THF. Moreover, it was also observed that IR spectrum of ZN-EtOH exhibited the alcohol functional group in the range of 3000 – 3600 cm^{-1} corresponding to O–H stretching, at 2780 – 3000 cm^{-1} and 1500 – 1300 cm^{-1} for C–H stretching and at 1100 cm^{-1} for C–O stretching[83]. This IR spectrum of the ZN-EtOH is in good agreement with the report by Huang *et al*[84].

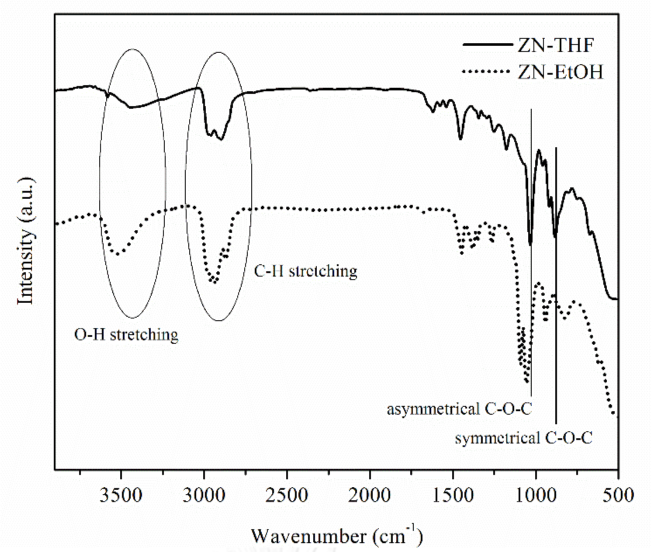

Figure 4.1 IR spectra of the catalysts

Moreover, the XRD patterns of α-$MgCl_2$ support and catalysts in the range of 10-80 degree are presented in **Figure 4.2**. The broad peak around 2θ = 26° was assigned as a Mylar film used to avoid air and moisture. The anhydrous $MgCl_2$ precursor showed the sharp peaks around 2θ = 14.9°, 30.2°, 34.8°, and 50.3°. Sharp peak at 2θ = 14.9° was assigned to the stacking of Cl–Mg–Cl triple layers along the crystallographic direction, whereas three peaks, at 2θ = 30.2°, 34.8° and 50.3° were defined as the stacking faults of the triple layers. The peaks at 2θ = 34.8° and 50.3° represented the (104) and (110) plane, respectively[84,85]. Chang *et al*. revealed that the characteristic peaks of $MgCl_2$/THF complex were presented at 2θ = 10.4°, 20.2°, and 32.3°[59,67]. Therefore, this XRD result of ZN-THF conforms to the result reported by Chang *et al*[59]. In case of ZN-EtOH, the XRD pattern exhibited the reduction of intensity in all peaks of α-$MgCl_2$. This is probably due to the interaction between Mg^{2+} and alcoholic oxygen. As a consequence, the insertion of alcohol between the Cl–Mg–Cl triple layers resulting in an increase in the interplanar distance or decrease in 2θ value[86], meaning that the crystallinity of catalysts is low.

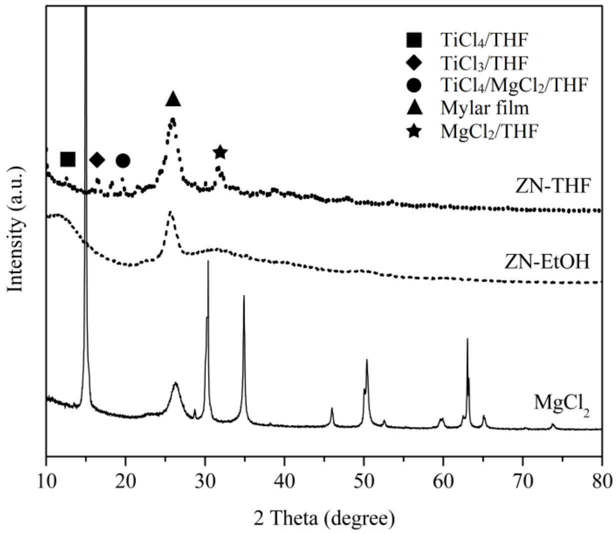

Figure 4.2 XRD patterns of $MgCl_2$ support and all catalysts

4.1.2 Catalytic activity of ZN catalysts prepared by different methods at various H_2/C_2H_4 molar ratios

It is well known that more hydrogen contents increase, the more catalytic activity decreases in ethylene polymerization even with small amounts of hydrogen in a system of Ziegler–Natta catalysts containing titanium and vanadium compounds as active components[16,87-89]. According to **Table 4.3**, effect of hydrogen on surface active sites is high even in the system having a small amount of hydrogen. However, it likely depends on its active centers distribution. In order to generate chain transfer reaction by hydrogen, Kouzai *et al.* reported that hydrogen dissociation sites are necessary in the surrounding of the active sites[90]. In this work only small amount addition of hydrogen at H_2/C_2H_4 molar ratio of 0.12 exhibits 42% reduction in activity indicating high hydrogen response for ZN-THF, while ZN-EtOH required more hydrogen amounts at H_2/C_2H_4 molar ratio of 0.30 to gain a decrease in activity of 41%. According to this result, it is confirmed that ZN-EtOH has a better active center distribution than that of ZN-THF. This is consistent with the specific surface area measurement. ZN-EtOH exhibited less active site deactivation and lower hydrogen response than the ZN-THF in the H_2/C_2H_4 molar ratio range of 0-0.12. This is because the active sites were still very active and plentiful. Moreover, there was a little amount of hydrogen in the system leading to less deactivation of some active sites to form further Ti-H bond[12,88,91]. When increasing the hydrogen contents (H_2/C_2H_4 molar ratio = 0.20-0.60) for ZN-THF, hydrogen response of ZN-THF was lower (30% activity decrease) compared with its hydrogen response in the range of H_2/C_2H_4 molar ratio = 0-0.12 (42% activity decrease). However, in case of the ZN-EtOH with higher hydrogen amount, activity decreased only 13% at H_2/C_2H_4 molar ratio = 0.60. This is also possible because ZN-THF has a poor Ti dispersion on the catalyst surface and its characteristics of good hydrogen response ability but moderate in activity[28].

Table 4.3 Activity of all catalysts at various H_2/C_2H_4 molar ratios

Catalyst	H_2/C_2H_4 molar ratio	Activity (kgPE/gTi*h)	Activity ratio
ZN-THF	0	732	1.00
	0.08	645	0.88
	0.12	431	0.58
	0.20	362	0.49
	0.30	313	0.43
	0.60	214	0.29
ZN-EtOH	0	1143	1.00
	0.08	1047	0.92
	0.12	1082	0.95
	0.20	744	0.65
	0.30	675	0.59
	0.60	521	0.46

Condition: Polymerization was performed in 2 L autoclave, reaction temperature = 80 °C, Ti = 0.008 mmol for ZN-THF and 0.004 mmol for ZN-EtOH, reaction time = 1 h, total pressure = 8 bars under 1 bar of nitrogen and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.12, 0.20, 0.30 and 0.60.

4.1.3 Effect of polymerization time on catalytic activity

Furthermore, polymerization time also has an influence on activity. According to **Figure 4.3** in case of ZN-THF, the hydrogen response at 60 minutes of polymerization time displayed a lower value of activity than its activity at hydrogen response at 15 minutes of polymerization time. This is possible because the occurrence of the initial accelerating stage in the ethylene polymerization with ethylene consumption rate attaining during the whole reaction at reaction time equal to 60 minutes was higher than that of reaction time equal to 15 minutes[87]. Thus, all catalysts showed the similar results that the increase in polymerization time can improve yield of polymer with decreased activity. These results are in agreement with some literatures[5,92-98]. This is because the ethylene monomers have more time to produce polymer resulting in an increase in polymer yield. As the time increases, the concentration of ethylene monomer at the catalyst active sites decreases. In addition, the longer reaction time leads to the possible decay of the active species[99]. The catalyst activity is therefore reduced.

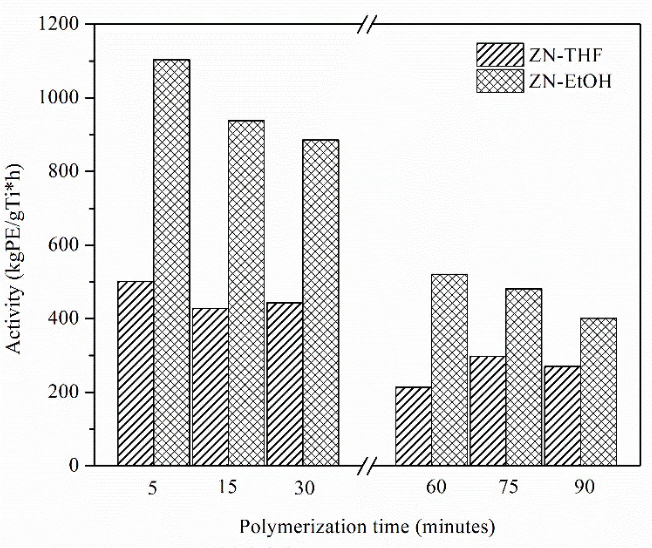

Figure 4.3 Catalyst activity in ethylene polymerization with various polymerization times at H_2/C_2H_4 molar ratio = 0.60

Condition: Polymerization was performed in 2 L autoclave at H_2/C_2H_4 molar ratio = 0.60, reaction temperature = 80 °C, Ti = 0.008 mmol for ZN-THF and 0.004 mmol for ZN-EtOH.

4.1.4 Effect of hydrogen on polyethylene properties

The resultant polyethylene was further characterized by DSC as shown in **Table 4.4**, which shows the influence of hydrogen amount on the polyethylene properties synthesized by ZN-THF and ZN-EtOH. This result showed that the melting temperature of all polyethylenes decreases with increased hydrogen pressure. This is because hydrogen acts as a chain transfer for the reaction causing the decrease in molecular weight and melting point of polyethylenes.[5] Furthermore, it is seen that an increase in hydrogen pressure leads to increase crystallinity of all polymers compared with in the absence of hydrogen. This is because hydrogen blocks the active sites of polymerization. As a consequence, the polymerization rate is reduced and crystallization rate is increased[5]. As mentioned previously, ZN-EtOH has a better active sites distribution than that of ZN-THF and could retard hydrogen effect. As the result, ZN-THF shows slightly higher crystallinity of polyethylenes than ZN-EtOH. From the GPC result, molecular weight of polymer decreased when hydrogen increased because chain termination reaction by hydrogen occurred.[16] Furthermore, ZN-EtOH gave broader MWD than ZN-THF. The MWD of all polymers did not significantly change at the different levels of hydrogen. This result is in agreement with Shan *et al*. and Mikenas *et al*[100,101]. Moreover, Ha *et al*. also confirmed that molecular weight distribution is independent of the hydrogen concentration[102]. In addition, surface Ti content has no correlation with molecular weight at the different level of hydrogen.

Table 4.4 Properties of synthetic polymer up on different catalysts and hydrogen pressures

Catalyst	$[H_2]/[C_2H_4]$	T_m[a] (°C)	χ_c[a] (%)	$Mw^b \times 10^{-3}$ (g/mol)	$Mn^b \times 10^{-3}$ (g/mol)	$Mw/Mw_{0.08}$[b]	MWD[c]
ZN-THF	0	132.9	55.4	-	-	-	-
	0.08	131.2	58.0	452	74	1.00	6.1
	0.12	130.2	58.6	275	52	0.61	5.3
	0.20	129.8	59.7	249	40	0.55	6.2
	0.30	129.0	56.2	179	31	0.40	5.7
	0.60	127.7	67.2	101	18	0.22	5.6
ZN-EtOH	0	133.5	54.9	-	-	-	-
	0.08	130.3	54.5	391	42	1.00	9.4
	0.12	130.3	60.3	370	35	0.95	10.5
	0.20	129.7	56.6	264	31	0.68	8.5
	0.30	128.1	58.3	191	21	0.49	9.0
	0.60	127.8	56.8	128	14	0.33	9.1

[a] Determined by DSC

[b] $Mw/Mw_{0.08}$ = Mw at any $[H_2]/[C_2H_4]$ level/ Mw at $[H_2]/[C_2H_4]$ = 0.08

[c] Determined by GPC

Condition: Polymerization was performed in 2 L autoclave, reaction temperature = 80 °C, Ti = 0.008 mmol for ZN-THF and 0.004 mmol for ZN-EtOH, reaction time = 1 h, total pressure = 8 bars under 1 bar of nitrogen and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.12, 0.20, 0.30 and 0.60.

4.2 A comparative study of $AlCl_3$ and $FeCl_2$-modified $TiCl_4/MgCl_2/THF$ catalytic system in the presence of hydrogen for ethylene polymerization

As described about the $TiCl_4/MgCl_2/THF$ catalytic system previously, the remaining THF in catalyst can decrease activity in olefin polymerization. In order to achieve better catalyst performance, $TiCl_4/MgCl_2/THF$ catalyst was modified with Lewis acid. Several researchers claimed that the added Lewis acid can make the defect on $MgCl_2$ structure which contributed to the enhancement of catalytic activity and polymer properties in ZN catalyst system[64,103,104]. Typically, some parts of cocatalyst can form complex with the remaining THF in catalyst leading to lowering in content of active cocatalyst. According to the capability of Lewis acid removing some THF in catalyst, this results the increase in content of active cocatalyst to activate active sites. Therefore, in this study, $AlCl_3$ and $FeCl_2$ were employed as promoter due to their benefits over alkylaluminium compounds like activity improvement, lower hazardous compound and cost[105]. Ethylene homopolymerization over $TiCl_4/MgCl_2/THF$ catalysts modified with different metal halide additives ($AlCl_3$ and $FeCl_2$) with and without hydrogen was investigated and then compared based on catalytic activity and polymer properties.

4.2.1 Characteristic of catalysts

Table 4.5 Abbreviation of the prepared catalysts

Catalyst abbreviation	**Components**
None-THF	$TiCl_4/MgCl_2/THF$
Al-THF	$TiCl_4/AlCl_3/MgCl_2/THF$
Fe-THF	$TiCl_4/FeCl_2/MgCl_2/THF$

Table 4.6 The elemental composition of the prepared catalysts

Catalyst	**ICP measurement**				**EDX measurement**			
	Element content (wt%)[a]			Ti/Mg (mol/mol)	Element content (wt%)[c]			Ti/Mg (mol/mol)
	Ti	Mg	M[b]		Ti	Mg	M[b]	
None-THF	4.07	6.87	-	0.30	6.52	24.32	-	0.14
Al-THF	2.96	6.51	0.97	0.23	9.56	24.50	2.65	0.20
Fe-THF	4.61	5.87	1.58	0.40	9.27	19.08	11.79	0.25

[a] Determined by ICP

[b] M = Al or Fe

[c] Determined by EDX

According to **Table 4.6**, the chemical compositions of catalysts were determined by ICP and EDX measurements. It was found that although the addition of $TiCl_4$

amount of all catalysts was fixed, the titanium contents in bulk, which were determined by ICP, were slightly changed compared with None-THF due to the presence of different Lewis acids on the support. This might be the fact that the Lewis acid modification can reduce free-vacancies of $MgCl_2$ crystallization and Ti insertion[59,106]. Thus, the titanium content of Al-THF slightly decreased. According to this result, it is also in good agreement with the report by Coutinho *et al*[1]. They observed that the addition of PCl_3 in $TiCl_4/MgCl_2$ via ball milling method decreased the Ti incorporation due to decrease of free-chloride crystal vacancies in the surface of milled $MgCl_2$ caused by the complexation of PCl_3. Furthermore, increasing of PCl_3 content can be attributed to the reduction of catalyst active sites resulting in drop in Ti incorporation. Nonetheless, Ti content in bulk of Fe-THF increased compared with None-THF. This is because the radius of iron (II) ions (Fe^{2+}) and the crystal compound structures ($FeCl_2$) were similar to Mg^{2+} and $MgCl_2$. Tanase *et al*. reported that the catalyst contained metal dichloride as a carrier material exhibited the relatively high activity compared with $MgCl_2$. Therefore, $FeCl_2$ was considered as one of an effective supports for anchoring $TiCl_4$[107] resulting in the improvement of Ti content. However, from the EDX result, all catalysts showed higher Ti content on catalyst surface than Ti content in bulk (It had some deviation from measured by XPS technique). This indicated that most Ti active sites were located on the surface of catalyst more than in the catalyst pores. In addition, the Lewis acid contained catalysts showed a higher Ti/Mg ratio than that of unmodified catalyst, especially Fe-THF. It displays the highest Ti/Mg ratio indicating a lot of Ti atoms can incorporate at the $MgCl_2$ support.

As seen from **Figure 4.4,** FT-IR spectra of all catalysts were analyzed in the range of 3900-500 cm^{-1}. Al-THF and Fe-THF exhibited a slightly shift to the lower wavenumbers compared with None-THF. None-THF, Al-THF and Fe-THF display the symmetrical C-O-C stretching bands at 883.4, 874.6 and 873.6, respectively and its asymmetrical C-O-C stretching bands at 1032.6, 1025.1 and 1024.6, respectively. It indicated that metal halides incorporated with the Ti-Mg-THF bimetallic complex resulting in the lower frequencies of the C-O-C stretching bands of THF. Therefore, this result may cause an increase in the Lewis acidity of the active center[28,60]. All catalysts also display the C-H stretching bands around 2885.2 – 2983.9 cm^{-1}. In addition, a neutral alkoxy Ti species, which are inactive for ethylene polymerization, were found in the range of 3440.1 – 3563.9 cm^{-1}. This is because the interaction of $MgCl_2$ and THF can change the nature of Ti species through creating a transient cationic Ti mononuclear species via the ring-opening of THF, which finally leads to a neutral alkoxy Ti species[82].

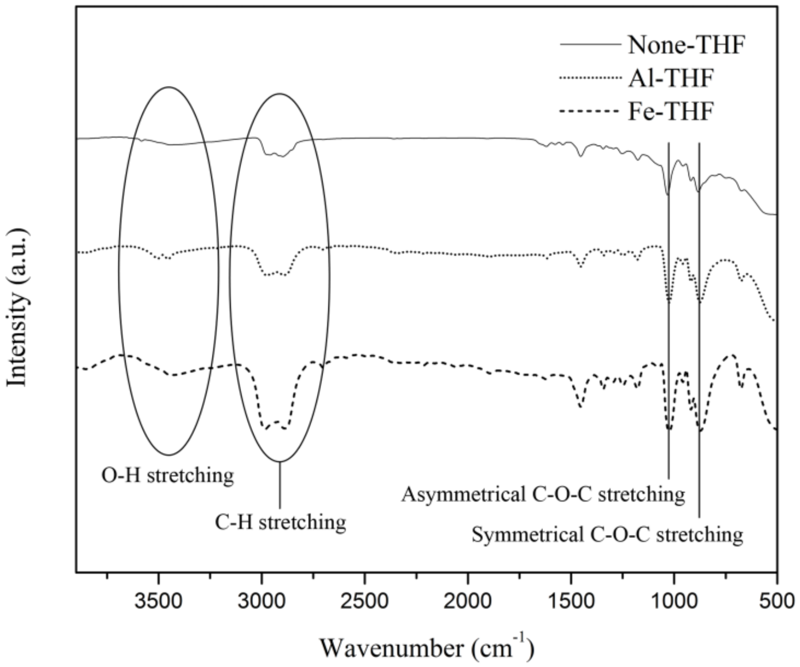

Figure 4.4 FTIR spectra of catalysts

XRD patterns of synthesized catalysts are reported in **Figure 4.5**. The peaks at 2θ = 14.9°, 30.2°, 34.8°, and 50.3° represent the α-form of $MgCl_2$ species, which are inactive for polymerization. The characteristic peaks of $MgCl_2$/THF complex were located at 2θ = 20.4°, and 32.0°[59,67]. The XRD peak around 2θ = 18.1° was also found and assigned as the creation of the $TiCl_4$/$MgCl_2$/THF complex[108]. Moreover, the characteristic peaks of $TiCl_4$/THF complex and the $TiCl_3$/THF complex were noticed at 2θ = 11.1° and 17.8°, respectively[59,67,108]. Lewis acid characteristic peak of Lewis acid modified catalysts could not be observed because Lewis acid completely participated in $TiCl_4$/$MgCl_2$/THF structure[4,109]. It can be suggested that the radius of Fe^{2+} (0.61 Å) is closer to Mg^{2+} (0.65 Å) than that of Al^{3+} (0.50 Å). Thus, the compatibility of $FeCl_2$ with $MgCl_2$ would be better than that of $AlCl_3$ with $MgCl_2$[27,67]. Due to the fact that Lewis acid can remove THF from $MgCl_2$/THF complex; therefore, Lewis acid presumably destroys the crystalline structure of $MgCl_2$/THF complex. This results in the lowering or loss in magnitude of XRD peaks at 2θ = 20.4°, and 32.0°.

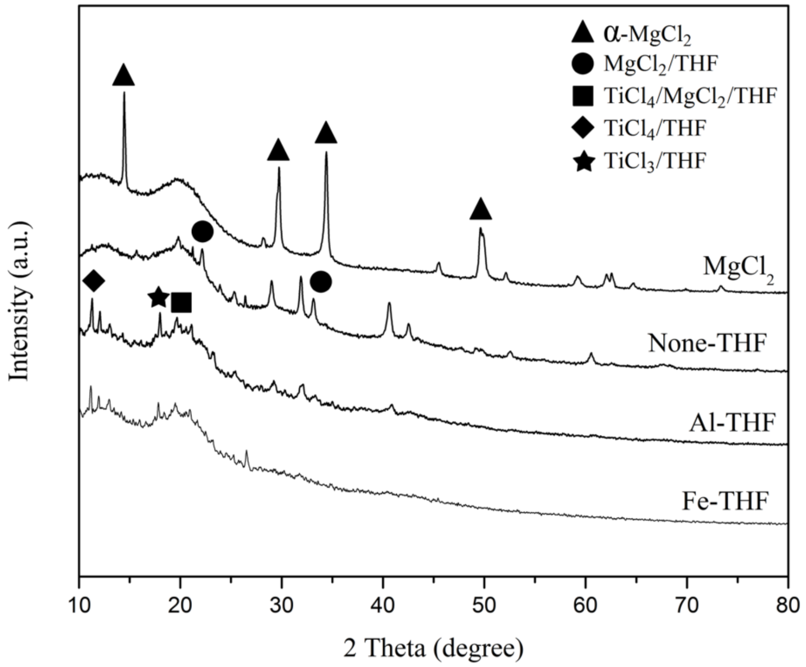

Figure 4.5 XRD patterns of prepared catalysts

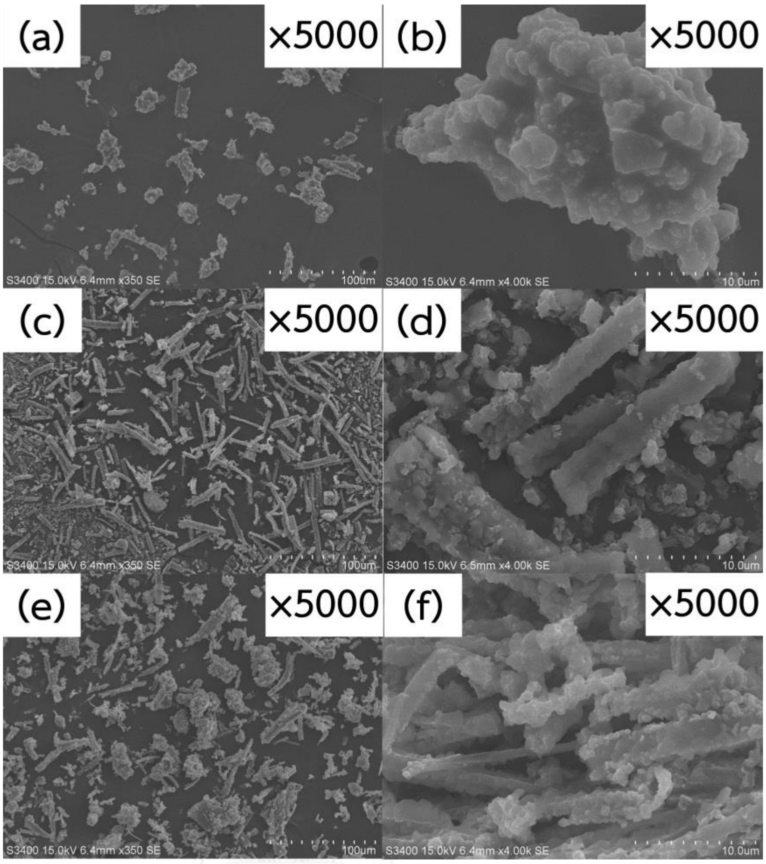

Figure 4.6 SEM images of prepared catalysts**:** [(a), (b)] None-THF, [(c), (d)] Al-THF and [(e), (f)] Fe-THF

Typical SEM images of catalysts, which are None-THF, Al-THF and Fe-THF, are shown in **Figure 4.6**. It can be seen that None-THF is in irregular shape while the modified catalysts with Lewis acid (Al-THF and Fe-THF) are in shape of bar.

4.2.2 Effect of $AlCl_3$ and $FeCl_2$ - modified $TiCl_4/MgCl_2/THF$ catalysts on catalytic activity

As reported in **Table 4.7**, Lewis acid modification by adding $AlCl_3$ and $FeCl_2$ can improve the activity around 17% and 86%, respectively compared with the activity of unmodified catalyst. This is because the formation of acidic sites by modifying the catalysts with Lewis acids[28]. One of the factors improving activities is the added $AlCl_3$ and $FeCl_2$ could also remove the THF in catalyst. The remaining THF of $MgCl_2 \cdot THF$ structure in the final catalyst leads to the reduction in catalytic activity because the remaining THF can poison the catalyst active sites[110]. THF occupies the coordination sites of Ti to make a neutral alkoxy Ti species, which is an inactive center, via the ring-opening of THF[82]. Moreover, TEA can also coordinate with THF, remove some THF from the Ti center, and then provide higher catalytic activity[110]. Chen *et al*. stated that the active center distribution of the $TiCl_4/MgCl_2$ could change by doping $AlCl_3$, which can be observed by the polymer GPC curves and Flory components. More types of active center, the Al-Mg-THF complex[2], were formed and led to an improvement of catalyst performance[105]. As mentioned earlier about the similar ionic radii of Fe and Mg, it could then be said that $FeCl_2$ was more efficient to incorporate with $MgCl_2$ than $AlCl_3$. Therefore, Fe-THF gave higher activity than Al-THF.

Table 4.7 Catalytic activity of different doped Lewis acid catalysts in ethylene polymerization

Catalyst	H_2/C_2H_4 molar ratio	Activity (kg PE/gTi*h)[a]	Activity ratio without H_2[b]	Activity ratio with H_2[c]
None-THF	0	732	1.00	1.00
	0.08	645	-	0.88
	0.20	362	-	0.49
	0.30	313	-	0.43
Al-THF	0	854	1.17	1.00
	0.08	560	-	0.66
	0.20	279	-	0.33
	0.30	246	-	0.29
Fe-THF	0	1364	1.86	1.00
	0.08	452	-	0.33
	0.20	330	-	0.24
	0.30	375	-	0.28

[a] Condition: Polymerization was performed in 2 L autoclave, Ti = 0.008 mmol for all catalysts, Al/Ti molar ratio = 140, co-catalyst = TEA, polymerization time = 1 h, reaction temperature = 80 °C, total pressure = 8 bars under 1 bar of nitrogen and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.20 and 0.30.

[b] Activity ratio without H_2 = activity of the modified catalyst/activity of the unmodified catalyst

[c] Activity ratio with H_2 = activity of the catalyst at that level of H_2/activity of that catalyst without H_2

In addition, $TiCl_4/MgCl_2$/THF catalysts modified with Lewis acids ($AlCl_3$ and $FeCl_2$) were conducted in ethylene polymerization in the presence of various hydrogen pressures for comparative study on catalytic activities. The polymerization activities results of $TiCl_4$/Lewis acid/$MgCl_2$/THF catalysts are summarized in **Table 4.7**. Catalysts modified with Lewis acid presented higher hydrogen response than unmodified catalyst, especially Fe-THF. Hydrogen response is high even in the system that has a small amount of hydrogen. Only small addition of hydrogen at H_2/C_2H_4 molar ratio of 0.08 results in 34% decrease in activity for Al-THF and 67% decrease in activity for Fe-THF. This indicates high hydrogen response for these catalysts in this H_2/C_2H_4 molar ratio period. From these results, this is probably due to increasing in acidic centers[28] by doping Lewis acid. Therefore, addition of Lewis acid causes the formation of more clustered active center leading to obtain more chances to proceed chain transfer reaction by hydrogen. This result is in good agreement with article reported by Kouzai *et al*. They revealed that chain transfer reactions by hydrogen will occur when hydrogen dissociation sites are located in the instant surrounding of polymerization sites[90]. Thus, the more clustered active species it had, the higher hydrogen response. In part of higher hydrogen amount at H_2/C_2H_4 molar ratio of 0.20-0.30, the increment of hydrogen pressure in the system was conducted. Activity of all catalysts did not remarkably change compared with its activity in the less-hydrogen system (the H_2/C_2H_4 molar ratio of 0.08). It could be implied that most of active sites were deactivated by hydrogen. The reason is the creation of titanium-hydride bond, which is less active, was higher and only the uncoordinated Ti-C_2H_5 group is capable reaction with ethylene monomer to generate the chain growth reaction[12,88,111]. This results in the reduction in activity and lower hydrogen response. Fe-THF is considered as a more clustered catalyst than Al-THF because it has higher Ti content than Al-THF. Moreover, catalyst having less titanium content, Al-THF, exhibited less deactivation effect than the catalyst having higher titanium content, Fe-THF, due to less number of surface active site being able to react with TEA. Therefore, Fe-THF indicated higher hydrogen response, which showed a rapid drop in activity, than Al-THF. However, catalyst having higher Ti content has higher stereospecificity than catalyst having lower Ti content[90,92,112]. As a consequence, one of the possible reasons was the aggregation of Ti species caused the reduction of active site concentration, resulting in a remarkable depression of the monomer consumption[112] and subsequently decrease in activity. This result is in good agreement with the report of Toshiaki *et al*. They investigated the catalytic performance through the isolated and clustered Zeigler-Natta catalysts in ethylene and propylene homo-polymerization. They also found that the isolated Ti species, located on the $MgCl_2$ surface, acted as the loss of the Ti-Ti interaction led to higher activity in both ethylene and propylene polymerization with the $TiCl_3/MgCl_2$ model catalyst[112].

4.2.3 Effect of Lewis acid modification on polyethylene properties

The morphologies of synthetic polyethylene are shown in **Figure 4.7**. It could be reported that all catalysts, including with and without Lewis acid modification, provided the morphology of lump which is similar for all synthetic polymer.

According to **Table 4.8**, polymers produced from Al-THF and Fe-THF without additional hydrogen exhibit a slight increase in melting temperature, but it decreases crystallinity when compared with None-THF. These are the results from utilizing of the different types of Lewis acids. All catalysts produce polymers which have relatively similar and narrow Mw/Mn. This is because the doped and undoped catalysts had basically the same types of active sites[27].

4.2.4 Effect of hydrogen on polyethylene properties

As reported in **Figure 4.7,** not only in the absence of hydrogen case, but also in the presence of hydrogen, the morphologies of resultant polymer were also similar.

As presented in **Table 4.8**, the molecular weight of polymer decreased when the concentration of hydrogen increased because chain termination reaction by hydrogen occurred. As a consequence, the melting temperature is lowered down due to the decrease in molecular weight of polyethylenes. In addition, more H_2 pressure tends to an increment in the crystallinity of all polymers[5]. This is because the polymerization rate is reduced by hydrogen resulting in an increase in crystallization rate[5]. Mw/Mn of all polymers did not significantly change at the different levels of hydrogen. This result is then in the agreement with that of Shan *et al*[100]. In addition, doping single Lewis acid has no correlation with hydrogen response of molecular weight.

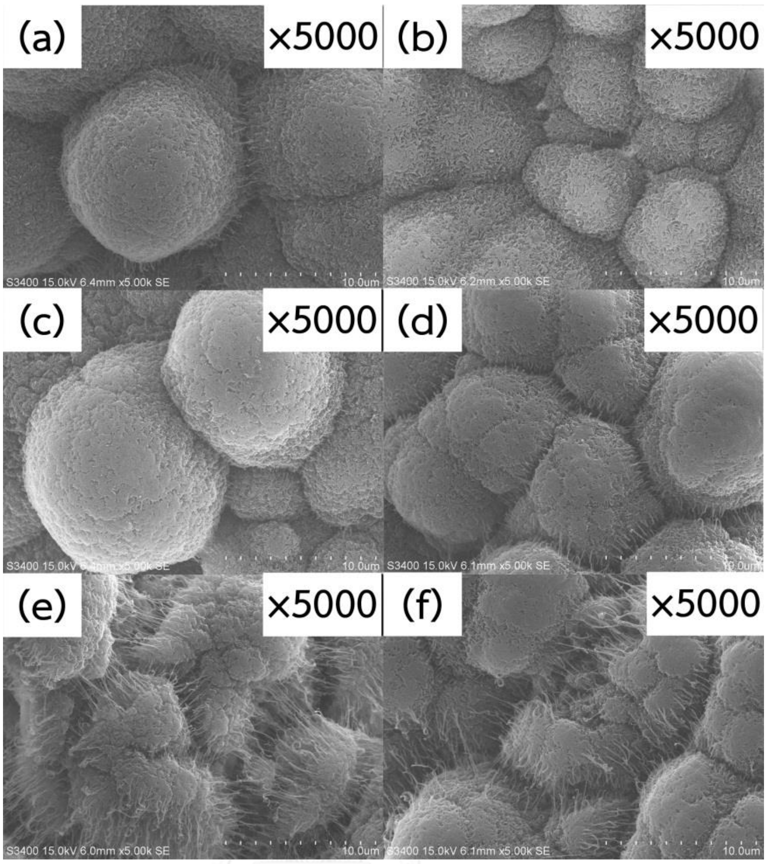

Figure 4.7 SEM images of the polyethylene obtained by: (a) None-THF, (c) Al-THF, (e) Fe-THF in the absence of H_2, and (b) None-THF, (d) Al-THF, (f) Fe-THF at H_2/C_2H_4 molar ratio = 0.30.

Table 4.8 Influences of Lewis Acids and hydrogen on polyethylene

Catalyst	$[H_2]/[C_2H_4]$	T_m[a] (°C)	χ_c[a] (%)	$Mw^b \times 10^{-3}$ (g/mol)	$Mn^b \times 10^{-3}$ (g/mol)	$Mw/Mw_{0.08}$[b]	MWD[c]
None-THF	0	132.9	55.4	-	-	-	-
	0.08	131.2	58.0	452	74	1.00	6.1
	0.20	129.8	59.7	249	40	0.55	6.2
	0.30	129.0	56.2	179	31	0.40	5.7
Al-THF	0	133.8	54.7	-	-	-	-
	0.08	131.2	60.7	336	54	1.00	6.2
	0.20	130.0	60.1	205	36	0.61	5.7
	0.30	130.1	68.5	190	34	0.57	5.7
Fe-THF	0	134.2	52.8	-	-	-	-
	0.08	131.9	55.7	370	57	1.00	6.5
	0.20	130.0	66.8	230	36	0.62	6.4
	0.30	130.0	62.8	201	29	0.54	6.9

[a] Determined by DSC

[b] $Mw/Mw_{0.08}$ = Mw at any $[H_2]/[C_2H_4]$ level/ Mw at $[H_2]/[C_2H_4]$ = 0.08

[c] Determined by GPC

Condition: Polymerization was performed in 2 L autoclave, Ti = 0.008 mmol for all catalysts, Al/Ti molar ratio = 140, co-catalyst = TEA, polymerization time = 1 h, reaction temperature = 80 °C, total pressure = 8 bars under 1 bar of nitrogen and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.20 and 0.30.

4.3 Effect of hydrogen response on $TiCl_4/MgCl_2$/THF catalysts with second Lewis acid addition for ethylene polymerization

Up to this point, the controlling of polymer properties can be done by the modification of $MgCl_2$ and hydrogen addition. The addition of Lewis acid with $MgCl_2$ support is one of the most effective ways to modify the catalyst system. Previously, $AlCl_3$[2,105,113], BCl_3[114], $GaCl_3$[114], LiCl[63], NaCl[65,66,115], $MnCl_2$[64] and PCl_3[1] doped catalysts were synthesized for α-olefin polymerization in the absence and/or presence of hydrogen. However, the modification of $MgCl_2$ with mixed metal chlorides is less studied. Therefore, it is interesting to investigate the mixed Lewis acids modification of $TiCl_4/MgCl_2$/THF catalytic system with hydrogen addition in ethylene polymerization. In this study, $ZnCl_2$ - , the mixed $ZnCl_2$ with $AlCl_3$ - and the mixed $ZnCl_2$ with $FeCl_2$-doped catalysts were tested for catalytic activity and their hydrogen responses. The properties of obtained polyethylene were also determined using GPC, SEM and DSC techniques.

4.3.1 Characteristic of catalysts

Ti content of all catalysts decreased slightly when adding Lewis acid as stated in **Table 4.9**. It is possible that the added Lewis acid formed complex compound with $MgCl_2$ support. This led to the drop in free-chloride crystal vacancies of $MgCl_2$ and contributed to declination in Ti incorporation[1].

Nevertheless, the addition of Lewis acid can improve Ti content on the outer surface as reported in **Table 4.10**. It can be noted that there is some deviation from XPS technique. Lewis acid modification can increase number of surface active sites in the catalyst, which can react with cocatalyst to catalyze further polymerization.

Table 4.9 The elemental composition of the prepared catalysts

Catalyst	**Components**	**Elemental content (wt%)[a]**				**Ti/Mg**
		Ti	Mg	Zn	M[b]	**(mol/mol)**
None-THF	$TiCl_4/MgCl_2/THF$	4.07	6.87	-	-	0.30
Zn-THF	$TiCl_4/ZnCl_2/MgCl_2/THF$	3.47	5.93	11.25	-	0.30
ZnAl-THF	$TiCl_4/ZnCl_2/AlCl_3/MgCl_2/THF$	3.24	5.83	2.77	0.26	0.28
ZnFe-THF	$TiCl_4/ZnCl_2/FeCl_2/MgCl_2/THF$	3.54	5.43	3.13	0.90	0.33

[a] Determined by ICP

[b] M = Al or Fe

Table 4.10 The elemental composition of the catalysts by EDX analysis

Catalyst	Elemental content on the surface of catalyst (wt%)[a]					Ti/Mg
	Ti	Mg	Cl	Zn	M[b]	(mol/mol)
None-THF	6.52	24.32	69.16	-	-	0.14
Zn-THF	12.63	22.36	62.00	3.01	-	0.29
ZnAl-THF	10.14	19.93	64.23	4.94	0.77	0.26
ZnFe-THF	11.71	20.05	57.77	5.45	5.02	0.30

[a] Determined by EDX

[b] M = Al or Fe

As seen from the **Figure 4.8**, all catalysts show the C-H stretching band around 2976-2875 cm^{-1}. The C-O-C symmetrical stretching band of all modified catalysts was found and displayed the IR spectra at 883.4, 871.6, 869.5 and 864.3 cm^{-1} for None-THF, Zn-THF, ZnAl-THF and ZnFe-THF, respectively, whereas the asymmetrical C-O-C stretching vibrations of these catalysts were also found at 1032.6, 1022.8, 1021.3 and 1019.2 cm^{-1} for None-THF, Zn-THF, ZnAl-THF and ZnFe-THF, respectively. These indicate the formation of titanium (III)-magnesium-THF complexes[28,60,116]. In addition, Chu *et al.* reported that the addition of $AlCl_3$ may adjust the acid-base property of $MgCl_2$ support due to the formation of Al-Mg-THF complex. According to Chen and Fan's report[105], they noted that the presenting of

$AlCl_3$, which has higher Lewis acidity than $MgCl_2$, might reduce electron density on some types of active site in the catalyst. Therefore, it suggested that the bimetallic complex may form resulting in lowering of an anion of $MgCl_2$. Thus, the second metal additive of Lewis acid modification can increase the acidity of active site. Then, it can efficiently eliminate the remaining THF in the catalyst. As a consequence, the alkoxy Ti species peak through the ring-opening of THF, which is expected to be around 3000-3600 cm^{-1}, could not be observed[82].

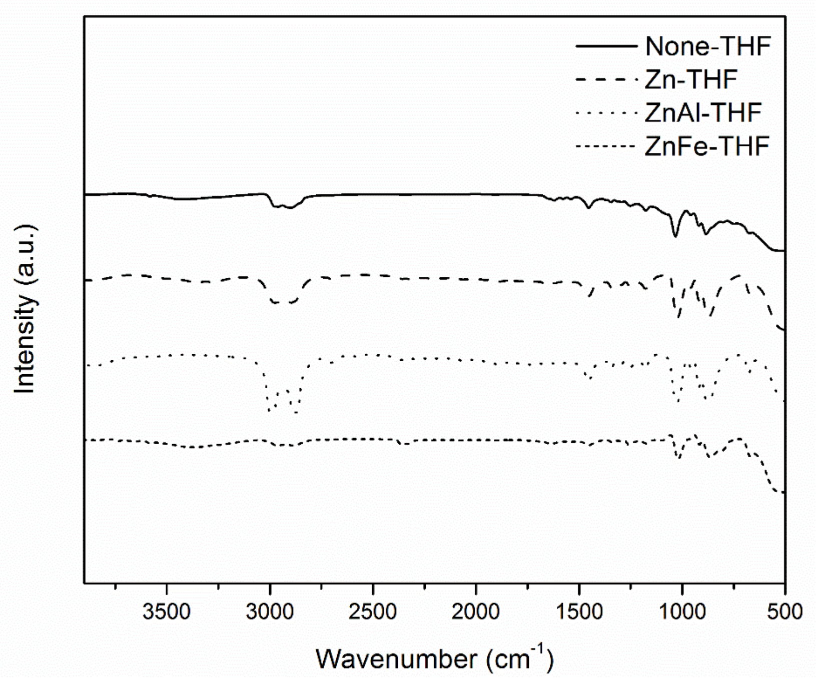

Figure 4.8 FTIR spectra of the prepared catalysts

The α-form of $MgCl_2$ exhibits the XRD peaks at 2θ = 14.9°, 30.2°, 34.8°, and 50.3°. The XRD peaks at 2θ = 20.4°, and 32.0° indicate the characteristic peaks of $MgCl_2$/THF complex[59,67]. As seen from the **Figure 4.9**, Lewis acid addition caused the decrease in the intensity of the $MgCl_2$/THF peaks in all modified catalysts. This could be attributed to the fact that a small amount of metal halide can possibly destroy the $MgCl_2$ structure[60]. Phiwkliang *et al*. stated that the $TiCl_4$/THF, $TiCl_3$/THF and $TiCl_4$/$MgCl_2$/THF complexes were revealed their characteristic peaks around 13.2°, 16.7° and 18.3°, respectively. However, these peaks were not observed because the addition of the second Lewis acid can increase the acidic site[67]. Therefore, it caused the elimination of the adherent THF of the catalyst. This result is in accordance with the IR measurement as reported in **Figure 4.8** that the O-H stretching band of the Lewis acid modified catalysts was not observed. As the result, modification of Lewis acid caused the lowering in intensity of the catalyst, especially with the second Lewis acid addition (ZnAl-THF and ZnFe-THF). Nonetheless, the Lewis acid characteristic peak of the modified catalysts was not detected because Lewis acid totally took part in $TiCl_4$/$MgCl_2$/THF structure[108,109]. Besides, morphology of None-THF, Zn-THF, ZnAl-THF and ZnFe-THF are presented in **Figure 4.10**. All catalysts are in bar shaped and have the similar morphology.

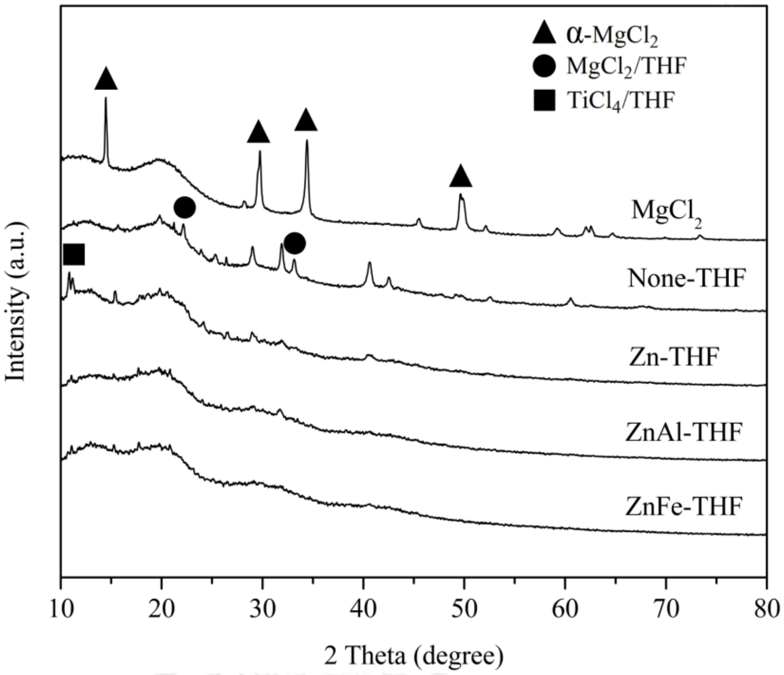

Figure 4.9 XRD patterns of the catalysts

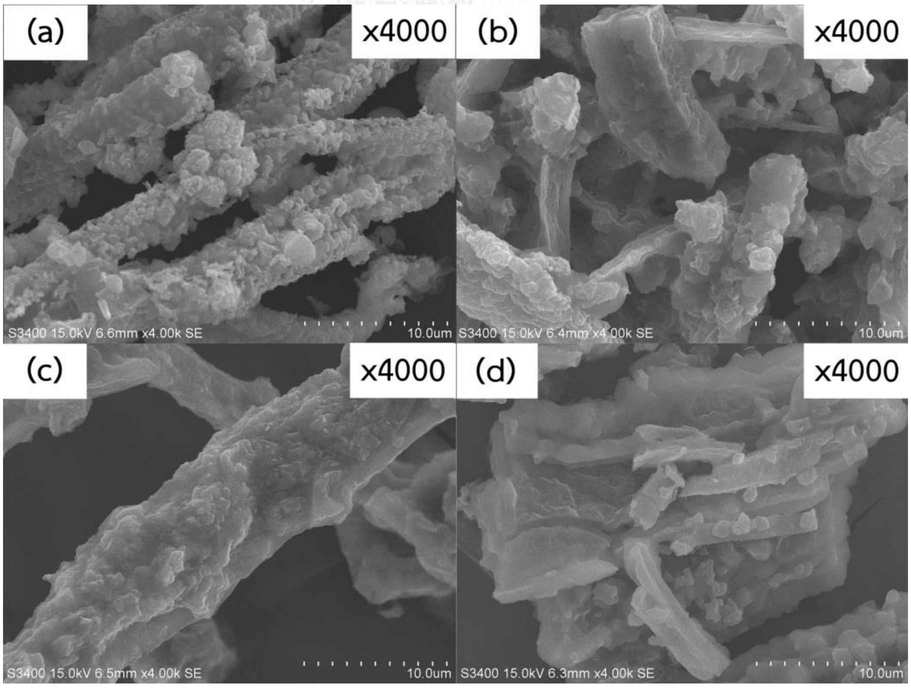

Figure 4.10 SEM images of the prepared catalysts: (a) None-THF, (b) Zn-THF, (c) ZnAl-THF and (d) ZnFe-THF

4.3.2 Effect of Lewis acid modification on catalytic activity

Lewis acid modification has a significant effect on catalytic activity in ethylene polymerization. $ZnCl_2$ as a doping metal salt in $MgCl_2$ support exhibited the strongest effect on the catalytic activity as summarized in **Table 4.11**. $ZnCl_2$ doped catalyst showed the lowest activity by following: None-THF > ZnFe-THF > ZnAl-THF > Zn-THF. According to this result, $ZnCl_2$ modification can reduce the activity compared with the unmodified catalyst. This is because $ZnCl_2$ acted as poison. This activity result is concordant with Fregonese *et al*. They reported that doping $ZnCl_2$ as salt in $MgCl_2$ supports could improve or reduce the activity of propylene polymerization; it however depended on $ZnCl_2$ concentration. Catalysts containing $ZnCl_2$ up to 0.73 wt% showed an increase of activity, whereas increased more $ZnCl_2$ content was found to decreased activity[27]. However, MWD of polypropylene did not significantly change with the added $ZnCl_2$ content. Therefore, in this study, the prepared catalysts containing zinc at least 3 wt% resulted in the reduction of activity as described earlier. The addition of the second metal halides such as $FeCl_2$ and $AlCl_3$ could improve the activity; however, their activities are still lower than those of None-THF. The second metal doped could increase the acidity of active site and therefore rise chain propagation rate constant[27,67]. This results in an enhancement of the activity with the catalyst containing the second metal chloride doped. ZnFe-THF displayed slightly higher activity than ZnAl-THF. It might be due to the fact that the ionic radii of Fe (0.75 Å) with Mg (0.86 Å) in the 6-coordinate, octahedral form is more similar than that of Al (0.68 Å) with Mg. As a consequence, $FeCl_2$ could participate in $MgCl_2$ structure in a better way than $AlCl_3$ with $MgCl_2$ as confirmed by XRD measurement. Moreover, $FeCl_2$ has higher electronegativity than $AlCl_3$, which led to the increase in acid property of active site being able to react with monomer. Then, ZnFe-THF had more monomer consumption and provided higher activity. This result is also in good agreement with many literatures[18,67]. Phiwkliang *et al.* reported that when compared with single metal chloride modification, the catalyst with mixed metal chlorides showed higher activity in ethylene polymerization, which could be attributed to increased Ti^{3+} species as confirmed by ESR measurement[67].

According to Ti content, all catalysts are considered as the clustered catalysts[112]. ZnFe-THF has the highest Ti/Mg ratio of the catalyst surface as shown in **Table 4.10**. The Higher Ti/Mg ratio of the catalyst surface means higher possible opportunities of active sites to react with cocatalyst, and then proceed chain propagation and chain termination further. Thus, in the presence of hydrogen system as reported in **Table 4.11**, ZnFe-THF exhibited the highest hydrogen response even in the system having small amount of hydrogen. At H_2/C_2H_4 molar ratio of 0.08, activity decreased by 54% from its original one. With higher hydrogen content, it was found that the activity of ZnFe-THF did not change significantly compared with its activity at H_2/C_2H_4 molar ratio of 0.08. The activity at H_2/C_2H_4 molar ratio of 0.60 decreased only 28% which might be due to its clustered Ti species, which most of them were rapidly deactivated by hydrogen. As already known, the addition of hydrogen is one of the most effective ways to proceed chain transfer reactions. Kouzai *et al*. stated that polymerization sites need to locate in an instant surrounding of hydrogen dissociation sites to produce the reactions of chain transfer[90]. Thus, the formation of more clustered active centers increases the chances to occur chain transfer reaction by hydrogen. Furthermore, the more clustered active species were formed leading to higher hydrogen response. Toshiaki *et al*. also found that one of the major deactivation mechanisms causing the activity suppression is the aggregation of Ti species, which results in the decrease in active site concentration. They studied about the catalytic performance using the isolated and clustered Ziegler-Natta catalysts in ethylene and propylene homopolymerization. They noted that the isolated Ti species located on the $MgCl_2$ surface acted as the loss of the Ti-Ti interaction. This gives rise to higher activity for both in ethylene and propylene polymerization with the $TiCl_3/MgCl_2$ model catalyst[112]. Furthermore, addition of hydrogen can produce Ti-H bond, which is inactive for polymerization. However, Ti-H bond can be reactivated by adding ethylene monomer. Only the uncoordinated Ti—C_2H_5 group can proceed with ethylene monomer to generate the chain propagation reaction[12,88,111]. As mentioned earlier, the second doped Lewis acid modification can improve the catalyst activity. Therefore, ZnAl-THF showed the similar trend of hydrogen response, but it performed only slightly higher activity ratio than Zn-THF. This is because of their Ti/Mg ratios of the catalyst surface as shown in **Table 4.10.** Ti/Mg ratio of Zn-THF is slightly higher than ZnAl-THF. It means that Zn-THF has more clustered active species than ZnAl-THF. Moreover, it was confirmed by FTIR measurement as presented in **Figure 4.8** that there was some of the remaining THF in the Zn-THF catalyst resulting in the slightly decreased activity. At the H_2/C_2H_4 molar ratio of 0.08, the activity of Zn-THF and ZnAl-THF decreased around 43% of their original one. For the higher hydrogen content, the activity decreased up to 81% at the H_2/C_2H_4 molar ratio of 0.60. This result can be explained using the similar reason as mentioned for that of ZnFe-THF. It was due to the fact that most of active sites were destroyed rapidly by hydrogen. Thus, when hydrogen concentration increased, activity did not considerably change compared with its activity at H_2/C_2H_4 molar ratio of 0.08.

Table 4.11 Catalytic activities of all catalysts in the presence of hydrogen for ethylene polymerization

Catalyst	$[H_2]/[C_2H_4]$	Activity (kg PE/gTi*h)[a]	Activity ratio without H_2[b]	Activity ratio with H_2[c]
None-THF	0	732	1.00	1.00
	0.08	645	-	0.88
	0.20	362	-	0.49
	0.60	214	-	0.29
Zn-THF	0	547	0.75	1.00
	0.08	311	-	0.57
	0.20	240	-	0.44
	0.60	104	-	0.19
ZnAl-THF	0	694	0.95	1.00
	0.08	400	-	0.58
	0.20	320	-	0.46
	0.60	149	-	0.21

Catalyst	$[H_2]/[C_2H_4]$	Activity (kg PE/gTi*h)[a]	Activity ratio without H_2[b]	Activity ratio with H_2[c]
ZnFe-THF	0	720	0.98	1.00
	0.08	330	-	0.46
	0.20	260	-	0.36
	0.60	132	-	0.18

[a] Condition: Polymerization was performed in 2 L autoclave, [Ti] = 0.008 mmol for all catalysts, Al/Ti molar ratio = 140, co-catalyst = TEA, polymerization time = 1 h, reaction temperature = 80 °C, total pressure = 8 bars under 1 bar of nitrogen and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.20 and 0.60.

[b] Activity ratio without H_2 = activity of the modified catalyst/activity of the unmodified catalyst

[c] Activity ratio with H_2 = activity of the catalyst at that level of H_2/activity of that catalyst without H_2

4.3.3 Effect of Lewis acid modification on polyethylene properties

As displayed in **Figure 4.11**, the Lewis acid modified catalysts provided lumpier polymer than None-THF. Moreover, when hydrogen was introduced, the obtained polymer was also lumpier than the polymer without hydrogen addition.

From **Table 4.12**, when compared with polyethylene produced by None-THF, the polyethylenes produced by Lewis acid modified catalysts exhibited a slight increase in crystallinity, but the melting temperature of them did not significantly change. These are the results from utilizing of the different types of Lewis acids[28]. In addition, broader MWD was obtained when using Lewis acid modified catalysts. This was because the added Lewis acid can form the new type of active centers.

4.3.4 Effect of hydrogen on polyethylene properties

The results of polyethylene with hydrogen addition are summarized in **Table 4.12**, the molecular weight of polymer declined with raised hydrogen content. This is due to the occurrence of chain termination reaction by hydrogen[16]. As a consequence, the melting temperature drops owing to the decrease in molecular weight of polyethylenes. Furthermore, the crystallinity of all polymers tends to increase with the increasing of hydrogen pressure. This is because hydrogen acting as a chain transfer agent for the reaction blocks the polymerization sites. As a result, the polymerization rate is reduced by hydrogen leading to a rise in crystallization rate[5]. In addition, the molecular weight distribution decreased with increased hydrogen concentration. This result is in accordance with Nikolaeva *et al*[117]. In addition, doping mixed Lewis acids has a correlation with hydrogen response of molecular weight due to the clustered Ti distribution.

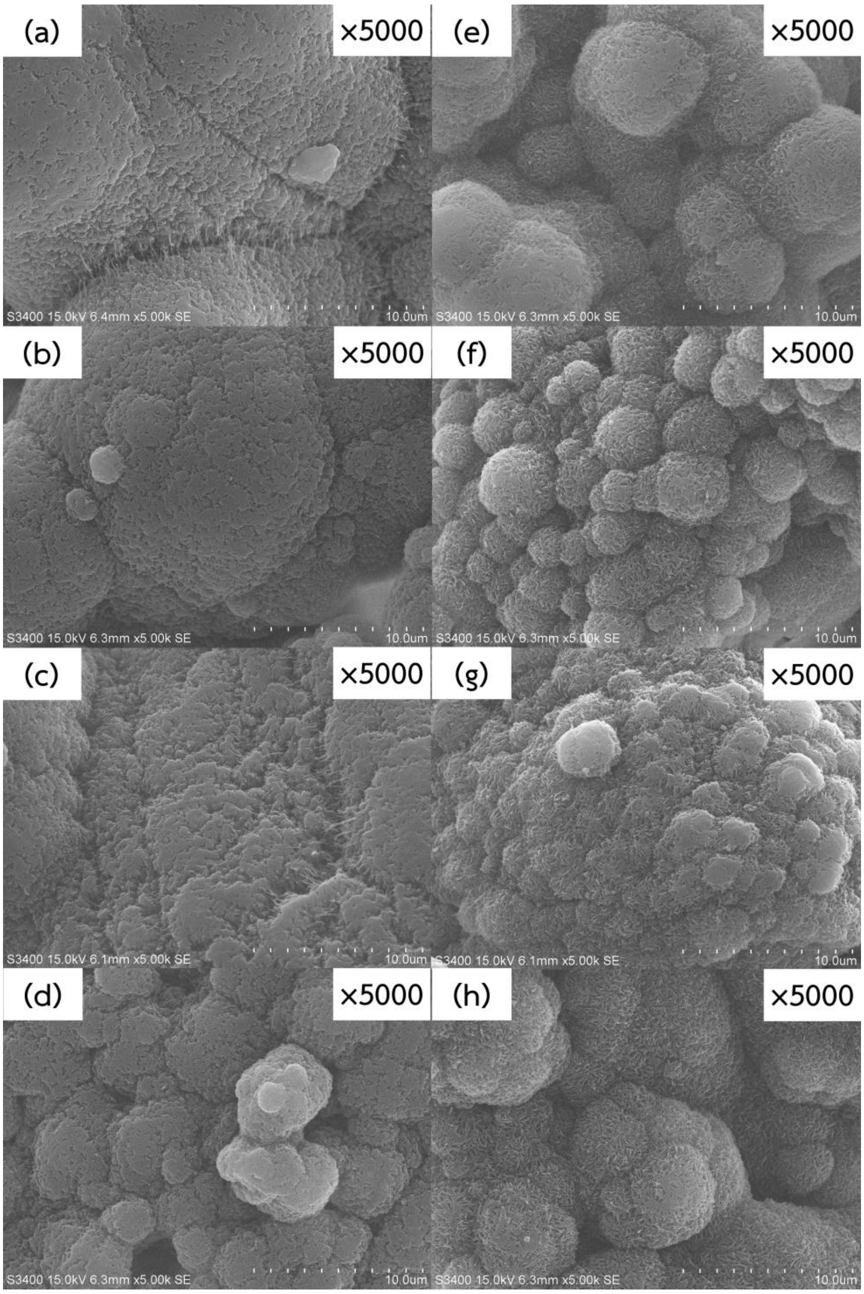

Figure 4.11 SEM images of the polyethylene obtained by: (a) None-THF, (b) Zn-THF, (c) ZnAl-THF, (d) ZnFe-THF without additional H_2, and (e) None-THF, (f) Zn-THF, (g) ZnAl-THF, (h) ZnFe-THF at H_2/C_2H_4 molar ratio = 0.60

Table 4.12 Influences of Lewis acids modification and hydrogen on polyethylene

Catalyst	$[H_2]/[C_2H_4]$	T_m [a] (°C)	χ_c [a] (%)	Mw [b] $\times 10^{-3}$ (g/mol)	Mn [b] $\times 10^{-3}$ (g/mol)	$Mw/Mw_{0.08}$ [b]	MWD [c]
None-THF	0	132.9	55.4	-	-	-	-
	0.08	131.2	58.0	452	74	1.00	6.1
	0.20	129.8	59.7	249	40	0.55	6.2
	0.60	127.7	67.2	101	18	0.22	5.6
Zn-THF	0	133.5	57.4	-	-	-	-
	0.08	131.3	57.5	406	40	1.00	10.0
	0.20	130.0	67.3	243	35	0.60	7.0
	0.60	128.2	68.2	121	18	0.30	6.6
ZnAl-THF	0	133.3	62.9	-	-	-	-
	0.08	131.6	56.7	334	40	1.00	8.3
	0.20	131.1	57.4	264	36	0.79	7.4
	0.60	128.4	62.4	110	18	0.33	6.2

Catalyst	$[H_2]/[C_2H_4]$	T_m[a] (°C)	χ_c[a] (%)	$Mw^b \times 10^{-3}$ (g/mol)	$Mn^b \times 10^{-3}$ (g/mol)	$Mw/Mw_{0.08}$	MWD[b]
ZnFe-THF	0	133.0	59.7	-	-	-	-
	0.08	131.8	54.6	403	44	1.00	9.2
	0.20	131.4	59.3	362	37	0.90	9.8
	0.60	128.5	67.0	128	18	0.32	7.2

[a] Determined by DSC

[b] $Mw/Mw_{0.08}$ = Mw at any $[H_2]/[C_2H_4]$ level/ Mw at $[H_2]/[C_2H_4]$ = 0.08

[c] Determined by GPC

Condition: Polymerization was performed in 2 L autoclave, [Ti] = 0.008 mmol for all catalysts, Al/Ti molar ratio = 140, co-catalyst = TEA, polymerization time = 1 h, reaction temperature = 80 °C, total pressure = 8 bars under 1 bar of nitrogen and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.20 and 0.60.

4.4 Investigation of alkoxysilanes in the presence of hydrogen with Ziegler-Natta catalysts in ethylene polymerization

There are numerous methods to improve catalyst like mechanical and chemical treatment[38,44,83,118,119]. The addition of Lewis base is one of the chemical routes to obtain the high active catalyst. Currently, the fourth generation of ZN catalyst is mostly synthesized and investigated in industry and academic aspects, especially in propylene polymerization. This catalyst generation consisted of $TiCl_4/MgCl_2$ supported catalyst, internal and external donor (Lewis bases). Phthalate based type or diester is used as internal donor while alkoxysilane is typically used as external donor[120]. Among various $R_1R_2Si(OMe)_2$ types of external donor, CHMDMS is more frequently used due to its effective performance to enhance the isotacticity of polypropylene without sacrificing the catalyst activity[121]. On the other side, ethanol is also used to improve $MgCl_2$ crystal structure for achieving high activity catalysts[116].

As mentioned previously, Lewis bases were studied in many aspects in propylene polymerization. For example, the combination of internal and external donor, the mixed internal donors and/or mixed external donors[122,123] including the different ratios of external donor to catalyst were investigated. However, the effect of external donor in ethylene polymerization is still opened for discussion and less mentioned in the literature. Therefore, the aim of this work, based on catalytic activity including polyethylene properties, was to study the effect of alkoxysilanes as external donor using two commercial ZN catalysts with and without internal donor in the presence of hydrogen.

4.4.1 Characteristic of commercial catalysts

The elemental composition of catalyst was determined by ICP as reported in **Table 4.13**. It shows that Cat-A and Cat-B contain 3.79 wt% of Ti and 2.47 wt% of Ti, respectively. However, the Ti/Mg ratios in bulk of them were similar.

Table 4.13 The elemental composition in bulk and on surface of catalysts

	ICP measurement			**EDX measurement**			
Catalyst	Element content (wt%)[a]		Ti/Mg	Element content (wt%)[b]			Ti/Mg
	Ti	Mg	(mol/mol)	Ti	Mg	Cl	(mol/mol)
Cat-A	3.79	14.89	0.11	5.09	24.99	67.44	0.10
Cat-B	2.47	16.66	0.08	5.26	23.07	71.27	0.12

[a] Determined by ICP

[b] Determined by EDX

EDX analysis was applied to identify roughly the surface elemental composition of catalyst as presented in **Table 4.13**. It can be seen that Ti content on catalyst surface is higher than Ti content in bulk measured by ICP technique. It indicated that most Ti active sites were located on the surface of catalyst more than in the catalyst pores. However, the ratios of Ti/Mg of these catalysts were almost equal. Cat-A showed the Ti/Mg ratio of 0.10, while Cat-B showed the Ti/Mg ratio of 0.12.

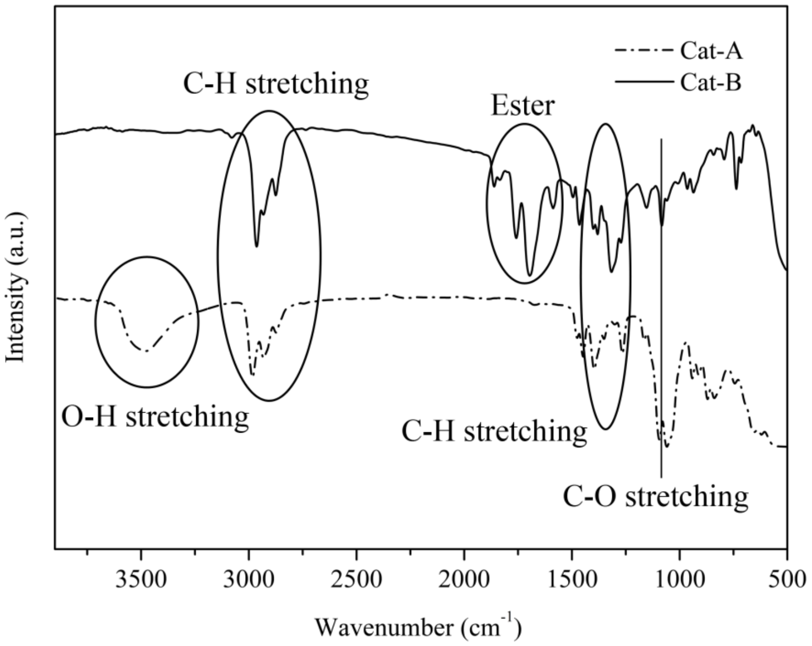

Figure 4.12 IR spectra of Cat-A and Cat-B

IR identification has been used to identify the interaction between $TiCl_4$ and $MgCl_2$ support. According to **Figure 4.12**, IR spectra of all catalysts are presented in the range of 3900-500 cm^{-1}. The analysis of the IR spectrum of Cat-A revealed that the alcoholate peak was found in the range of 3100 – 3700 cm^{-1} corresponding to O–H stretching[38]. Moreover, the bands at 2874 – 2983 cm^{-1} and 1266 – 1476 cm^{-1} corresponded to C–H stretching, while the vibration at 1095 cm^{-1} corresponded to C–

O stretching[83]. This IR spectrum of Cat-A is in good agreement with the report by Huang *et al*[84]. and Parada *et al*[38]. Similarly, the spectra of Cat-B showed the band around 2800 - 3000 cm^{-1} and 1273 – 1495 cm^{-1} corresponding to C–H stretching. The characteristic peaks of ester occurred at 1696 – 1758 cm^{-1} and 936 – 1154 cm^{-1}. Moreover, the aromatic ring stretching is located at 1588 cm^{-1}, while the vibration is at 737 cm^{-1} indicating the ortho aromatic ring. As a result, it confirmed that there is phthalate type as internal donor in Cat-B. This IR spectrum is in accordance with that of Higgins *et al*[124].

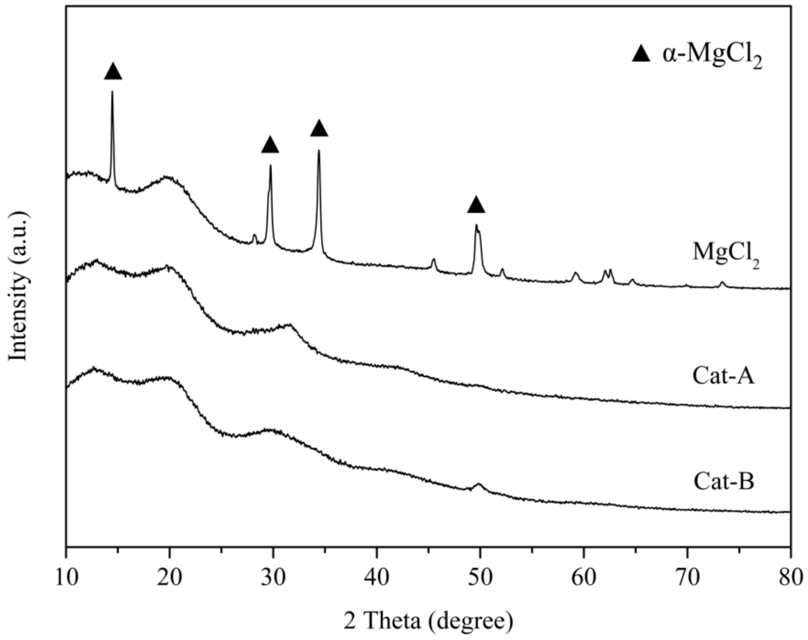

Figure 4.13 XRD patterns of $MgCl_2$ support and catalysts

The XRD patterns of α-$MgCl_2$ support and catalysts in the range of 10-80 degree are presented in **Figure 4.13**. The characteristic peak of anhydrous $MgCl_2$

showed the sharp peaks at 2θ = 14.4°, 29.7°, 34.3°, and 49.5°. Sharp peak at 2θ = 14.4° was defined as the stacking of Cl–Mg–Cl triple layers along the crystallographic direction. While three peaks at 2θ = 29.7°, 34.3° and 49.5° were found and assigned to be the stacking faults of the triple layers. The peaks at 2θ = 34.3° and 49.5° represented the (104) and (110) plane, respectively[84,85]. Huang *et al.* reported that the δ-$MgCl_2$ support has a single Cl–Mg–Cl structural layers (monolayers)[84]. Regarding to XRD data, Cat-A and Cat-B exhibited the reduction of intensity in all peaks of α-$MgCl_2$. This is because the insertion of alcohol between the Cl–Mg–Cl triple layers. It increases the interplanar distance of Cl–Mg–Cl triple layers[86] resulting in a disappearance of peak at 2θ = 14.4°, 29.7°, 34.3°and 49.5°.

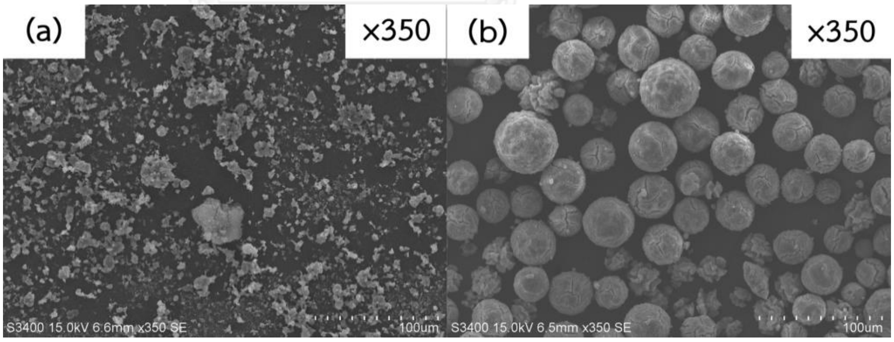

Figure 4.14 SEM images of catalysts: (a) Cat-A and (b) Cat-B

As seen in **Figure 4.14**, morphology of catalyst was investigated by SEM technique. The result revealed that Cat-A is in irregular shapes, whereas Cat-B is quite uniformly spherical shape.

4.4.2 Effect of alkoxysilanes on catalytic activity

According to **Table 4.14**, it could be noticed that catalytic activity was lower when adding external donor. This is because electron donor can form a complex with both cocatalyst and active sites[49,51,121,123]. As a consequence, the content of active cocatalyst, which can activate the active center, was lowered. The efficiency of the formation of active site was therefore reduced. In addition, CHMDMS and DMDMS have the bulky substituents, which cause the steric hindrance to neighborhood active sites. This restricted the direction of monomer insertion. Thus, this caused the decrease in activity for both catalysts[53]. However, Zhang *et al*. reported that alkoxysilane requires bulky hydrocarbon groups to prevent the removal of silane from the surface of catalyst via the complexation with cocatalyst[51,120,121]. Moreover, the CHMDMS can reduce more catalytic activity than the DMDMS. It might be due to the fact that cyclohexyl group of the CHMDMS has more bulkiness than methyl group of the DMDMS which results in the decrease in monomer insertion as mentioned earlier. Cat-A exhibited the decrease in activity ratio more than Cat-B when external donor was added. It is probably because alkoxysilane has some poisoning effect on non-stereospecific active sites for Cat-A[51,52]. In case of Cat-B, it has phthalate type as internal donor, which can turn less stereospecific active site to become more stereospecific one. Although, most of internal donor can be easily removed from the catalysts surface through complexation with cocatalyst[51,123], Cat-B still has external donor to replace the lost internal donor. Therefore, when combined the left internal donor with the external one, Cat-B still had higher activity ratio than Cat-A which has no internal donor. Yet it was still lower than the case with has no external donor. This is because alkoxysilane has a slight deactivating effect on catalyst[125].

As it has been already known, hydrogen is commonly used as an effective chain transfer agent to reduce molecular weight of polymer in olefin polymerization[121,126]. Therefore, the polymer molecular weight can be controlled by changing the volume of added hydrogen[121]. According to **Table 4.14**, hydrogen was introduced into the system. It was found that both catalysts exhibited lower activity than that in the system without hydrogen addition. This is because hydrogen can block active site for polymerization. This reduced opportunity of ethylene monomer to the catalyst active sites and favored the termination reaction[5]. It means that hydrogen can suppress the ethylene polymerization rate due to the formation of Ti-H bond. This Ti-H bond is less active and can generate the stabilized Ti-C_2H_5 bond further[126]. Thus, the activity declined when hydrogen concentration was raised for both catalysts in ethylene polymerization.

Moreover, when external donor was added in H_2/C_2H_4 molar ratio range of 0 - 0.20, much more hydrogen was needed when DMDMS was used as external donor than CHMDMS. For example in case of Cat-B, small amount addition of hydrogen at H_2/C_2H_4 molar ratio of 0.08 led to a drop of 14% in activity ratio for CHMDMS, while DMDMS required more hydrogen amounts at around H_2/C_2H_4 molar ratio of 0.20 to gain the similar decrease in activity ratio. It interpreted that CHMDMS is more sensitive to hydrogen[121]. However, in higher H_2/C_2H_4 molar ratio range of 0.20 - 0.60, it showed a different result in hydrogen response compared to the less hydrogen system. It was seen that there was a slight change in activity for both catalysts when CHMDMS was employed. It indicated that CHMDMS showed lower hydrogen response than DMDMS in higher hydrogen concentration. From the previous result, CHMDMS is more sensitive to hydrogen than DMDMS. Therefore, when hydrogen concentration was increased, most of active sites, when CHMDMS acted as external donor, can react quickly with hydrogen and turn into inactive centers. As a consequence, hydrogen response of CHMDMS was lower. Compared between these two catalysts, the results implied that the bulkiness of external donor showed the significant effect on the activity of the internal donor absent catalyst in the hydrogen-present system, while the catalyst having internal donor was less influenced by the structure of external donor. This was because the addition of internal donor decreased sensitivity of catalyst activity to hydrogen. This result is in good agreement with that of Zhang *et al*. They reported that the addition of phthalic anhydride or anisole as internal donor can depress the sensitivity of catalyst activity to hydrogen in ethylene /1-hexene copolymerization[127].

Table 4.14 Catalytic activity of the commercial catalysts in ethylene polymerization

Catalyst	External donor	H_2/C_2H_4 molar ratio	Activity[a] (kgPE/gTi*h)	Activity ratio without H_2[b]	Activity ratio with H_2[c]
Cat-A		0	845	1.00	1.00
		0.08	608	-	0.72
		0.20	606	-	0.72
		0.60	511	-	0.61
	CHMDMS	0	253	0.30	1.00
		0.08	110	-	0.43
		0.20	110	-	0.43
		0.60	96	-	0.38
	DMDMS	0	313	0.37	1.00
		0.08	259	-	0.83
		0.20	235	-	0.75
		0.60	184	-	0.59

Catalyst	External donor	H_2/C_2H_4 molar ratio	Activity[a] (kgPE/gTi*h)	Activity ratio without H_2[b]	Activity ratio with H_2[c]
Cat-B	-	0	558	1.00	1.00
		0.08	489	-	0.88
		0.20	430	-	0.77
		0.60	282	-	0.51
	CHMDMS	0	304	0.54	1.00
		0.08	262	-	0.86
		0.20	190	-	0.62
		0.60	211	-	0.69
	DMDMS	0	330	0.59	1.00
		0.08	294	-	0.89
		0.20	287	-	0.87
		0.60	177	-	0.53

[a] Condition: Polymerization was performed in 2 L autoclave, [Ti] = 0.008 mmol for all catalysts, [Al]/[Ti] = 140, [Al]/[Si] = 10, co-catalyst = TEA, polymerization time = 1 h, reaction temperature = 80 °C, total pressure = 8 bars under 1 bar of nitrogen and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.20 and 0.60.

[b] Activity ratio without H_2 = activity of the modified catalyst/activity of the unmodified catalyst

[c] Activity ratio with H_2 = activity of the catalyst at that level of H_2/activity of that catalyst without H_2

4.4.3 Effect of alkoxysilanes on polyethylene properties

From **Table 4.15**, it can be seen that the addition of alkoxysilane as external donor can improve molecular weight of the polymer[49,53]. This results in a slight increase in melting point of the polymer[5]. Furthermore, alkoxysilane can also enhance crystallinity, but it has no significant change in MWD[52,125].

4.4.4 Effect of hydrogen on polyethylene properties

Polymer molecular weight and MWD were determined by GPC as presented in **Table 4.15**. The result showed that when hydrogen was introduced, the melting point decreased and crystallinity of the polymer increased. This is due to the fact that the added hydrogen acts as a chain transfer agent to reduce the polymer molecular weight which resulted in lower molecular weight and melting temperature of the polymer[5]. In addition, Sperling *et al.* reported that the polymer having lower molecular weight will have lower surface area. It indicated lower physical attraction between the polymer chains and low melting point[128]. In case of crystallinity of the polymer, the added hydrogen blocked catalyst active centers as mentioned previously. This ended up in the reduction of the polymerization rate. Then, the crystallinity was improved[5,129]. The MWD of polymer remained unchanged with hydrogen concentration[117]. This consequence is in accordance with that of Ha *et al.* They confirmed that the polymer polydispersity is independent with hydrogen concentration[102]. No relationship between surface Ti content and H_2 response of MW.

Table 4.15 Influences of alkoxysilanes and hydrogen on polyethylene properties

Cat.	ED	$[H_2]/[C_2H_4]$	T_m^a (°C)	χ_c^a **(%)**	$Mw^b \times 10^{-3}$ (g/mol)	$Mn^b \times 10^{-}$ (g/mol)	$Mw/Mw_{0.08}^b$	MWD^c
Cat-A	-	0	134.0	55.3	-	-	-	-
		0.08	130.5	62.3	317	33	1.00	9.7
		0.20	129.9	58.3	257	29	0.81	8.8
		0.60	128.9	59.1	150	16	0.47	9.6
	CHMDMS	0	134.8	66.8	-	-	-	-
		0.08	132.0	73.3	501	57	1.00	8.8
		0.20	130.7	73.8	308	36	0.61	8.7
		0.60	128.9	70.1	154	20	0.31	7.9
	DMDMS	0	134.4	65.2	-	-	-	-
		0.08	131.2	69.8	417	41	1.00	10.1
		0.20	131.0	75.5	347	40	0.83	8.7
		0.60	128.5	71.1	133	20	0.32	6.8

Cat.	ED	$[H_2]/[C_2H_4]$	$T_m{}^a$ (°C)	$\chi_c{}^a$ (%)	$Mw^b \times 10^{-3}$ (g/mol)	$Mn^b \times 10^{-}$ (g/mol)	$Mw/Mw_{0.08}{}^b$	MWD^c
Cat-B	-	0	130.4	52.9	-	-	-	-
		0.08	131.6	57.8	475	51	1.00	9.4
		0.20	130.2	56.9	295	32	0.62	9.2
		0.60	128.1	60.6	130	17	0.27	7.6
	CHMDMS	0	135.4	55.8	-	-	-	-
		0.08	132.4	59.3	493	63	1.00	7.8
		0.20	130.6	56.7	269	35	0.55	7.7
		0.60	128.4	62.7	239	20	0.48	11.3
	DMDMS	0	135.0	66.4	-	-	-	-
		0.08	132.0	70.8	420	69	1.00	6.1
		0.20	131.0	68.8	328	51	0.78	6.4
		0.60	128.6	71.5	129	13	0.31	6.7

[a] Determined by DSC

[b] $Mw/Mw_{0.08}$ = Mw at any $[H_2]/[C_2H_4]$ level/ Mw at $[H_2]/[C_2H_4]$ = 0.08

[c] Determined by GPC

Condition: Polymerization was performed in 2 L autoclave, [Ti] = 0.008 mmol for all catalysts, [Al]/[Ti] = 140, [Al]/[Si] = 10, co-catalyst = TEA, polymerization time = 1 h, reaction temperature = 80 °C, total pressure =8 bars under 1 bar of nitrogen and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.20 and 0.60.

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Ti content on surface of catalysts and it distribution play an important role in catalytic productivity including hydrogen response. Catalyst preparation method and the modification of $MgCl_2$ support have an effect on Ti content and its distribution on surface of catalysts.

In the first part of this work, ZN-THF and Zn-EtOH, which were prepared by different methods, were investigated. It can be concluded that ZN-EtOH had a better active center distribution than that of ZN-THF. Therefore, ZN-EtOH was found to hinder the effect of hydrogen and show higher activity in every hydrogen content. Moreover, catalytic activity was lower when increased hydrogen pressure.

According to the $MgCl_2$ modification, Lewis acids were employed to improve Ti content on the surface of catalyst. In the second part, a comparative study of $AlCl_3$ and $FeCl_2$-modified $TiCl_4/MgCl_2$/THF catalytic system in the presence of hydrogen was studied. $FeCl_2$ showed higher competency to remove the remaining THF in $MgCl_2$ structure than $AlCl_3$. Thus, the activity was in the order of Fe-THF > Al-

THF > None-THF. Due to $FeCl_2$ having higher Ti content than $AlCl_3$, it showed better hydrogen response than Al-THF.

Then, effect of the second Lewis acid addition on hydrogen response was explored. The presence of $ZnCl_2$ reduced the activity because it acted as a poison donor. The activity was in the order of None-THF > ZnFe-THF > ZnAl-THF > Zn-THF. The addition of the second Lewis acid could improve the activity. However, activity is still slightly lower than undoped $ZnCl_2$ catalyst. ZnFe-THF exhibited slightly higher activity than ZnAl-THF because $FeCl_2$ could remove the remaining THF more than $AlCl_3$. In part of additional hydrogen, the activity was in the order of ZnFe-THF > Zn-THF > ZnAl-THF > None-THF at H_2/C_2H_4 molar ratio of 0.08 due to its clustered active sites on the catalyst surface. For higher hydrogen concentration, the activity of the modified catalysts did not considerably change because most of active sites were deactivated by hydrogen.

Not only Lewis acids, but also Lewis bases can modify the $MgCl_2$ structure. Alkoxysilanes as external donor were studied using two commercial Ziegler-Natta catalysts ($TiCl_4/MgCl_2{\bullet}nEtOH$ and $TiCl_4$/phthalate type/$MgCl_2$). CHMDMS can decrease the activity more than DMDMS. This was because CHMDMS has bulkier hydrocarbon groups than DMDMS and led to restrict the direction of monomer insertion to active sites. In addition, when hydrogen was added into the system, CHMDMS is more sensitive to hydrogen than DMDMS. However, CHMDMS showed lower hydrogen response with increased hydrogen concentration. Among the two catalysts, catalyst having internal donor can decrease sensitivity of catalyst activity in the system with hydrogen.

Based on GPC and DSC results, the molecular weight decreased with hydrogen concentration due to chain termination reaction by hydrogen. This results in a decrease of melting point and the increase in crystallinity of polyethylene. Moreover, hydrogen response of molecular weight depends on each catalyst system.

5.2 Recommendations

In order to further improve the $TiCl_4/MgCl_2$ catalytic systems, some ideas derived from this research are suggested:

- To measure the remaining THF content in $TiCl_4/MgCl_2/THF$ catalysts, Gas chromatography (GC) should be used.
- To determine Lewis acid sites of the modified $TiCl_4$/Lewis acid/$MgCl_2$/THF catalyst, IR spectra of pyridine should be employed.

- To measure the amount of Ti atom on the catalyst surface of the modified $TiCl_4$/Lewis acid/$MgCl_2$/THF catalysts, X-ray photoelectron spectroscopy (XPS) should be used.
- To understand for more detail, the same catalysts preparation in the topic of investigation of alkoxysilanes in the presence of hydrogen with Ziegler-Natta catalysts in ethylene polymerization should be studied.
- Effect of hydrogen on MWD of polyethylene should be investigated.
- Effect of $ZnCl_2$ on MWD should be investigated.
- Effect of Lewis acid/$MgCl_2$ ratio should be investigated.
- How internal donor can reduce catalyst sensitivity should be studied for more detail.
- Steric hindrance effect of internal donor on hydrogen response should be investigated for more detail.
- Effect of hydrogen response on molecular weight in each catalyst system should be investigated further.

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APPENDIX

APPENDIX A

LIST OF PUBLICATIONS

A-1 Publications

- Thanyathorn Niyomthai, Aniroot Ratchadaphet, Bunjerd Jongsomjit and Piyasan Praserthdam, “Influence of hydrogen on catalytic properties of Ziegler-Natta catalysts prepared by different methods in ethylene polymerization”, Advances in Polymer Technology (2016), DOI 10.1002/adv.21753

- Thanyathorn Niyomthai, Aniroot Ratchadaphet, Bunjerd Jongsomjit and Piyasan Praserthdam, “A comparative study of $AlCl_3$ and $FeCl_2$-modified $TiCl_4$/$MgCl_2$/THF catalytic system in the presence of hydrogen for ethylene polymerization”, *International Journal of Polymer Science* (2016), 9.

A-2 Conference contributions

- Poster: Thanyathorn Niyomthai, Aniroot Ratchadaphet, Bunjerd Jongsomjit and Piyasan Praserthdam, Effect of hydrogen on Ziegler-Natta catalysts in ethylene polymerization, Asian Polyolefin Workshop 2015 with World Polyolefin Congress 2015, Tokyo, Japan, November 23-27, 2015.

VITA

Thanyathorn Niyomthai was born on September 24, 1990 in Bangkok, Thailand. In 2011, she completed the Bachelor’s Degree of Chemical Engineering with 1st class honor from the Department of Chemical Engineering, Faculty of Engineering, King Mongkutt’ s University of Technology Thonburi. Thereafter, she continued studying Doctoral Degree of Chemical Engineering at Chulalongkorn University and joined catalysis and catalytic reaction engineering research group under the supervision of Prof. Dr. Piyasan Praserthdam with the Royal Golden Jubilee program of Thailand Research Fund (TRF).