ผลของปริมาณไทเทเนียมต่อสมรรถนะของตัวเร่งปฏิกิริยาซีเกลอร์-นัตตา

นางสาวนิตยา สุดส่ง

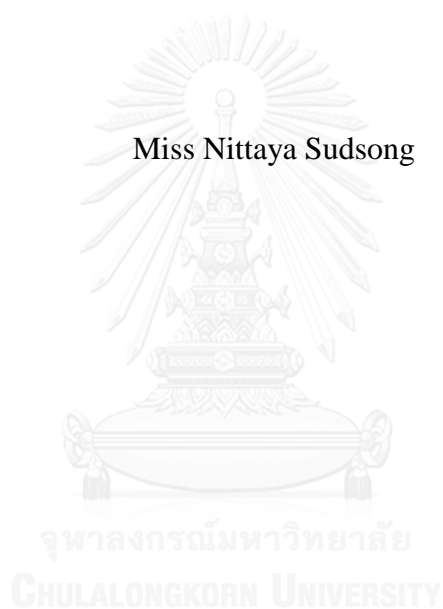วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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EFFECT OF TITANIUM CONTENT ON ZIEGLER-
NATTA CATALYST PERFORMANCE

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A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering Program in Chemical Engineering

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วิทยานิพนธ์ฉบับนี้ได้ศึกษาผลของปริมาณไทเทเนียมในตัวเร่งปฏิกิริยาซีเกลอร์-นัตตา ผ่านการกำจัดเบสลิวอิสในโครงสร้างของแมกนีเซียมคลอไรด์โดยใช้กรดลิวอิสชนิดต่างๆ ซึ่งเบสลิวอิสที่ได้ทำการศึกษาแบ่งเป็น 2 ชนิด ได้แก่ เอทานอลและเตตระไฮโดรฟูแรน สำหรับความว่องไวของตัวเร่งปฏิกิริยาได้ถูกทดสอบในปฏิกิริยาพอลิเมอร์ไรเซชันของเอทีลีน กรดลิวอิสที่เลือกใช้ในระบบที่มีเอทานอลเป็นเบสลิวอิส ได้แก่ ไดเอทธิลอลูมินัมคลอไรด์ (DEAC) เอทธิลอลูมินัมไดคลอไรด์ (EADC) และสารผสมของ DEAC/EADC จากผลการทดลองเมื่อเพิ่มปริมาณของ DEAC ในการกำจัดเอทานอล พบว่าปริมาณไทเทเนียมในตัวเร่งปฏิกิริยาเพิ่มขึ้น อย่างไรก็ตามความว่องไวสูงสุดของตัวเร่งปฏิกิริยาขึ้นอยู่กับปริมาณของ DEAC ที่เหมาะสม เมื่อพิจารณาเปรียบเทียบการใช้ DEAC และ EADC ในการกำจัดเอทานอล พบว่าตัวเร่งปฏิกิริยาที่ใช้ DEAC มีความว่องไวกว่าการใช้ EADC นอกจากนี้สารผสมของ DEAC/EADC ที่เหมาะสมยังทำให้ตัวเร่งปฏิกิริยามีความว่องไวที่สูง ทั้งนี้การกำจัดของเอทานอลด้วยสารเหล่านี้ทำให้ช่วยเพิ่มพื้นที่ผิวและลดความความเป็นผลึกของแมกนีเซียมคลอไรด์ ส่งผลให้เกิดปฏิกิริยาที่เหมาะสมระหว่างไทเทเนียมเตตระคลอไรด์และแมกนีเซียมคลอไรด์ จึงทำให้ตัวเร่งปฏิกิริยามีความว่องไวสูง สำหรับอีกระบบที่ใช้เตตระไฮโดรฟูแรนเป็นลิวอิสเบส ในระบบนี้กรดลิวอิสที่ถูกเลือกใช้ ได้แก่ อลูมิเนียมไตรคลอไรด์ แคลเซียมไดคลอไรด์ ไอรอนไดคลอไรด์ และซิงค์ไดคลอไรด์ ผลการทดลองพบว่าการสังเคราะห์ตัวเร่งปฏิกิริยาโดยใช้กรดลิวอิสผสมระหว่างอลูมิเนียมไตรคลอไรด์และไอรอนไดคลอไรด์ ทำให้ได้ตัวเร่งปฏิกิริยาที่มีความว่องไวสูงสุด เนื่องจากตัวเร่งปฏิกิริยานี้สามารถกำจัดเตตระไฮโดรฟูแรนออกจากโครงสร้างของแมกนีเซียมคลอไรด์ได้มากที่สุด ซึ่งผลนี้ถูกยืนยันจากการวิเคราะห์ของ XRD และ FT-IR อย่างไรก็ตามปริมาณไทเทเนียมในระบบนี้ไม่ได้เพิ่มขึ้นตามปริมาณการกำจัดของเตตระไฮโดรฟูแรนที่เพิ่มขึ้น

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NITTAYA SUDSONG: EFFECT OF TITANIUM CONTENT ON ZIEGLER-NATTA CATALYST PERFORMANCE. ADVISOR: PROF. PIYASAN PRASERTHDAM, Dr.Ing., 90 pp.

In this study, the effect of titanium content through using Lewis acid in the removal of Lewis base (EtOH and THF) in $MgCl_2$ structure was investigated. The catalytic activity of synthesized catalysts was tested in ethylene polymerization. For $MgCl_2$/EtOH system, the type of Lewis acid such as alkylaluminum chloride (DEAC, EADC and its mixture) was used. It was found that titanium content was increased with an increase of DEAC/$MgCl_2$ molar ratio. However, the suitable molar ratio of $MgCl_2$/DEAC exhibited the highest catalytic activity. In comparison between the use of DEAC and EADC, it was found that using of DEAC showed higher catalytic activity than the use of EADC. In addition, the suitable molar ratio of DEAC/EADC mixture also showed the high catalytic activity. The removal of ethanol using alkylaluminum chloride caused an increase in surface area and a decrease in the crystallinity of $MgCl_2$. This led to the suitable interaction of $TiCl_4$ and $MgCl_2$. For $MgCl_2$/THF system, the type of Lewis acid such as metal chloride ($AlCl_3$, $CaCl_2$, $FeCl_2$ and $ZnCl_2$) was selected. The results showed that the modification of $AlCl_3$ + $FeCl_2$ provided the highest activity because it had an efficiency to remove higher amount of THF, which can be confirmed by XRD and FT-IR. However, the titanium content was not increased by the removal of THF.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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CHAPTER I
INTRODUCTION

1.1 Introduction

The Ziegler-Natta (ZN) type catalyst was discovered in 1953 for production of polyethylene. After that, it is well known that ZN catalyst was used in industrial polymerization of olefins and there has been continuous research. The performance of the catalyst depends on the reaction between the catalytic active species and aluminum organic compound as co-catalyst to the formation of active site for polymerization with monomer [1, 2]. The ZN catalyst not only produced many new commercial polymers but also enhanced our basic knowledge of polymer properties and structures as well as polymerization processes.

Typical ZN catalyst is titanium tetrachloride supported on a magnesium dichloride ($TiCl_4/MgCl_2$). $MgCl_2$ has been almost invariably used for all the supported catalyst of practical interest, because it allows the realization of catalyst with the highest activity [3]. There are several preparation methods for ZN catalyst, such as ball milling, recrystallization, chemical reaction and alcohol adduct-based solution. Each method leads to the different nature of the active site, distribution of active site, shape or size distribution of the catalyst particle, etc. [4, 5]. It has been also found that the chemical treatment of $MgCl_2$ is more effective than the mechanical treatment [6, 7].

The treatment of α-$MgCl_2$ with a Lewis base such as esters, ethers, ketones and alcohols [8, 9] was called the adduct form. In the type of alcohol, ethanol is most extensively that react with $MgCl_2$ in order to the adduct formation ($MgCl_2 \cdot n$EtOH). It can increases the defects in the $MgCl_2$ support that leads to the suitable support structure for the ZN catalyst [10, 11]. Moreover, it can prevents the unsaturated Mg from re-aggregation [6]. In addition, introducing of ether such as THF in the form bound with the $MgCl_2$ support ($MgCl_2(THF)_n$) into a catalytic system yields a very stable and active titanium catalyst [12].

However, the remaining Lewis base in the final catalyst can be decrease in catalytic activity. In the case of $MgCl_2 \cdot n$ROH adducts, the remaining alcohol in

catalyst can react with $TiCl_4$ leading to produces titanium alkoxide which inactive to polymerization reaction [13, 14]. For in case of THF, the excess THF may have poisoned the catalyst sites too [15]. Therefore, the removal of the Lewis base in the adduct structure is very important to achieve the good final support and the high catalytic activity.

The removal of the Lewis base also makes the different amount of Ti content in final catalyst. However, all total number of Ti content found that some Ti species are not active (or dormant site) [16]. The preparation of catalyst containing high Ti content may leads to increase or decrease in the catalyst activity.

In this study, the ZN catalysts were synthesized in order to get different amount of Ti content. The various Lewis acids (such as DEAC, EADC, $AlCl_3$, $CaCl_2$, $FeCl_2$ and $ZnCl_2$) were used for the removal of Lewis bases (such as ethanol and THF). The effect of Ti content on catalysts was investigated on the catalytic activity for ethylene polymerization.

1.2 Objective

The objectives of this research are to study the effect of Lewis acid, both the molar ratio of Lewis acid/$MgCl_2$ and the various type of Lewis acid in the ZN catalyst system that consists of Lewis base (ethanol and THF). This is to obtain the different amount of loaded titanium and investigate the effect on the catalytic activity for ethylene polymerization.

1.3 Research scopes

1) $MgCl_2$ was selected as support of catalyst.

2) In $MgCl_2$/EtOH system, using of Lewis acids is DEAC and EADC, the polymerization of ethylene was carried out in a 2 L stainless steel reactor.

3) In $MgCl_2$/THF system, using of Lewis acids is $AlCl_3$, $CaCl_2$, $FeCl_2$ and $ZnCl_2$, the polymerization of ethylene was carried out in a 100 mL stainless steel autoclave reactor.

1.4 Research Methodology
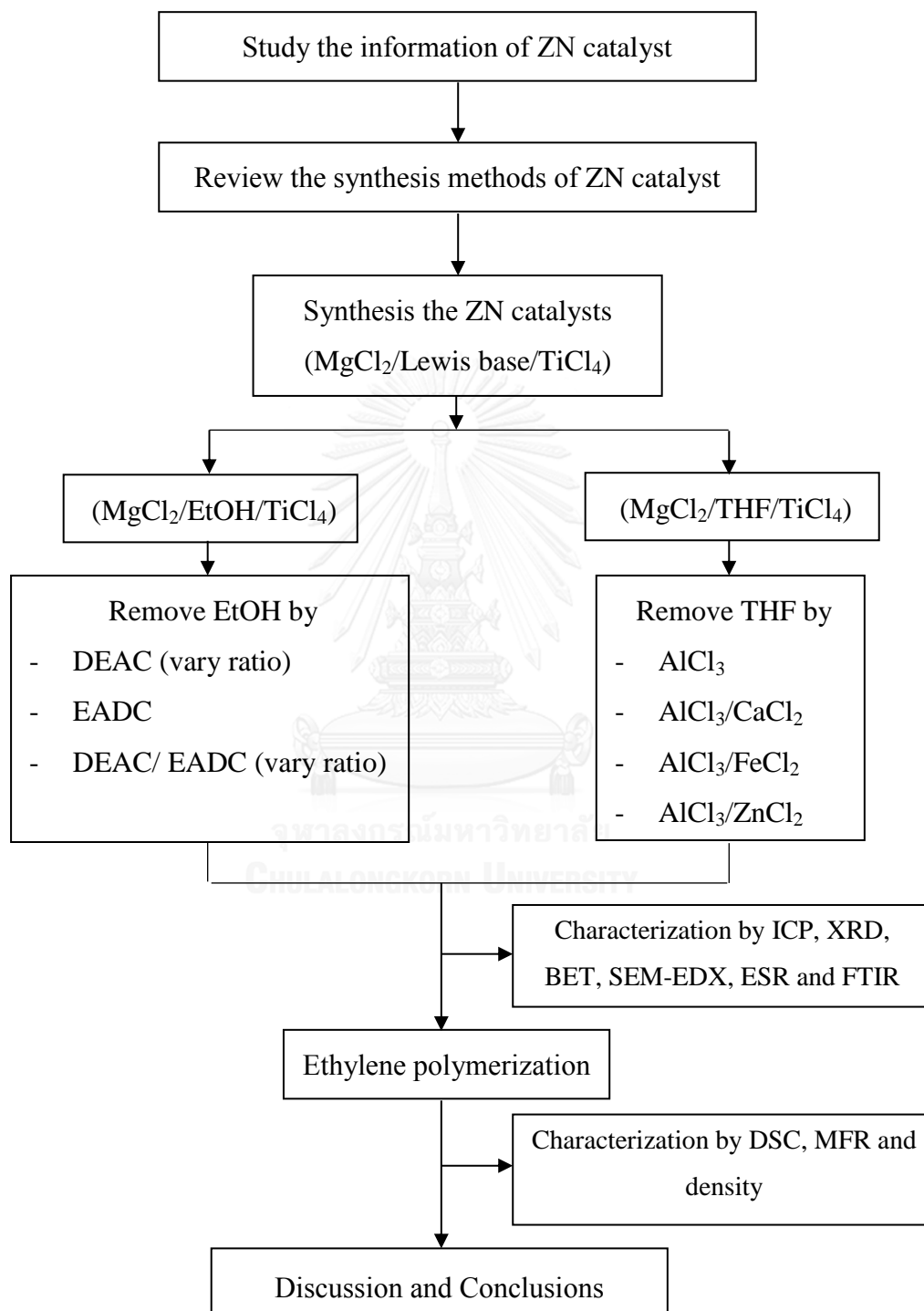
Figure 1.1 Flow diagram of research methodology for this work

CHAPTER II
THEORY AND LITERATURE REVIEWS

2.1 Introduction of Ziegler-Natta Catalyst

One the most important discoveries in polymer science and catalysis are polymerization of olefins using transition metal-based catalysts. In the early 1950s, Karl Ziegler (Germany) was the first to discover that transition metal halides such as $TiCl_4$, $TiCl_3$, $ZrCl_4$ and so on, in combination with aluminum organic compounds as co-catalysts convert ethylene to high molecular weight linear polyethylene. Later, Giulio Natta (Italy) independently discovered stereoregular polymers of α-olefins such as propylene, 1-butane and styrene. The monumental contributions of Karl Ziegler and Giulio Natta received universal recognition. In 1963, they were jointly awarded the Nobel Prize for chemistry in their discoveries of the polymerization catalysts named after them, Ziegler-Natta (ZN) catalyst.

The discoveries changed polymer chemistry forever, and provoked a worldwide research and development effort that terminated in many new commercial plastics and elastomers. The ZN catalyst became prominent in a special period in the history of polymer science, a period that not only produced many new commercial polymers but also enhanced our basic knowledge of polymer properties and structures as well as polymerization processes. [5, 17, 18]

It is well known that heterogeneous ZN catalyst has multiple active centers. It can produced the polyolefins with broad molecular-weight distribution (MWD) and broad chemical composition distribution (CCD) [16, 19, 20]. Polymers produced with ZN catalyst include many widely known commercial materials: high-density polyethylene (HDPE); linear low-density polyethylene (LLDPE); ethylene-based plastomers; crystalline isotactic polyolefins such as upolypropylene, poly(1-butene) and poly(4-methyl-1-pentene); crystalline syndiotactic polypropylene and polystyrene; ethylene-propylene elastomers; ethylene-cycloalkene engineering plastics, and synthetic rubbers based on polybutadiene and polyisoprene. [5]

The majority of transition metal ZN catalyst system consists of two components. The first component is a derivative of a transition metal such as titanium,

vanadium, zirconium, nickel, palladium, iron, cobalt, etc. For example, typical transition metal compound that was used in the early ZN catalyst and are still universally used for the manufacture of modern catalyst is $TiCl_4$, $TiCl_3$, VCl_4 and $VOCl_3$. The second components of the ZN catalyst system called co-catalyst such as organometallic compounds, mostly organoaluminum compounds. Typical organoaluminum co-catalysts are $Al(CH_3)_3$, $Al(C_2H_5)_3$, $Al(i-C_4H_9)_3$, $Al(C_2H_5)_2Cl$, $Al(i-C_4H_9)_2Cl$, $Al_2(C_2H_5)_3Cl_3$, etc.; and methylalumoxane, $[Al(CH_3)O]_n$. Neither of these two catalyst components, if used alone, can polymerize alkenes. However, when the two components of the catalyst systems are mixed, a series of chemical reactions takes place and some of the products of these reactions, called active centers, readily polymerize alkenes and dienes. [5]

The heterogeneous ZN catalyst, Mg-based support began to be explored around 1960s, several highly efficient catalysts for olefins polymerization were developed. There was studied by based on the reaction between transition metal halides (mostly $TiCl_4$) and Mg compounds such as $Mg(OH)_2$, $MgCl_2 \cdot 3Mg(OH)_2$ or $MgSO_4 \cdot 3Mg(OH)_2$, which was believed to lead to the formation of $Mg\text{-}O\text{-}TiCl_3$ bonds. But finally found that the most active catalysts were based on active $MgCl_2$ or on reactions that led to its formation such as the reaction between $TiCl_4$ and Mg alkoxides, Grignard compounds or Mg-alkyls. [21]

In the current, the heterogeneous ZN catalyst is based on titanium tetrachloride supported on magnesium dichloride ($TiCl_4/MgCl_2$) is very important. It has been widely studied and continuous developed for both the academic researches and the industrial production of polyolefins [6, 11, 22, 23].

2.2 $MgCl_2$-supported catalysts

Anhydrous $MgCl_2$ is known as the principal support precursor for ZN catalyst. It was discovered since 1975 that as the highly active support ZN catalyst for the production of polypropylene [21]. In 1986, Norio Kashiwa reported liquid $TiCl_4$ supported on $MgCl_2$ which provide the higher activities than solid $TiCl_3$ 100 times [3]. $MgCl_2$ is suitable support for $TiCl_4$ due to its crystal and electronic structure including a similarity of ionic radii of $MgCl_2$ and $TiCl_4$ (Mg^{2+} and Ti^{4+} have ionic radii as 0.68 and 0.65 Å, respectively [24]). The $MgCl_2$ not only make the catalyst is

highly active with low cost, but it also good control of polymer particle morphology [25-28]. In addition, the morphology of the catalyst can also affect the polymer morphology [29].

Soga and Shiono [27] reported the investigation of additive various metal chlorides (MCl_x) effects on both the propylene and ethylene polymerization using the homogeneous catalyst system. Combination of the catalyst and MCl_x exhibited stationary polymerization rates. The correlation between the stationary rate and the electron negativity (X_i) of the metal ion in MCl_x was showed in Figure 2.1. In general, the chlorides of metal ions with X_i smaller than that of Ti^{3+} (10.5) enhanced the polymerization rate, while chlorides of metal ions with X_i larger than 10.5 decreased the polymerization rate. The enhancement of polymerization rate by the metal chlorides is mainly caused by the electron donation from the metal chloride to the active transition metal (Ti^{3+}). They also reported the $MgCl_2$-supported catalyst system; show the highest activity for both propylene and ethylene polymerization.

In general, anhydrous $MgCl_2$ is in form of α-$MgCl_2$, has a rhombohedral structure with a close packed stacking of double chlorine layers with interstitial Mg^{2+} ions in six fold coordination as showed in Figure 2.2. The less crystalline β-$MgCl_2$ can be obtained by dehydration of $MgCl_2 \cdot 6H_2O$ with $SOCl_2$. The X-ray pattern of $MgCl_2$ was also showed in Figure 2.3, a strong peak (104) for d = 2.56 Å in form of α-$MgCl_2$ due to the cubic packing of the Cl atoms. For in form of β-$MgCl_2$ is less stable, has hexagonal close packed structure and a strong peak at d = 2.78 Å [21].
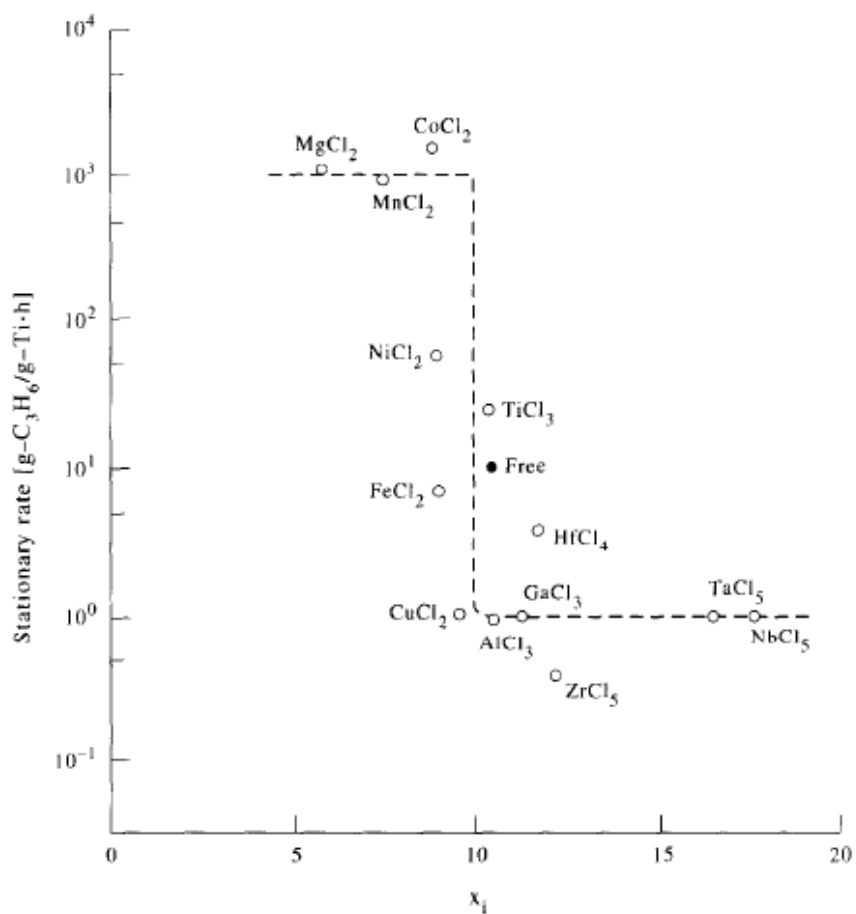
Figure 2.1 Relationship between stationary rate and electron negativity of the metal ion in metal chloride compound [27]
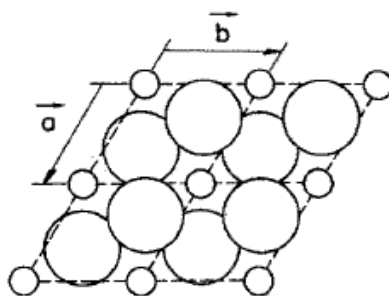
Figure 2.2 The form structure of α-MgCl$_2$ (Large spheres is chloride atoms) [21]
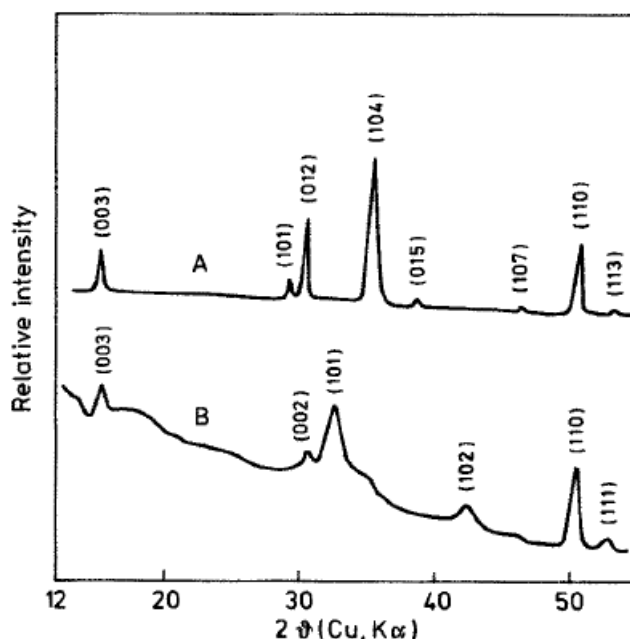
Figure 2.3 The XRD patterns of α-MgCl$_2$ (A) and β-MgCl$_2$ (B) [21]

However, the δ-MgCl$_2$ is form that active for preparation of ZN catalyst [21]. Figure 2.4 shows the XRD patterns of δ-MgCl$_2$ [30]. The dominant coordination in MgCl$_2$ supports are (104) and (110) surfaces, which five- and four-coordinate Mg cations, respectively. General, the XRD pattern of MgCl$_2$ has the peak at $2\theta = 15°$ corresponding to the Cl–Mg–Cl triple layers and reflections at $2\theta = 35°$ and $2\theta = 50°$ corresponding to (100 or 104) and (110) peaks, respectively. The Cl–Mg–Cl triple layers are bound via van der Waals forces thus can most easily cleave between adjacent Cl layers [31, 32]. Comparison between α-MgCl$_2$ and active δ-MgCl$_2$, the δ-MgCl$_2$ are characterized that (104) peak become the broad halo. The diffraction peak at $2\theta = 15°$ may be absent, indicating that the support has a single Cl–Mg–Cl structural layers (monolayers) [7].

Due to MgCl$_2$ has high crystallinity with low pore volume and surface area which poor interaction with TiCl$_4$ [33]. So, the anhydrous MgCl$_2$ need to have been improved to change α-MgCl$_2$ to active δ-MgCl$_2$ form together with improvement in its structure and morphology before the addition of TiCl$_4$ to obtaining a high dispersion of the active titanium species on the lower crystallinity and large surface of MgCl$_2$.

There are many methods of morphological improvement of $MgCl_2$ support for highly active ZN catalysts, both mechanical and chemical treatment such as ball-milling, chemical conversion of Mg compounds, recrystallization or $MgCl_2$-Lewis base adducts [13, 33-36] which in combination with other methods, for example; melt quenching, spray drying and spray cooling etc. [3, 29]. These methods can change α-$MgCl_2$ form into the active δ form of $MgCl_2$.
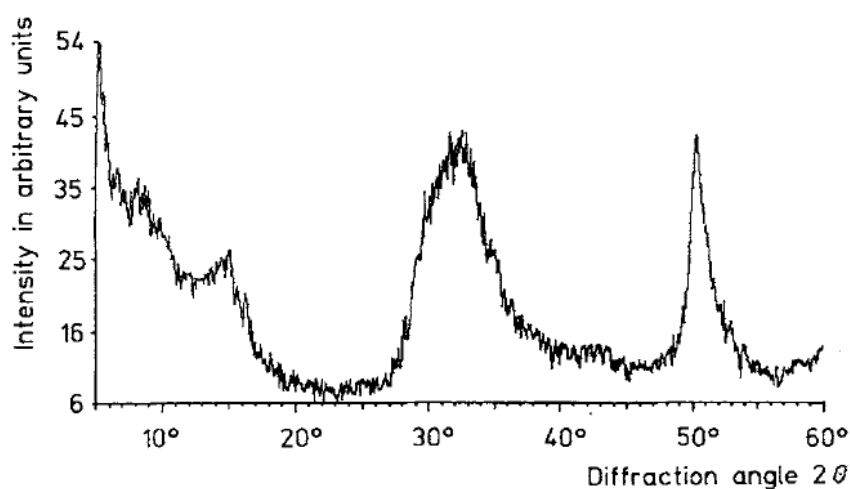
Figure 2.4 The XRD patterns of δ-$MgCl_2$ [30]

Ball-milling method

For the ball-milling method, results in a significant increase in the specific surface area and province the very small crystallites of the support. This process can be monitored by X-ray diffraction which shows a broadening of the some typical peaks [5]. Although the main advantage is obtaining small crystallites of $MgCl_2$ lead to introduce an amount of titanium species in its crystal lattice, the disadvantage of the ball-milling method is difficult to control the morphology of polymer. [13, 34, 37]

Chemical reaction method

Chemical reaction method can prepared from the reaction between $TiCl_4$ and magnesium alkoxides such as $Mg(OEt)_2$ show a very high activity for the polymerization of ethylene and propylene. Magnesium alkoxide compounds consist of crystals with layers of magnesium cations and alkoxy anions with loose layers of

alkyl chains of the alkoxy groups. Solvent can penetrate into these loose layers. These layers swell and the bonds are weakened. During the reaction with $TiCl_2$, hydrocarbon solvent are incorporated and a reaction with $TiCl_4$ takes place in this layer to form $MgCl_2$ and $TiCl_{4-n}(OEt)_n$ compounds. The in petrol suspended magnesium ethoxide is transformed into the $MgCl_2$ support and at the same time, $TiCl_4$ is absorbed. The soluble $TiCl_{4-n}(OEt)_n$ compounds are removed by washing with petrol. A catalyst particle with spherical shape, high porosity and high specific surface area is achieved. [38, 39]

Recrystallization method

The recrystallization method consists of a chemical activation by reaction of crystalline $MgCl_2$ with alcohol or ether to form adducts (such as $MgCl_2 \cdot nROH$ and $MgCl_2 \cdot THF$), followed by a controlled regeneration of the active support through recrystallization by removing the added compound (quick cooling, solvent evaporation, titanation or spray drying etc.). In consequence, the assemblies of spherically fined $MgCl_2$ crystallites with highly distort and high number of uncoordinated magnesium sites is produced. [38, 39]

These methods lead to catalysts which differ from each other in the nature of the active sites, spatial distribution of active sites, shape or size distribution of the catalyst particles, etc. Therefore the synthetic methods of ZN catalysts strongly affect the kinetic profiles and morphology development [4]. It has been also found that the chemical treatment of $MgCl_2$ is more effective than the mechanical treatment [6, 7].

Pokasermsong and Praserthdam [39] have prepared two different methods of ZN catalysts to comparison. The first catalyst was synthesized by forming the adduct of $MgCl_2 \cdot EtOH$ (recrystallization method) and the second catalyst was synthesized using $Mg(OEt)_2$ as the starting material for support (chemical reaction method). The results showed that the catalytic activity from chemical reaction was lower than recrystallization method because $Mg(OEt)_2$ was converted to $MgCl_2$ (confirmed by XRD and TGA), which transformed from alkyl group to Cl group. Thus probability of titanium was attached to support. And may be due catalyst reacted with cocatalyst to

form active site, which formed at the outer support (surface), titanium attached inner support was more than outer support, thus probability of formation to active site in chemical reaction was low led to lower activity than recrystallization method. Although, the specific surface areas and Ti content from chemical reaction was higher than recrystallization method.

Rojanotaikul et al. [3] studied the preparation of the $MgCl_2$-alcohol adduct with difference of alcohol (such as ethanol, *n*-propanol and *n*-butanol) using spray drying method. This method can produce the porous particles of support from droplets using heat transfer between hot gas and droplets. The results from the XRD pattern as shown in Figure 2.5, indicate that ethanol can destroy the most crystal structure of α-$MgCl_2$ which it is in contrast with propanol. The surface area and pore volume that increased in order of $MgCl_2$/EtOH > $MgCl_2$/BuOH > $MgCl_2$/PrOH > $MgCl_2$ which corresponding result to residual alcohol that decreased. The $MgCl_2$/EtOH can remove the alcohol by spray drying was the lowest because ethanol has the lowest boiling point, leaded to the highest surface area and pore volume. Whereas, the $MgCl_2$/PrOH can destroy the crystal structure of α-$MgCl_2$ that was very well. It was probably that propanol can attach within particle of $MgCl_2$.
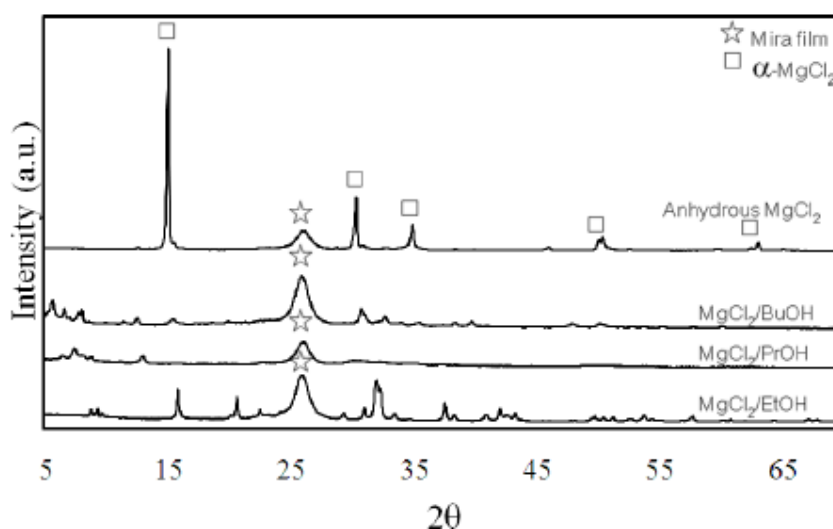
Figure 2.5 The results from the XRD pattern of α-$MgCl_2$
and $MgCl_2$-alcoholadduct [3]

Sozzani et al. [11] mentioned the method of preparing $MgCl_2$, supporting the titanium species, affects the catalytic properties markedly. Mechanical and chemical routes were pursued for the formation of "active" $MgCl_2$ loaded with the catalyst. In particular, the reaction of $MgCl_2$ with a Lewis base, typically an alcohol, treated with an excess of $TiCl_4$ can produce super active catalyst. The use of $MgCl_2$/EtOH adducts with a restricted range of compositions yields, after inserting the transition metal, a most efficient and selective catalytic system. The key point for the enhanced performances of the supported catalyst is the nature of the $MgCl_2$ precursors, obtained as complexes with Lewis bases, which undergo direct titanation. In fact, Lewis base/$MgCl_2$ ratios in the precursor determine, among other features, the activity and the isotacticity degree of the resulting polymer.

2.3 Preparation of Ziegler-Natta catalysts with MgCl₂-Lewis base Adducts

An adduct (come from the Latin *adductus*, "drawn toward") is the product of a direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components. The treatment of α-$MgCl_2$ with a Lewis base (such as esters, ethers, ketones and alcohols [8, 9]) was called the formation of adducts. The reaction between $MgCl_2$ and Lewis base can be represented as follows Reaction 2.1:

$$MgCl_2 + n\text{B} \ \leftrightarrow \ MgCl_2 \cdot n\text{B} \ ; \text{ where B is Lewis base} \tag{2.1}$$

For examples include the adducts such as $MgCl_2 \cdot 6CH_3OH$, $MgCl_2 \cdot 6C_2H_5OH$ and $MgCl_2 \cdot 4C_4H_8O$ are obtained by dissolution of $MgCl_2$ in methanol, ethanol or tetrahydrofuran (THF), respectively [29, 37].

The $MgCl_2$-Lewis base adduct as chemical treatment in order to improve of $MgCl_2$ crystal structure which leading to the active ZN catalysts for olefin polymerization [10, 12]. The $MgCl_2$-Lewis base adducts can prepare by recrystallization method [29, 33, 36, 37, 40] or melt quenching method [6, 14, 29] which could be useful for controlling the supported catalyst and polymer morphology.

The alcohols which react with $MgCl_2$ can give adducts of different stoichiometry, depending on the type of alcohol (the length of alkyl group) [13]. All

of the alcohol, ethanol is most extensively that react with $MgCl_2$ in order to the adduct formation ($MgCl_2 \cdot n$EtOH), it was believed that can increases defects in the $MgCl_2$ support lead to the formation of a very perfect crystal in the preparation of suitable support structures for the ZN catalyst [10, 11]. Moreover, it can prevents the re-aggregation of unsaturated Mg from [6]. In addition, introducing a ether such as THF in the form bound with the $MgCl_2$ support ($MgCl_2(THF)_2$) into a catalytic system yields a very stable and active titanium catalyst, applicable in ethylene polymerization [12].

2.3.1 MgCl₂-EtOH Adducts

The Mg ions interact with ethanol through the oxygen of ethanol [9]. The formation is $MgCl_2 \cdot n$EtOH that was believed to be formed according to Reaction 2.2 and Figure 2.6 [10].

$$MgCl_2 + nC_2H_5OH \rightarrow MgCl_2 \cdot nC_2H_5OH \tag{2.2}$$
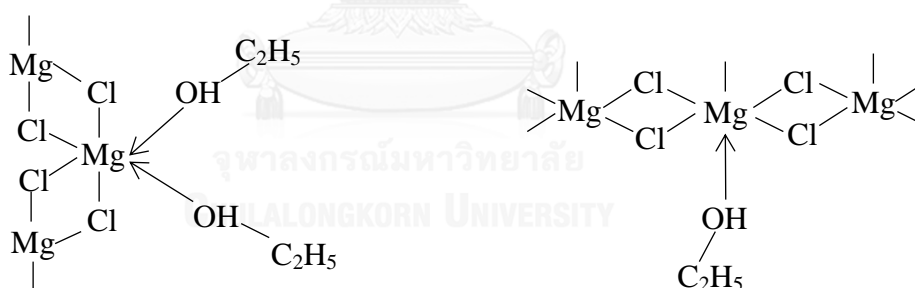
Figure 2.6 Proposed complexes of $MgCl_2$ and C_2H_5OH [10]

Reaction of akylaluminum with alcohol give the corresponding aluminum alkoxide [41]. For the reaction between $MgCl_2 \cdot n$EtOH and DEAC was proposed according to Reaction 2.3 and Figure 2.7.

$$MgCl_2 \cdot C_2H_5OH + C_4H_{10}AlCl \rightarrow MgCl_2 + C_6H_{15}OAl + HCl \tag{2.3}$$
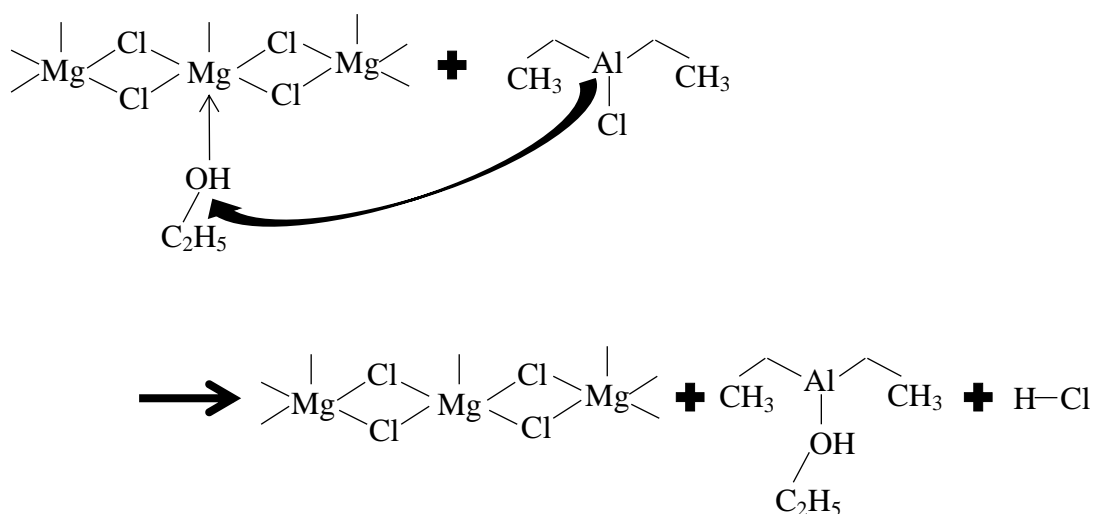
Figure 2.7 Proposed reaction between $MgCl_2 \cdot C_2H_5OH$ and $C_4H_{10}AlCl$ (DEAC)

An excess of $TiCl_4$ was added in order to of leads to $TiCl_4$ supported on $MgCl_2$. However, $TiCl_4$ is reduced to a lower valence state with remaining aluminum alkyl compound in catalyst (reduction from Ti^{4+} to Ti^{3+} or Ti^{2+}) [4]. For example, the reduction of $TiCl_4$ due to the large amount of DEAC shows in Reaction 2.4 [42].

$$(CH_3)_2AlCl + TiCl_4 \rightarrow CH_3TiCl_3 + CH_3AlCl_2 \tag{2.4}$$

In addition, the remaining alcohol in catalyst was also removed by $TiCl_4$. Forte and Coutinho [43] have been described reactions during the support titanation. The reaction between $TiCl_4$ and EtOH represented follow Reaction 2.5;

$$MgCl_2 \cdot EtOH + TiCl_4 \rightarrow MgCl_2 + EtOTiCl_3 + HCl \tag{2.5}$$

$$MgCl_2 + TiCl_4 \rightarrow MgCl_2 \cdot TiCl_4 \text{ (catalyst)} \tag{2.6}$$
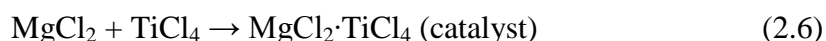
It is highly exothermic reaction, so the addition of $TiCl_4$ in during the catalyst preparation must be carried out at low temperature to prevent the above reaction. The by-product $EtOTiCl_3$ is soluble in hot $TiCl_4$, thus it is well removed from the catalyst by washing at high temperature. Finally, the obtained final catalyst as follow as Reaction 2.6.

2.3.2 MgCl₂-THF Adducts

The use of THF in catalyst synthesis is an important industrial route to prepare catalysts for the production of polyethylene. Grau et al. [44] reported that the nature of Ti species is modified by the interaction with $MgCl_2$ and THF to give Ti mononuclear species. the example of $MgCl_2 \cdot THF$ complex shows in Figure 2.8.
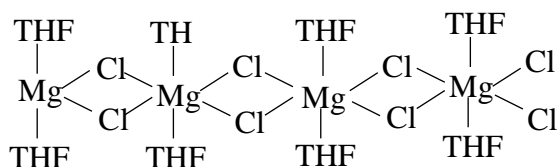
Figure 2.8 The example of $MgCl_2 \cdot THF$ complex [12]

Chang et al. [45] studied the THF in $TiCl_3(AA)/3MgCl_2/THF$ catalyst system. The XRD patterns showed in Figure 2.9, it was exhibited the anhydrous $MgCl_2$ and $TiCl_3(AA)$ structural transformation through the interactions with THF. The new peaks were believed to be complex of THF.

Table 2.1 shows the FT-IR spectra of pure THF had an asymmetrical and a symmetrical stretching bands at 912 cm^{-1} and 1071 cm^{-1} of C–O–C and also represents different kinds of complexes.
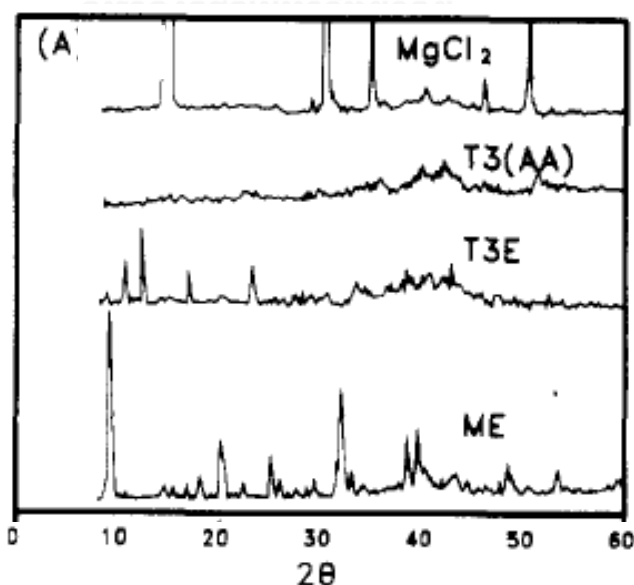
Figure 2.9 The XRD patterns of anhydrous $MgCl_2$, $TiCl_3(AA)$ (T3(AA)),
$TiCl_3(AA)/THF$ (T3E) and $MgCl_2/THF$ (ME) [45]

Table 2.1 FT-IR bands of different kinds of complexes [46]

Sample	Absorbance (cm^{-1})	
THF	1071	912
$TiCl_4/3MgCl_2/THF$	1027	876
$MgCl_2/THF$	1036	891
$TiCl_3(AA)/THF$	1010	854
$TiCl_3(AA)/3MgCl_2/THF$	1027	876
$TiCl_3/2.5MgCl_2(0.5MgEt)/THF$	1035	885
$TiCl_3/2.5MgCl_2(0.5MgEt)/THF(0.2)$	1032	880
$TiCl_3/2.5MgCl_2(0.5MgEt)/THF(0.4)$	1028	878
$TiCl_3/2.5MgCl_2(0.5MgEt)/THF(0.8)$	1027	876
$TiCl_3/2.5MgCl_2(0.5MgEt)/THF(1.2)$	1022/997	876

Ochezdzan-Siodłak and Nowakowska [47] studied the modification of the $MgCl_2(THF)_2$ with akylaluminium compound such as DEAC, MAO, TEA and TMA on heterogenisation of the metallocene catalyst (bis(cyclopentadienyl) zirconium(IV) dichloride; Cp_2ZrCl_2). It was found that the $MgCl_2(THF)_2$ support modified with $AlEt_2Cl$ gave the heterogeneous catalyst whereas modified by MAO, TEA and TMA gave the homogeneous zirconocene catalyst.

2.4 The removal of Lewis base

The suitable elimination of the Lewis base from adducts can provide a good support, affect the crystal structure leading to very active in the polymerization catalysis [6, 48]. However, the excess remaining Lewis base in the final catalyst can be decrease in catalytic activity. In the case of the $MgCl_2·nROH$ adducts, the remaining alcohol in catalyst can react with $TiCl_4$ (exothermic reaction) leading to produces titanium alkoxide which inactive to polymerization reaction [13, 14]. For in case of THF, the excess THF may have poisoned the catalyst sites too [15]. Therefore, the removal of the Lewis base in preparation of the support before the impregnation with $TiCl_4$ (active phase) is very important to achieve good final support and high

catalytic activity. In addition, the removal of Lewis base in adducts form is very important factor in control the size and shape of the catalyst particles, which the resulting on the morphology of polymer particles [43].

The removal of Lewis base has been used since 1980 [14]. There are many methods to remove of Lewis base from support particles both physical and chemical methods such as

a) heating under nitrogen flow [7]

b) evaporation with heating or no heating under vacuum [11, 13, 33]

c) treatment with alkyl aluminum or alkyl aluminum chloride [37, 40, 49]

d) treatment with metal halide such as $SiCl_4$, $ZnCl_2$ [13, 50, 51]

e) direct titanation with $TiCl_4$ [43, 52]

f) treatment by silanation [53, 54]

Jalali Dil et al. [14] prepared the spherical support using melt quenching method. Produced particles were dealcoholated using hot nitrogen flow. Three dealcoholated samples of different alcohol contents were used in the catalyst preparation. Results showed that by decrease in alcohol content of support particles, specific surface area, and pore volume of catalysts increased. Moreover, titanium content of final catalysts increased slightly. An increase in catalyst activity and enhancement of polypropylene powder morphology were observed as the alcohol content of support particles decreased.

Patthamasang et al. [55] studied the effect of $EtOH/MgCl_2$ molar ratios on the catalytic properties of ZN catalyst. The $[EtOH]/[MgCl_2]$ ratio is a very important parameter to control the morphology and catalyst performance for $MgCl_2$-supported catalysts. In this research, $MgCl_2$-supported catalysts and $MgCl_2$-SiO_2-supported catalysts were synthesized with various $MgCl_2 \cdot nEtOH$ adducts (n values ranging from 6 to 10). The catalytic activities for ethylene polymerization decreased markedly with increased molar ratios of $[EtOH]/[MgCl_2]$ for the $MgCl_2$-supported catalysts, while for the bi-supported catalysts, the activities only decreased slightly. For bi-supported catalysts was found that the optimized $[EtOH]/[MgCl_2]$ value for preparation of having high activity and good spherical morphology with little agglomerated $MgCl_2$

was 7. However, in the case of $MgCl_2$-supported catalysts, an excess amount of EtOH in the support could react with $TiCl_4$ and produce inactive species like titanium alkoxide. In contrast, the bi-supported catalysts showed the interesting result that the activity was relatively independent of the [EtOH]/$MgCl_2$] ratio. This indicates that the SiO_2 probably prevents the titanium active species from reacting further with ethanol. However, for the $MgCl_2$-SiO_2-supported catalyst, $MgCl_2$ can agglomerate on the SiO_2 surface at low [EtOH]/[$MgCl_2$] thus not being not suitable for $TiCl_4$ loading.

Park and Lee [33] studied the recrystallization of $MgCl_2$ by dissolved in ethanol with *n*-decane, ethanol was removed under vacuum drying and treating it with TEA before impregnation of $TiCl_4$. The XRD pattern was presented in Figure 2.10, Anhydrous $MgCl_2$ exhibited a cubic close packing structure giving strong reflection patterns at $2\theta = 35°$ (004 plane), $15°$ (003 plane) and $50°$ (110 plane). For $MgCl_2 \cdot 6C_2H_5OH$, at $35°$, $15°$ and $50°$ disappeared and showed of new shape and different strength appeared at new positions. The XRD pattern of $MgCl_2/TiCl_4$ showed no reflections, meaning that it does not form a crystal.
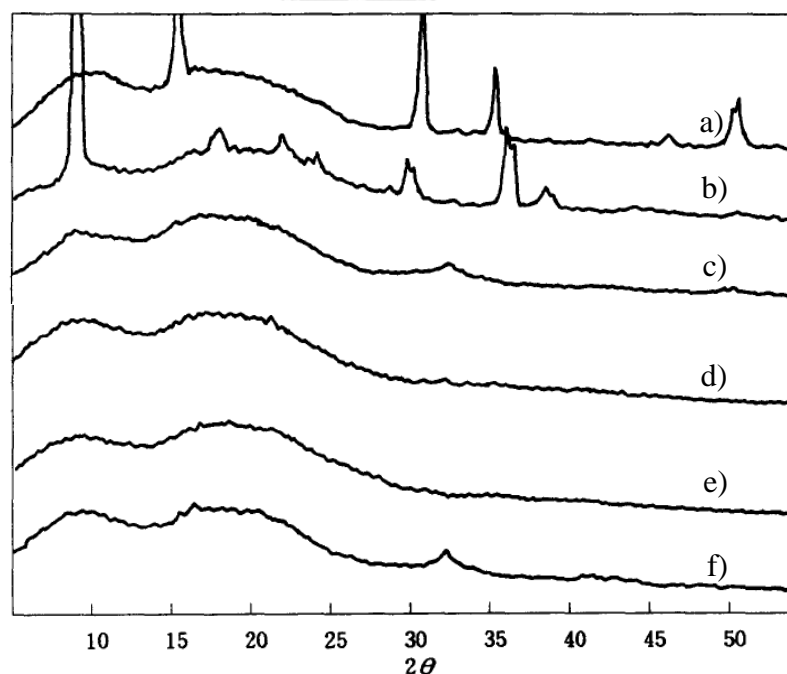
Figure 2.10 XRD Patterns of a) $MgCl_2$, b) $MgCl_2 \cdot 6C_2H_5OH$, c) $MgCl_2/TiCl_4$
d) $MgCl_2/TEA$, e) $MgCl_2/EB/TEA$ and f) $MgCl_2/EB/TEA/TiCl_4$
(EB is ethylbenzoate as an electron-donor)

Hadian et al. [6] studied the thermal dealcoholation in MgCl$_2\cdot$3.3EtOH adduct that was prepared by melt quenching method. Difference of obtained MgCl$_2\cdot n$EtOH support from different temperature and time in dealcoholation process was in the range of 2.1 – 3.3 molar ratios. The surface areas of MgCl$_2\cdot n$EtOH support by BET method showed a significant increase by the progression of the dealcoholation (in range of 7.4 – 12.8 m^2/g). The results of final catalysts were also showed the high surface area in range of 205 – 360 m^2/g. The performance of the catalyst was tested by propylene polymerization reaction. Figure 2.11 presented the relationship between Ti content (0.824 – 1.402 %wt) and the catalytic activity. It indicated that the activity was increased by increasing Ti content, but more increase in Ti showed lower activity. That means that Ti species were not all active in the polymerization reaction. So, the Ti content about 0.9 %wt gave the highest catalytic activity.
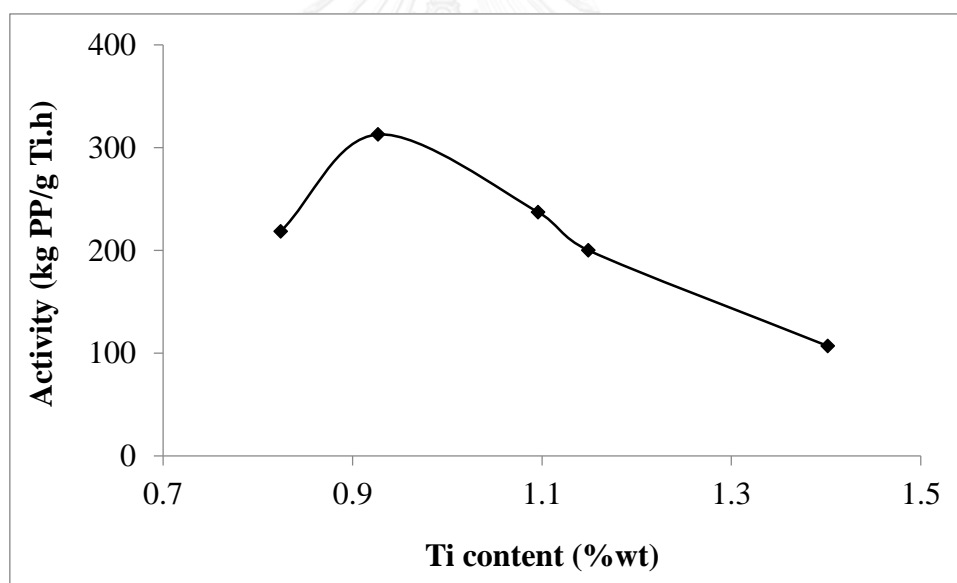
Figure 2.11 The relationship between Ti content and activity of catalysts prepared by thermal dealcoholation method [6]

Forte and Coutinho [43] studied the preparation of ZN catalyst form MgCl$_2\cdot n$EtOH adducts. The EtOH/MgCl$_2$ molar ratio for the support was varied in the range 0.4 – 1.7. The results of the surface area for prepared supports and catalysts were listed in Table 2.2. It was observed that the surface area of prepared support increased with decreasing in molar ratio of EtOH/MgCl$_2$. In contrast, after titanation

reaction at 120 °C in order to the catalyst, the surface area decreased with lower amount of ethanol in the support.

Table 2.2 The surface area for the preparation using different $MgCl_2 \cdot nEtOH$ molar ratio [43]

mol EtOH (support)	Surface area (m^2/g)	
	Support	Catalyst
1.7	9.2	249
1.5	9.1	221
1.0	11.5	66.5
0.4	36.3	66.5

Phiwkliang et al. [50, 51] studied the homo- and co-polymerization system using $TiCl_4/MgCl_2/THF$ catalysts modified with different metal halide additives ($ZnCl_2$, $SiCl_4$, and combined $ZnCl_2$-$SiCl_4$) were investigated. It was found that the catalyst modified with mixed $ZnCl_2$-$SiCl_4$ revealed the highest activities for both homo- and co-polymerization system. The increase in activities was due to the formation of acidic sites by modifying the catalysts with Lewis acids. And it can be observed the reduction in the peak intensity of $MgCl_2/THF$ complexes with Lewis acid compounds as proven by XRD techniques.

Almeida et al. [53] studied the different dealcoholation in the adduct $MgCl_2 \cdot nEtOH$. Both thermal treatment and chemical treatment (such as $TiCl_4$, TEA, dichlorodimethylsilane; $Cl_2(CH_3)_2Si$, and chlorotrimethylsilane; $Cl(CH_3)_3Si$) were used for dealcoholation. It was found that the different dealcoholation affect the specific area, pore volume, and size increase, and consequently on the increase of titanium content fixed on the surface of the crystal $MgCl_2$, as shown in Table 2.3. The treatment with $TiCl_4$ showed low activity due to reduction on texture properties led to low Ti content. Moreover, the titanium chloride alkoxides (inactive for polymerization) formed through reaction of $TiCl_4$ and ethanol in the adduct structure were not effectively removed during catalyst washing. The treatment with dichlorodimethylsilane also shows the low polymerization activity. It is possible that,

due to the presence of two chlorine atoms in the structure of dichlorodimethyl-silane, this becomes fixed in $MgCl_2$ surface defects in the form of diethoxysilane, filling positions where potentially active titanium could be fixed, which explains the decrease in activity of catalysts.

Table 2.3 The textural properties of support and Ti content on the catalyst and the catalytic activity [53]

Dealcoholation method	Surface area[a] (m^2/g)	Pore volume[a] (cm^3/g)	Ti content[b] (wt %)	Activity[b] (kgPE/(gTi.h.atm))
Thermal	17.6	0.1	8.0	0.6
$TiCl_4$	7.0	0.005	6.8	0.1
TEA	18.4	0.05	4.8	1.2
$Cl(CH_3)_3Si$	-	-	5.5	1.5
$Cl_2(CH_3)_2Si$	7.2	0.04	7.4	0.004
Thermal + $Cl_2(CH_3)_2Si$	20.2	0.1	6.5	0.006

[a] Support

[b] Catalyst

Chung et al. [34] studied the effect of the ethanol treatment in the $MgCl_2$ support by the recrystallization method. The $MgCl_2$ treatment performed with ethanol in an n-decane medium. Di-n-butyl phthalate (DNBP) was used as an internal electron donor. The $MgCl_2.EtOH$ was also treated with triethylaluminium (TEA) before impregnated with $TiCl_4$. They found that $MgCl_2.EtOH$ was treated with TEA led to change in an amorphous of support due to the removal of ethanol in the form of aluminum ethoxide. The result was also confirmed by data form surface area as shown in Table 2.4. This result can be seen that the ethanol content decreased after the treatment with TEA. Moreover, the impregnation with $TiCl_4$ also could remove ethanol in the form of titanium ethoxide (by reaction of ethanol with $TiCl_4$).

Table 2.4 Characterization of supports and catalysts (ethanol adduct) [34]

Sample	Surface area	Ethanol content
	m^2/g	wt %
$MgCl_2$/DNBP/EtOH	8.1	62.3
$MgCl_2$/DNBP/EtOH (30 mL)/TEA	101.5	19.7
$MgCl_2$/DNBP/EtOH (30 mL)/TEA/$TiCl_4$	112.6	5.57

In later year (1996), Choi et al. [35] studied the effect of different alcohols (such as ethanol, propanol) treatment in the $MgCl_2$ support by the recrystallization method which a similar method but without the treatment with TEA. The surface area of the catalyst showed in Table 2.5 that indicate the surface area of the catalyst was large when propanol-treated in the $MgCl_2$ support. The propanol-treated also showed a lower alcohol content and Ti content than the ethanol-treated catalyst. The propylene polymerization, the ethanol-treated catalyst shows the lower catalytic activity than the propanol-treated catalyst. It is likely that large amount of alcohol in ethanol-treated react much more with TEA (cocatalyst) in polymerization to form aluminium ethoxide.

Table 2.5 Characterization of supports and catalysts (ethanol and propanol adduct) [35]

Sample	Surface area	Alcohol content	Ti content
	m^2/g	wt %	wt %
$MgCl_2$/DNBP/EtOH/$TiCl_4$	122.53	13.9	13.6
$MgCl_2$/DNBP/PrOH/$TiCl_4$	182.24	9.3	12.1

Magalhaes et al. [37] studied the adduct of $MgCl_2$ with both methanol and ethanol. The $MgCl_2{\cdot}6MeOH$ and $MgCl_2{\cdot}6EtOH$ supports showed melting points by DSC of 118 °C and 76 °C, respectively. The IR spectrum of $MgCl_2{\cdot}6MeOH$ and $MgCl_2{\cdot}6EtOH$ supports showed in Table 2.6. The catalysts was prepared by treatment of adducts with $TiCl_4$ as single and double. It was found that Ti content in the obtained catalyst by double treatment with $TiCl_4$ had lower Ti contents than the obtained catalyst by single treatment. These results indicate that, in the second

treatment with TiCl$_4$, the catalyst surface was "cleaned" by removing some titanium derivatives soluble in TiCl$_4$. The result of ethylene polymerization also shown that, the second treatment with TiCl$_4$ had higher activities. This result indicates that the double treatment with TiCl$_4$ removed titanium derivatives which were inactive sites in ethylene polymerization. Moreover, the obtained catalyst from methanol adduct showed higher the catalytic activity than the obtained catalyst from ethanol adduct for propylene polymerization.

Table 2.6 The IR spectrum of MgCl$_2$·6MeOH and MgCl$_2$·6EtOH supports [37]

Stretching	Absorption bands (cm^{-1})	
	MgCl$_2$.6MeOH	**MgCl$_2$·6EtOH**
O--H stretching	3600 – 3100 cm^{-1}	3600 – 3000 cm^{-1}
C--H stretching	2950, 2850, 2780, 1410 cm^{-1}	2980, 2900, 1500 – 1300 cm^{-1}
C--O stretching	1 100 cm^{-1}	1100 cm^{-1}

Bosowska and Nowakowska [12] studied the catalytic activity in ethylene polymerization of TiCl$_4$ supported on a MgCl$_2$(THF)$_2$/Al(C$_2$H$_5$)$_2$Cl support which involving bimetallic Mg–Al complexes system by THF as the Lewis base. The catalytic activity was evaluated as well as its influence on the polymer properties (molecular weight and grain size distribution). The results also confirmed that the bimetallic system [MgCl$_2$(THF)$_2$/Al(C$_2$H5)$_2$Cl/TiCl$_4$] showed very active than monometallic system [MgCl$_2$(THF)$_2$/TiCl$_4$], while the stability is similar.

Parada et al. [13] prepared the adduct of MgCl$_2$ in 1-hexanol/isooctane by recrystallization method through different dealcoholation techniques such as evaporation of the solvent, cooling, precipitation with silicon tetrachloride (SiCl$_4$) and precipitation with TiCl$_4$. The FT-IR spectra of each catalyst as shown in Figure 2.12, they showed bands around at 3500 cm^{-1} corresponding to the OH group and a strong peak at 1065 cm^{-1} corresponding to C–O of titanium chloride alkoxide. It was also observed that disappearance the band of OH group in dealcoholation of catalyst by precipitation with SiCl$_4$. (For dealcoholation by TiCl$_4$ not was showed the IR spectra that it was similar the dealcoholation by evaporation and cooling.) The amount of Ti

content and catalytic activity also increased in order of the higher degrees of dealcoholation. In the case of the amount of alcohol present is greater led to lower catalytic activity due to the reaction between $TiCl_4$ with alcohol and the formation of $Cl_3Ti-O(1-hexyl)$, that is inactive for polymerization.
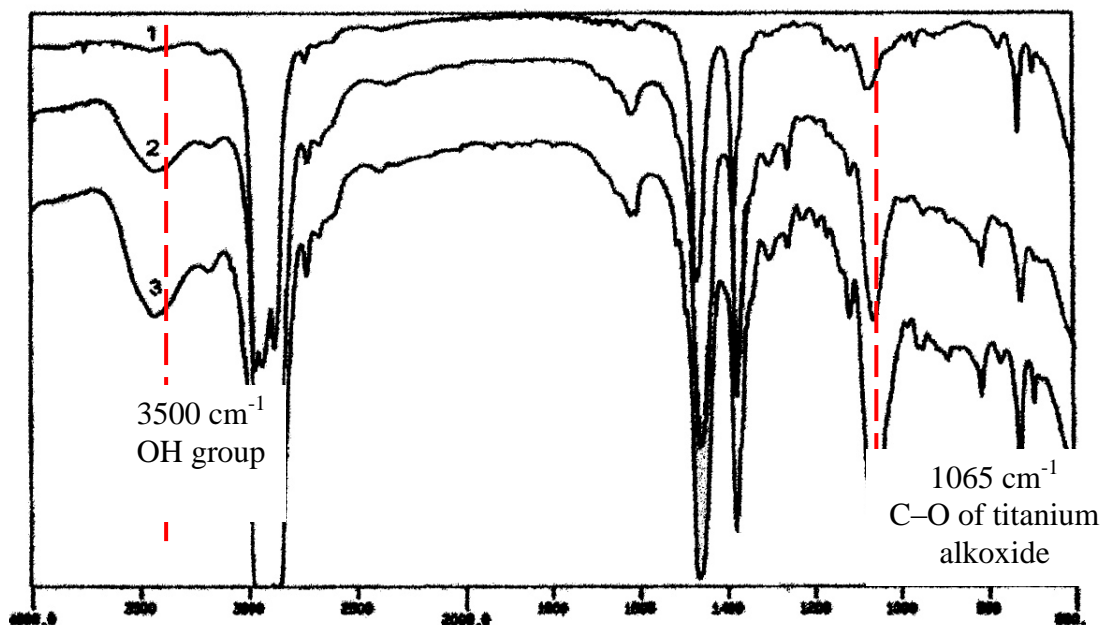
Figure 2.12 The FT-IR spectra of catalyst in dealcoholation by 1) precipitation with SiCl₄, 2) evaporation of the solvent and 3) cooling [13]

Jamjah et al. [29] studied the $MgCl_2 \cdot nEtOH$ that was prepared by melt quenching method and was remove of EtOH by heating increases the surface area of the support. Effect of molar ratio of $[EtOH]/[MgCl_2] = 2.8 - 3.0$ were studied. Treatment of the support with excess $TiCl_4$ increased its surface area from 13.1 to 184.4 m^2/g, as shown in Table 2.7. The best adduct of spherical morphology was obtained that is $[EtOH]/[MgCl_2] = 2.9$.

Table 2.7 The surface area of the $MgCl_2 \cdot nEtOH$ adduct, support and catalysts [29]

Sample	Surface area (m^2/g)
$MgCl_2 \cdot nEtOH$	2.7
Support[a]	13.1
Catalyst ($TiCl_4/MgCl_2$)	184.4

[a]Support is dealcoholated $MgCl_2 \cdot nEtOH$ using heating

2.5 Polymerization reactions

The polymerization reaction [5] consists of the formation of active center, initial reaction, chain propagation reaction and chain termination reaction. The active centers in the catalysts are formed in reactions between M–X bonds in catalyst precursors (X is usually Cl, M is Ti or V) and the Al–R´ bond in a cocatalyst. The reaction produces the M–R´ group, as shown in Reaction 2.7.

$$[M]–Cl + Al\,R_3´ \rightarrow [M]–R´ + Al\,R_2´Cl \tag{2.7}$$
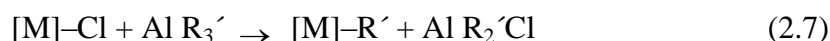
Arlman and Cossee explained how active sites are formed at the surface of $TiCl_3$ crystal by the reaction with alkyl aluminum compounds. Each titanium cation is surrounded octahedrally by six chlorine anions. At the surface, titanium centers and chlorine anions are exposed, and thus accessible to other components. One chlorine ion is exposed in such a way that it can react with alkyl aluminum compounds and be replaced by an alkyl group.

The growth of a polymer chain with any transition metal catalyst occurs via the insertion reaction of the C=C bond of an alkene molecule CH_2=CH–R into the transition M–C bond of an active center (Reaction (2.8)). This reaction is called the chain growth reaction (chain propagation reaction). In each insertion step of the activated complexed monomer into the Ti–C bond, a new Ti–C bond is formed, and the vacant site is regenerated for complexation of the next monomer molecule as shown in Figure 2.13.

$$[M]–R´ + nCH_2=CH–R \rightarrow [M]–(CH_2–CHR)_n–R´ \tag{2.8}$$
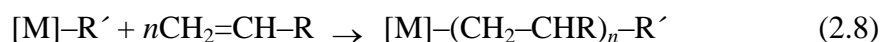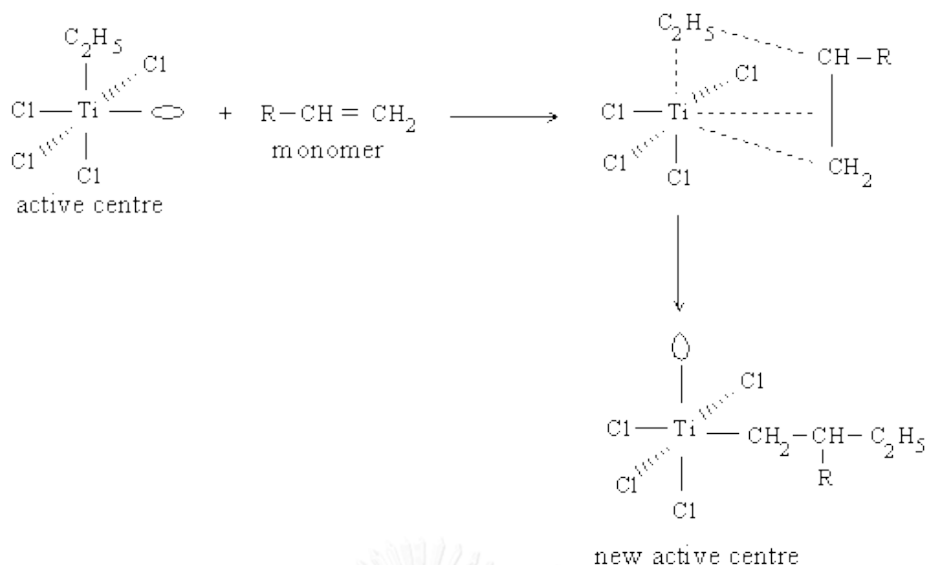
Figure 2.13 The polymerization reaction between active center and monomer for ZN catalyst [56]

The chain growth reaction usually occurs many thousands times before any other reaction intervenes. Very infrequently, an alkene molecule reacts with a growing polymer chain in a different way compared to that in Reaction (2.8).

$$[M]–(CH_2–CHR)_n–R´ + CH_2=CH–R \rightarrow [M]–CH_2–CH_2–R +$$
$$CH_2=CR–(CH_2–CHR)_{n-1}–R´ \qquad (2.9)$$
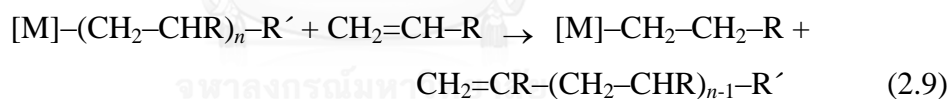
This reaction is called the chain transfer reaction to a monomer. Reaction (2.9) results in disengagement of the polymer chain from the active center, but the active center remains intact; it contains a short alkyl group $CH_2–CH_2–R$ attached to the transition metal atom and it retains ability to insert double bonds of alkene molecules in Reaction (2.8) and to grow a new polymer chain. A special agent (nearly always, hydrogen) is usually added to polymerization reactions with ZN catalysts. It hydrogenates the M–C bond in the growing polymer chain.

$$[M]–(CH_2–CHR)_n–R + H_2 \rightarrow [M]–H + CH_3–CHR–(CH_2–CHR)_{n-1}–R \quad (2.10)$$
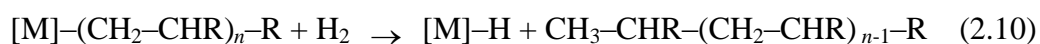
Reaction (2.10) is called the chain transfer reaction to hydrogen. The center with the M–H bond remains active; it also can insert double bonds of alkene molecules, similarly to Reaction (2.8). Reaction (2.10) proceeds with a much higher rate than Reaction (2.9), and the molecular weight of polymers produced in the presence of hydrogen is always much lower. It also has the b-hydride elimination which leads to removal of the polymer chain from the active center along with the formation of a vinyl group at the chain end.

Kissin [57] have studied on the formation rates of active centers (C^*) in polymerization reactions of ethylene with solid Ti-based ZN catalysts (γ and δ forms of $TiCl_3$, $TiCl_2$). The catalytic conversion of ethylene into a polymer $(CH_2=CH_2)_n$ This reaction can be presented as Reaction (2.11).

$$C^* + nCH_2=CH_2 \overset{k_p}{\rightarrow} \text{Polymer } (CH_2–CH_2)_n + C^* \qquad (2.11)$$

The consumption rate of ethylene and the accumulation rate of polyethylene in Reaction (2.5) are both proportional to $[C^*]$ as Reaction (2.12).

$$\text{Polymerization rate (R)} \approx k_p[C^*][CH_2=CH_2] \qquad (2.12)$$

where k_p is in L/mol min, $[C^*]$ is in mol/g catalyst, $[CH_2=CH_2]$ is in mol/L, and R is in mol(ethylene)/(g catalyst·min). Effects of the factors on the center formation in ethylene polymerization reactions are discussed. The C^* formation rate strongly depends on temperature but does not depend on the concentration of the free monomer and depend on the concentration of the $Al(C_2H_5)_3$ cocatalyst. Even a small amount of ethylene is sufficient to convert Ti species on the catalyst surface into C^*. Introduction of H_2 into reactions significantly accelerates the C^* formation stage independently of the catalyst type. Introduction of 1-alkenes into reactions significantly accelerates the C^* formation rate only if the 1-alkenes can copolymerize with ethylene. And C^* formation rates with various solid and supported catalysts based on different Ti^{4+} and Ti^{3+} species are quite similar, which suggests that the nature of immediate precursors to the active centers is similar. However, the C^* formation rates are noticeably higher when the catalysts are derived from Ti^{2+} species

2.6 Polyethylene

The type of catalyst are known and used for production of polyethylene (PE) such as Phillips catalyst, ZN catalyst and metallocene catalyst. Each catalyst can produce PE with difference of MWD, for Phillips CrO_x/SiO_2 catalyst is in ultra-broad range of 10 – 30, ZN catalyst is in medium range of 3 – 6 and metallocene catalyst is a narrow MWD that is less than 3. The broader MWD of polymer induces greater flow ability in the molten state at higher shear rate, which is the most important factor for processability in the blowing and extrusion techniques. Phillips catalyst can produce PE with the highest broad MWD show good processability but the existence of residual toxic Cr species. For the operation of metallocene, its disadvantage is high cost and poor processibility for PE. Thus, ZN catalyst is still the main industrial catalysts for production of PE [23, 58].

Generally, the most simple of polymer is polyethylene. It consists of several repeated-CH_2-cell connections by polymerization process as shown in Figure 2.14. Polyethylene is classified into several types. It depends on its density and molecular structure. The polyethylene properties depend on condition such as temperature, pressure and catalyst type during polymerization. These conditions affect polyethylene shape because it can promote and break the chains of molecular branching. Thus, prepared polyethylene using different condition is main factor to produce various polyethylene types. Because of several types, Polyethylene is widely applied in many products. The products which are produced from polyethylene are trash bag packaging, containers, toys and various house wares.
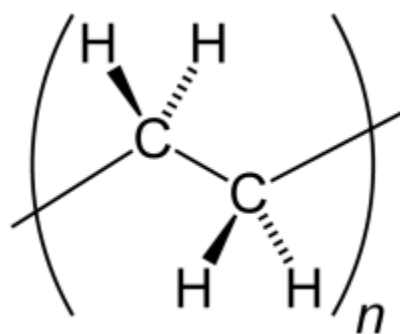
Figure 2.14 Repeating units of polyethylene [17]

In 1937, The Society of the Plastics Industry (SPI) can separate three main types of polyethylene based on density:

- Low density: $0.910 - 0.925$ g/cm^3
- Medium density: $0.926 - 0.940$ g/cm^3
- High density: $0.941 - 0.965$ g/cm^3

After that the American Society for Testing and Materials (ASTM) has also identified more several types of polyethylene than SPI, but also based on density as well. Polyethylene types which are classified by ASTM are shown in Table 2.8.

Table 2.8 Density of polymer classification

Polymer types	Density (g/cm^3)
High density polyethylene (HDPE)	> 0.941
Linear medium density polyethylene (LMDPE)	$0.926 - 0.940$
Medium density polyethylene (MDPE)	$0.926 - 0.940$
Linear low density polyethylene (LLDPE)	$0.919 - 0.925$
Low density polyethylene (LDPE)	$0.910 - 0.925$

LDPE is produced under high temperature and pressure. Its density range can be defined in $0.910 - 0.940$ g/cm^3. LDPE highly consists of short and long chain branching. For this reason, the chains of LDPE are not press closely. Thus its structure is amorphous. The important properties of LDPE are lightweight, good impact resistance, extremely flexible, easily cleaned, thermoforming performance, no moisture absorption, chemical- and corrosion-resistant. From the properties of LDPE, it can be produced in many products such as corrosion-resistant work surfaces, plastic wrap, various containers, and parts of computer hard.

Products which are produced from the polymerization at low temperature under low pressure are called High-density polyethylene (HDPE). HDPE cannot be produced by free radical polymerization. The structure of high-density polyethylene types consists of dense short branches, giving its stronger intermolecular forces, tensile strength and more linear than LDPE, but less flexible than LDPE. Nevertheless, due to the high crystalline structure, HDPE cannot match the clarity of

LDPE or LLDPE film. The applications of HDPE are bottles for bleach, shampoo, detergent, extruded pipe for potable water and gas distribution, etc.

LLDPE is polyethylene which was produced from 1-butene, 1-hexene, and 1-octene as comonomers. Therefore, LLDPE consists of short chain branches of ethyl, n-butyl, and n-hexyl groups. Density if this polymer is shown in $0.915 - 0.930$ g/cm^3. LLDPE has developed and improve properties. They are employed as a film in the packaging industry. Nevertheless, the produced film from LLDPE is not as clear as from LDPE because of the lower amorphous content and heterogeneous composition distribution.

2.7 Ti Oxidation State

Because the oxidation state of the transition metal of the active center significantly affects the structure of that center, much work has been done to establish its value for different ZN catalysts. It is, however, important to distinguish between the measured average oxidation state of the whole catalyst and the oxidation state or states of the individual centers. The first can usually be determined easily, but a direct assignment of oxidation state of the active centers is more difficult. First of all, the fraction of the total transition metal atoms that are active centers is small, about 1% or less. Suggestions that traces of the transition metal in an unmeasured oxidation state actually form the active centers in some catalysts cannot be lightly dismissed. [38]

The key concept of this study is to assume the variation in the oxidation state of the titanium species, depending upon the reactivity of the alkylaluminium used in the catalyst system. The determination of the Ti^{n+} species on the TiCl$_4$/MgCl$_2$ systems can carry out after contact it with cocatalyst by various methods such as potentiometric, polarographic or EPR or ESR methods and redox titration [59]. Fregonese et al. determined the Ti^{3+} and Ti^{2+} species by redox titration, while Ti^{4+} was calculated by difference, the total titanium amount being known [59]. XPS was applied to analyze the oxidation state and distribution of the titanium species on the supported catalysts [60, 61]. Garoff et al. [62] also determined of Ti^{4+} and Ti^{3+} by titration method. Moreover, The Ti Oxidation state also can formed by different types of Ti^{3+} species (isolates and clusters) as well as Ti^{2+} species in the catalysts [63]. However, the ESR technique is widely used to study Ti^{3+} species in the catalysts [63,

64]. The results from ESR technique are associated with a g value which depending on the type of Ti^{3+} species.

It is well known that the reduction of $TiCl_4$ to Ti^{3+} and Ti^{2+} by reacting with alkylaluminum or cacatalyst. Ti^{3+} and Ti^{2+} species are active for ethylene polymerization while only Ti^{3+} species are active for propylene and other olefin polymerization [64]. However, titanium dichloride is also active in ethylene polymerization without organoaluminum cocatalyst [63]. In the experiments of Tregubov et el. [63], it were tested in the polymerization of ethylene using $[\eta^6\text{-}$BenzeneTiAl$_2$Cl$_8$]/MgCl$_2$ catalyst system that comprise the only isolated Ti^{2+} species, indicated that this catalyst showed high activity by absence of organoaluminum cocatalyst. However, when $[\eta^6\text{-}BenzeneTiAl_2Cl_8]/MgCl_2$ catalyst was treated with chloropentafluorobenzene (it became isolated Ti^{3+} species which was determined by ESR), is completely inactive in ethylene polymerization without cocatalyst.
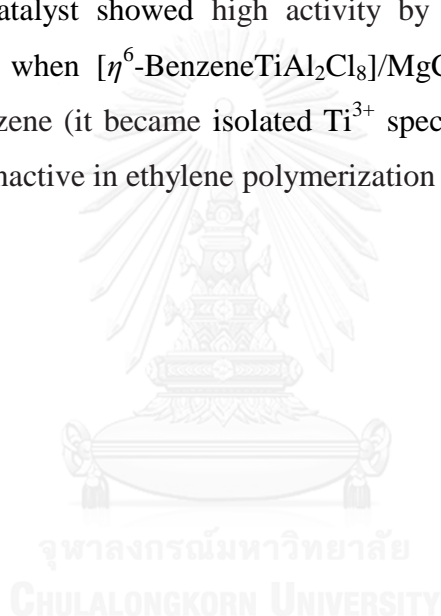
CHAPTER III
EXPERIMENTAL

In experimental chapter comprise of chemicals, preparation of catalyst, ethylene polymerization and characterization techniques.

3.1 Chemicals

1. Ethylene (C_2H_4) was purchased from Thai Industrial Gas Co., Ltd.

2. *n*-Hexane (C_6H_{14})was used as solvent, supplied from Thai Polyethylene Co., Ltd., dehydrated with molecular sieves 3Å and stored under nitrogen atmosphere. Some was purified by distillation and refluxing over sodium metal and benzophenone as an indicator.

3. Titanium tetrachloride ($TiCl_4$) was supplied from Thai Polyethylene Co., Ltd. and purchased from Merck Ltd.

4. Anhydrous magnesium chloride ($MgCl_2$) was used as support, supplied from Thai Polyethylene Co., Ltd.

5. Diethylaluminum chloride ((C_2H_5)$_2$AlCl or DEAC) was supplied from Thai Polyethylene Co., Ltd.

6. Ethylaluminum dichloride ($C_2H_5AlCl_2$ or EADC) was supplied from Thai Polyethylene Co., Ltd.

7. Ethanol (C_2H_5OH or EtOH) was dehydrated with molecular sieves 3Å

8. Triethylaluminum ((C_2H_5)$_3$Al or TEA) was used as a cocatalyst, supplied from Thai Polyethylene Co., Ltd.

9. Hydrochloric acid (HCl) was purchased Roongsub Chemical Ltd., Part**.**

10. Methanol (CH_3OH or MeOH) was purchased Roongsub Chemical Ltd., Part**.**

11. Ultra-high purity nitrogen (N_2) and argon (Ar) (99.999%) were purchased from Thai Industrial Gas Co., Ltd.

12. Anhydrous aluminium trichloride ($AlCl_3$), calcium dichloride ($CaCl_2$), iron dichloride ($FeCl_2$) and zinc dichloride ($ZnCl_2$) were purchased from Sigma-Aldrich Inc.

13. Tetrahydrofuran (THF) was purchased from Sigma-Aldrich Inc.

Because of the sensitivity of the ZN catalyst system to air and moisture, all the operations were carried out under an inert atmosphere of nitrogen (standard Schlenk techniques) and argon (glove box).

3.2 Preparation of catalyst

3.2.1 $TiCl_4$/$MgCl_2$/EtOH

The catalyst was prepared according Mitsui Petrochemical Industries Ltd. [65]. As shown in Figure 3.1, 1 or 2 g of anhydrous $MgCl_2$ was added in a four-necked of 500 mL round bottom flask equipped with a magnetic stirrer. Then, 150 mL of n-hexane was added into the flask as a medium reagent. After, dried ethanol with the molar ratio of EtOH/$MgCl_2$ as 6 was added dropwise into the flask and stirred for 2 h. DEAC or EADC or DEAC/EADC mixture was added dropwise into the flask under stirring and constantly stirred for 2 h. Finally, the desired amount of $TiCl_4$ was injected dropwise into the flask. The reaction was controlled at 20 °C. After injecting of $TiCl_4$, the temperature was gradually increased to 80 °C within 2 h and then holds at this temperature for 2 h. The mixture was refluxed under nitrogen atmosphere and stirred. After the reaction was cooled to room temperature, the solid was washed 7 times with 100 mL of n-hexane. The obtained suspension catalyst was transferred to storage bottle and stored under argon atmosphere in glove box.
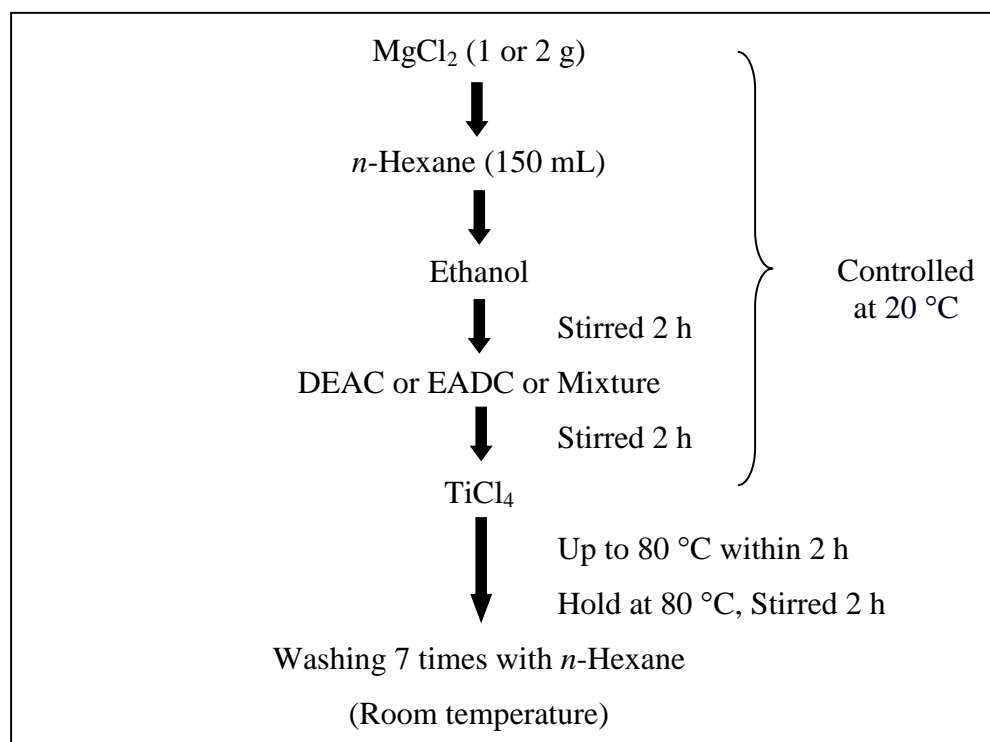
Figure 3.1 Preparation of TiCl$_4$/MgCl$_2$/EtOH catalytic system

3.2.2 TiCl$_4$/MgCl$_2$/THF

The catalyst of type TiCl$_4$/MgCl$_2$/THF/AlCl$_3$ + MxCl$_2$ (Mx is Ca, Fe and Zn) was prepared via a chemical route using MgCl$_2$ as a support precursor according to a procedure that was previously published [50] and showed in Figure 3.2. 2 g of anhydrous MgCl$_2$ was added in a four-necked 500 mL round bottom flask equipped with a magnetic stirrer. Then, 150 mL of THF was added into the flask. Later, AlCl$_3$ and MxCl$_2$ (molar ratio of AlCl$_3$/MgCl$_2$ and MxCl$_2$/MgCl$_2$ is equal to 0.063) were added. After that, 2 mL of TiCl$_4$ was injected dropwise into the flask under continuous stirring. The temperature was gradually increased to 68 °C and held at this temperature for 3 h. After the reaction mixture was cooled to 40 °C, the solid part was filtered and washed with 100 mL of n-hexane for 6 times. Finally, the catalyst obtained was dried under a vacuum at room temperature and catalyst powder was stored under argon atmosphere in a glove box.

MgCl$_2$ (2 g)

↓

THF (150 mL)

↓

MxCl$_2$/AlCl$_3$

↓

TiCl$_4$

↓ Heating 68 °C, Stirred 3 h

Washing 6 times with *n*-Hexane
(40 °C)
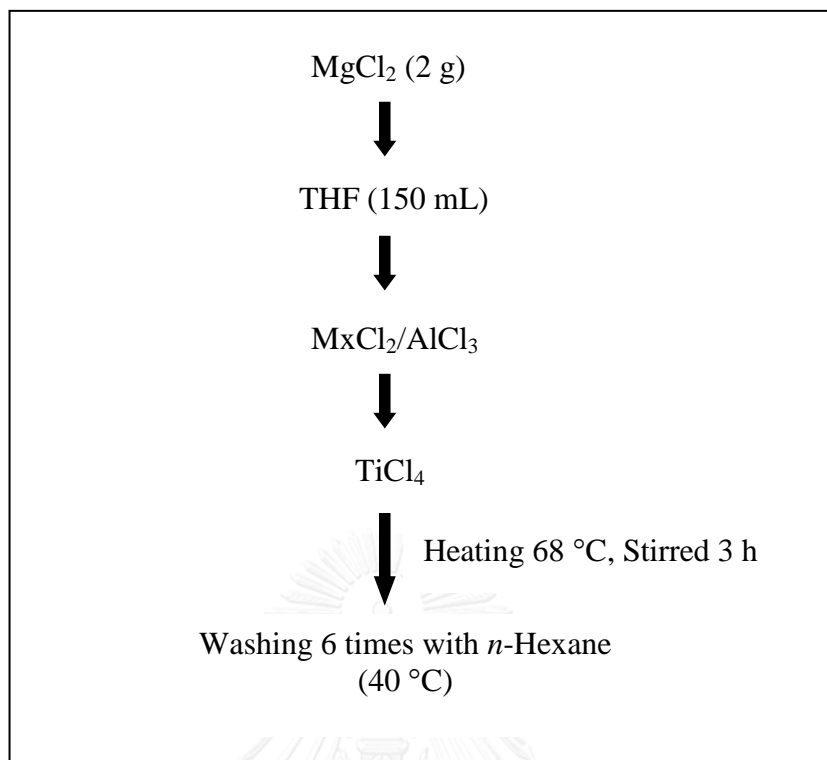
Figure 3.2 Preparation of TiCl$_4$/MgCl$_2$/THF catalytic system

3.3 Ethylene polymerization

3.3.1 Reactor 1: 2 L Reactor

For $TiCl_4/MgCl_2/EtOH$ catalytic system, the ethylene polymerization was carried out in a 2 L BuchiGlasUster stainless steel reactor fitted with a thermocouple and a mechanical stirrer (speed of 350 rpm). At 70 °C, the reactor was evacuated for 20 min and purged with nitrogen gas for 1 h. After that, reactor was cooled to room temperature. Then 1 L of *n*-haxane was fed into the reactor. TEA cocatalyst and the catalyst suspension were injected to the reactor by a syringe at room temperature, which the molar ratio of Al/Ti as 100. Hydrogen was used as a chain transfer agent to control molecular weight of polyethylene with hydrogen pressure at 2.5 bar, constant ethylene pressure at 8 bar and polymerization temperature at 80 °C. The catalytic activity was calculated from the amounts of consumed ethylene measured by a mass flow meter. Finally, the catalytic activities of each series of the synthesis catalyst were compared with the catalytic activity of commercial catalyst.

3.3.2 Reactor 1: 100 mL Reactor

For $TiCl_4/MgCl_2/THF$ catalytic system, the polymerization of ethylene was carried out in a slurry 100 mL semi-batch autoclave reactor equipped with magnetic stirrer. *n*-haxane as medium agent for reaction (total volume of 30 mL), TEA solution as cocatalyst were injected into the reactor (Al/Ti molar ratio of 140). Then, 10 mg of catalyst powder was added into the autoclave reactor. The feeding of ethylene with the pressure of 50 psi was performed to start polymerization reaction at 80 °C and the amount of ethylene was fixed at 0.018 mmol. Finally, the reaction was terminated by adding acidic methanol. The product was washed with methanol and dried under vacuum.

3.4 Characterization techniques

3.4.1 Characterization of supports and catalysts
3.4.1.1 Inductively Coupled Plasma (ICP)

The inductively coupled plasma optical emission spectroscopy equipment (ICP-OES optima 2100 DV from PerkinElmer) was used to identify Ti, Mg and Al

content in catalyst. The solid catalysts was weighed and digested with HCl. The mixtures were stirred about 30 min. After catalyst was completely dissolved, the solution sample was diluted with DI water. The weight percentage of element content was calculated by analysis of value from ICP. The concentrations of each element standard solutions used for calibration range are 0 − 15 ppm.

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

SEM and EDX were used to determine the morphologies and elemental distribution, respectively. The SEM of JEOL mode JSM-6400 was applied. The EDX was performed using Link Isis series 300 program. The solid catalyst sample was prepared on stub in a glove box and store in bottle with Ar atmosphere. Under the N_2 gas flow, the sample was coated with platinum particles by ion sputtering device to provide electrical contact to the specimen.

3.4.1.3 X-ray Powder Diffraction (XRD)

The X-ray powder diffraction patterns were performed to determine the crystalline phase of samples and identify the type of powders sample. It was carried out using a Bruker D8 Advance Diffract meter at 40 kv, 40 mA with CuKα radiation (λ = 1.54056 A°). The XRD was recorded follow conditions: reflection mode at room temperature, scans from diffraction angle 2θ = 10 to 80°, scan speed of 0.3 sec/step and a step size of 0.02. All samples were prepared under argon atmosphere in glove box and loaded into a holder covered with a Mylar film to prevent air and moisture.

3.4.1.4 Electron Spin Resonance (ESR)

The electron spin resonance spectra of catalyst samples were recorded at ambient temperature, with the use of JEOL JES-FE1XG spectrometer under N_2 atmosphere. ESR was used to determine Ti^{3+} content in the catalysts. Because Ti^{3+} has an unpaired electron in the 3d orbital, this can detect by ESR. The slurry catalyst sample was put not more than 4 cm in an ESR tube (the length of 30 cm) and sealed to prevent air and moisture, which prepared in a glove box. If the catalyst was

activated with cocatalyst, it should be cooled with liquid N_2 to stop the interaction during awaiting analysis.

3.4.1.5 N_2 Physisorption

The specific surface area of catalyst was measured by physical adsorption of N_2 molecules on a solid surface (single point). The solid sample was prepared in a glove box by sample was put in a tube and sealed to prevent air and moisture. The adsorption was performed at -196 °C with liquid N_2. The obtained peak area signal from desorption were used to calculate as follow: Surface area = Peak area (m^2) / Weight of sample (g).

3.4.1.6 Fourier Transforms Infrared Spectroscopy (FTIR)

The FT-IR was applied with a Nicolet 6700 FTIR spectrometer. It was used to identify the function group of sample. For this work, want to identify the EtOH or EtOH-complex and THF or THF-complex in supports and catalysts. A scanning range from 400 cm^{-1} to 4000 cm^{-1} with scanning of 400 times was applied.

3.4.2 Characterization of polymers
3.4.2.1 Differential Scanning Calorimetry (DSC)

The melting temperature (T_m) and percentage of crystallinity (χ_c) of polyethylene were determined by DSC-TGA with TA Instruments SDT Q600 V8.1 Build 99. The characterizations were performed at a heating rate of 10 °C/min in the temperature range of 20-600 °C. However, the appearance of T_m is in the range of 100-200 °C. The crystallinity of polymers was calculated by the following equation:

$$\chi_c = [\Delta H/(\Delta H°)]\times100)$$

where ΔH is heat of fusion of polyethylene sample.

$\Delta H°$ is the heat of fusion of standard (for linear polyethylene as 290 J/g) [50].

3.4.2.2 Measuring Flow Rate (MFR)

The MI of polyethylene determined by Extrusion Plastometer (Melt Indexer) measuring flow rate throughout Orifice diameter and length fixed at 10 min using load weights (2.16 kg) on the piston at temperature 190 ± 0.2 °C. Then can calculate the Melt Index in units of g/10 min.

CHAPTER IV
RESULTS AND DISCUSSIONS

4.1 The MgCl$_2$ support

MgCl$_2$ is known as the best support for the ZN catalyst polymerization. Several researches confirm that using MgCl$_2$ as a support catalyst exhibited high catalytic activity [25-28]. In Figure 4.1, anhydrous MgCl$_2$ was characterized by XRD analysis shows sharp peaks at 2θ = 15, 26, 32, 35 and 50°. Sharp peak at 2θ = 15° was involved with the stacking of Cl–Mg–Cl triple layers along the crystallographic direction, where two peaks, at 2θ = 32, 35 and 50° with stacking faults of the triple layers, which at 2θ = 35 and 50° was involved represent of (104) and (110) peaks, respectively. [6, 7]. The peaks at 2θ = 26° is Mylar film. Figure 4.2 (a) shows the morphology of anhydrous MgCl$_2$ supports. The smooth surface morphology and crystalline layers indicates the Cl–Mg–Cl triple layer structure.
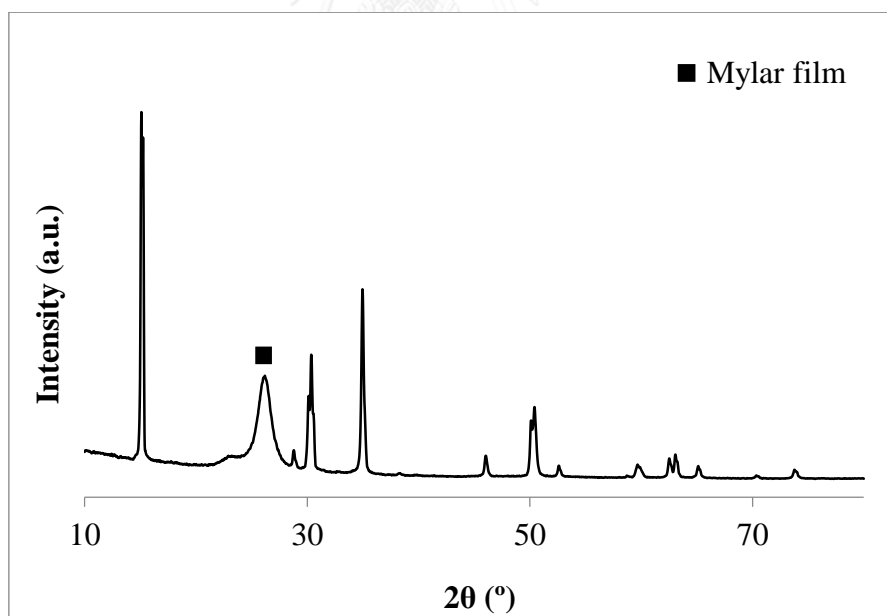
Figure 4.1 XRD pattern of anhydrous MgCl$_2$ support

The anhydrous MgCl$_2$ was used as support precursor into the ZN catalyst synthesis by complexes with Lewis base such as ethanol and THF in order to activate catalyst. However Lewis base can poison the catalyst sites. Thus these Lewis base

must be removed from the catalyst before the addition of $TiCl_4$, which can be removed with Lewis acid, for this work such as DAEC, EADC, $AlCl_3$, $CaCl_3$, $ZnCl_3$, $FeCl_3$ and their mixture. However, the some kind of these compound can cause the over-reduction of Ti species at high concentration [15].

4.2 The TiCl₄/MgCl₂/EtOH catalytic systems

In this part, ethanol is type of Lewis base, which was used in this preparation to form molecular adduct in order to change α-$MgCl_2$ to δ-$MgCl_2$ form which as the active form for polymerization [6]. For the reaction of $MgCl_2$/EtOH adduct, in this work, we combine of 1 mole of $MgCl_2$ and 6 mole of ethanol ($MgCl_2 \cdot 6EtOH$). The morphology of formation of $MgCl_2$ and ethanol as shown in Figure 4.2 (b) indicated that the destruction of layers of $MgCl_2$ structure became rough surface. The surface area of $MgCl_2 \cdot 6EtOH$ was also measured and compared with anhydrous $MgCl_2$ by N_2 physisorption technique, showed in Table 4.1 It indicates that ethanol can cause a porous $MgCl_2$ led to an increase of surface area.

Table 4.1 The surface area of anhydrous $MgCl_2$ and $MgCl_2 \cdot 6EtOH$ adduct

Sample	Surface area (m^2/g)
anhydrous $MgCl_2$	2.00
$MgCl_2 \cdot 6EtOH$	6.05
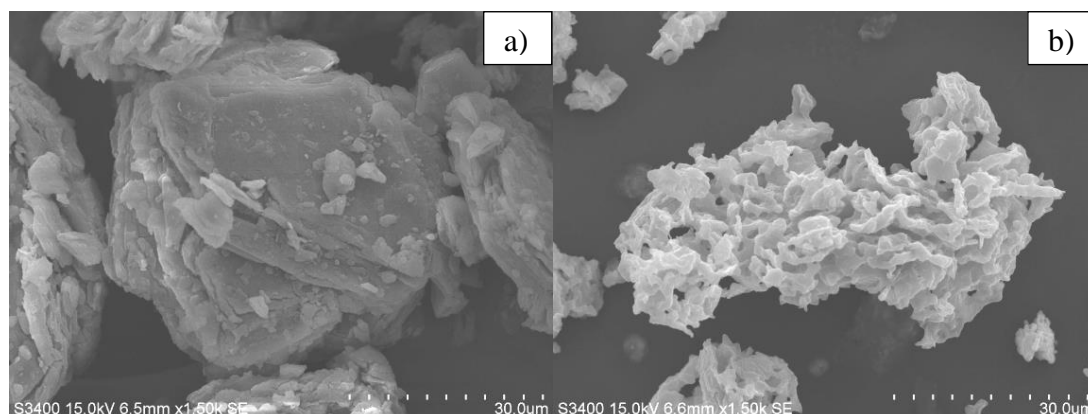
Figure 4.2 The morphology of a) anhydrous $MgCl_2$ and b) $MgCl_2 \cdot 6EtOH$ adduct

The next step for preparation of support involving removal of ethanol from $MgCl_2 \cdot EtOH$ adduct using alkylaluminum chloride compound such as DEAC, EADC and their mixture. The reaction between $MgCl_2 \cdot EtOH$ adduct and alkylaluminum compound lead to the removal of ethanol in the adduct structure. An excess of $TiCl_4$ was added in to reaction to obtain $TiCl_4$ supported on $MgCl_2$. However, $TiCl_4$ can be reduced to a lower valence state with remaining alkylaluminum compound in catalyst (reduction from Ti^{4+} to Ti^{3+} or Ti^{2+}) [4, 15]. Therefore, the suitable amount of alkylaluminum compound was considered.

4.2.1 Effect of different molar ratio of DEAC/MgCl$_2$ in the synthesized catalyst

The molar ratio of DEAC/MgCl$_2$ in range from 2.0 to 3.3 was used to prepare the catalyst support. Table 4.2 presented the element contents and surface area in catalysts which were characterized by ICP and N_2 physisorption technique, respectively. It was found that Ti content was increased with an increase of DEAC/MgCl$_2$ molar ratio, whereas the Mg content was decreased led to increasing in the Ti/Mg ratio. This is because DEAC can react with ethanol in structure of MgCl$_2$/EtOH adducts and can be removed ethanol from the structure. An increase in the amount of DEAC lead to reaction between DEAC and ethanol is more; makes removal of ethanol is greater. The amount of remaining alcohols in support was confirmed by FT-IR as shown in Figure 4.3. It was observed that IR spectrum of the MgCl$_2 \cdot$6EtOH exhibits peak involving alcoholate such as in the regions of $3600 - 3000$ cm^{-1} corresponding to O–H stretching, at $2980 - 2900$, $1500 - 1300$ cm^{-1} corresponding to C–H stretching and at 1100 cm^{-1} corresponding to C–O stretching [37]. After removal of ethanol with DEAC, it clears that the large amount of DEAC can reduce in these peaks involving alcoholate.

Table 4.2 Effect of different molar ratio of DEAC/MgCl$_2$ on element content

Catalyst[a]	DEAC/MgCl$_2$	Element content (%wt)			Ti/Mg	Surface area (m^2/g)
	(molar ratio)	Ti	Mg	Al	(mol/mol)	
TMC-160214	2.0	6.72	15.60	0.47	0.22	300
TMC-020214	2.5	7.07	14.74	0.75	0.24	283
TMC-211113	2.7	7.77	14.33	0.83	0.28	262
TMC-271113	3.0	8.39	13.51	1.07	0.32	220
TMC-091113	3.3	12.11	9.93	0.77	0.62	81

[a] TMC refers to Titanium Magnesium Catalyst, where the six numbers presents the order of the day, month and year in the synthesis
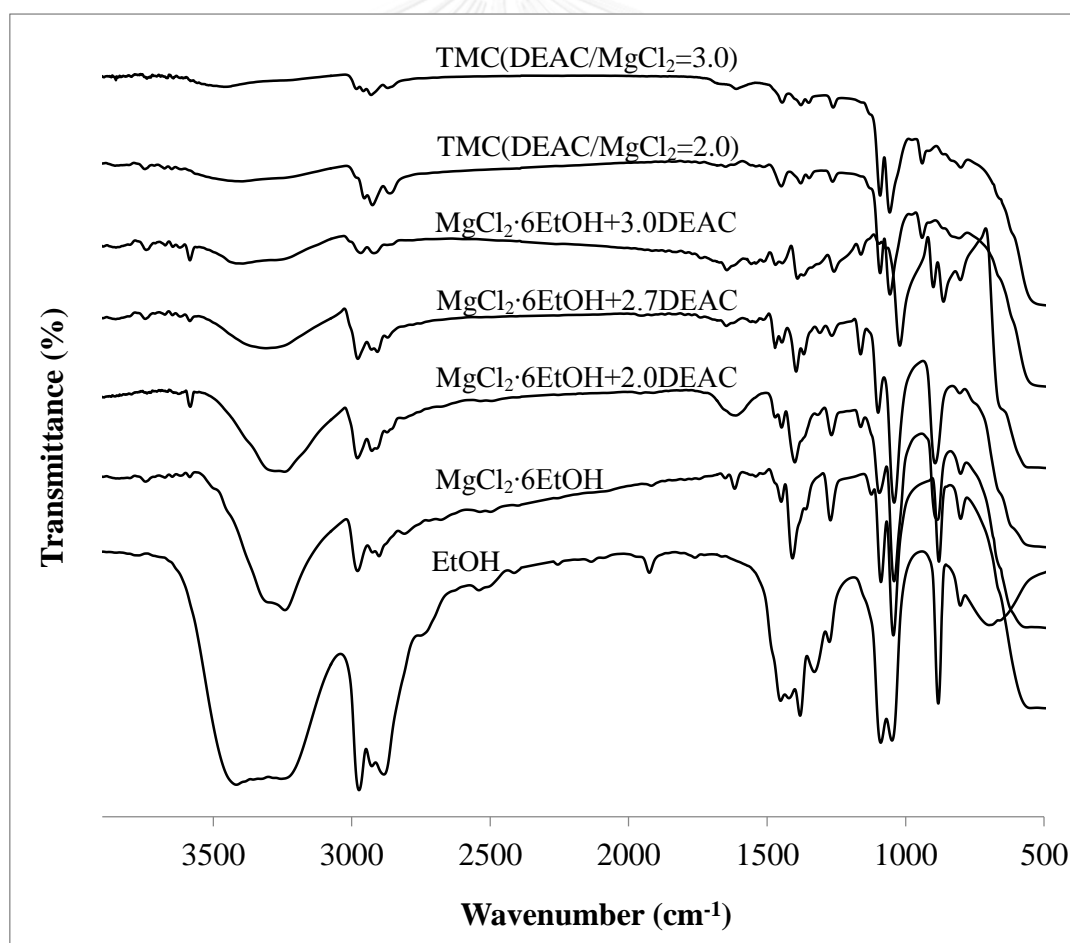
Figure 4.3 FT-IR of EtOH, MgCl$_2$·EtOH adducts and catalysts with different molar ratio of DEAC/MgCl$_2$

As a result, there is an increase in the surface area of support which was confirmed by N_2 physisorption technique. Table 4.3 shows the support which was selected to prepare for this characterization. It noticed that a decrease of ethanol with the large amount of DEAC relationship to an increase the surface area of support. Huang et al. [7] was also reported that the reaction between an alkyl aluminium compound and $MgCl_2 \cdot n$EtOH support led to significant increases in pore size and porosity.

Table 4.3 The surface area of prepared support using the different molar ratio of DEAC/MgCl$_2$

Support	Surface area (m^2/g)
MgCl$_2$·6EtOH + 2.0DEAC	15.37
MgCl$_2$·6EtOH + 2.7DEAC	17.20
MgCl$_2$·6EtOH + 3.0DEAC	18.85

After TiCl$_4$ was fixed and added in to the reaction, it was found that Ti content increased with increasing of DEAC/MgCl$_2$ molar ratio but the surface areas in the catalyst became decreased as showed in Table 4.2. This is due to TiCl$_4$ will react with remaining ethanol in support, at the temperature rose up to 80 °C, the large of ethanol caused the strong interaction with TiCl$_4$ and led to increasing the surface area rather than in the small of ethanol. After that, the remaining TiCl$_4$ will impregnate on catalyst, due to the amount of TiCl$_4$ was fixed, thus Ti content did not increased by increasing the surface area. The results are also consistent with research that has been published [43]. However, the reaction between TiCl$_4$ and ethanol will be formed as titanium chloride ethoxide (TiCl$_3$(OC$_2$H$_5$)) which is inactive for the polymerization [54]. So, it needs to be washed in final step of preparation.

The effect of Ti content on the catalytic activity of catalysts in ethylene polymerization system was indicated in Figure 4.4 and Table 4.4. It can be seen that an increase of DEAC/MgCl$_2$ molar ratio from 2.0 to 2.7, the activity was increased with an increase of Ti content. But when the molar ratio of DEAC/MgCl$_2$ was 3.0 or more, it was found that the activity decreased. It means that the Ti species were not all active.

In the polymerization process, the reaction between catalyst ($TiCl_4$) and cocatalyst (TEA) is important to form active site, which cause from reduction of $TiCl_4$ to Ti^{3+} and Ti^{2+} by reacting with TEA. It is well known that Ti^{3+} and Ti^{2+} species are active for ethylene polymerization. The ESR was used to characterize the Ti^{3+} species both before and after the catalyst react with TEA as shown in Table 4.4. In case of catalyst not reacted with TEA, it was observed that synthesized catalyst with $DEAC/MgCl_2$ mole ratio equal to 3.3 showed the highest in amount of Ti^{3+} species, while the other catalysts showed in only small amounts. This means that titanium species were reduced due to the large amount of DEAC [15], which the reaction of $TiCl_4$ with DEAC as follows Reaction 4.1 [42]:

$$(CH_3)_2AlCl + TiCl_4 \leftrightarrow CH_3TiCl_3 + CH_3AlCl_2 \tag{4.1}$$
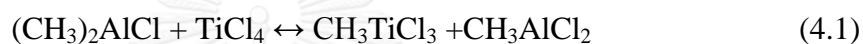
It can also noticed, the reduction of $TiCl_4$ with DEAC cause a change of color of the synthesized catalyst due to changes of Ti state. For this molar ratio of $DEAC/MgCl_2$ =3.3, it showed the dark brown color of catalyst. After this catalyst reacted with TEA, the amount of Ti^{3+} species is less compared to other catalysts due to over-reduction and led to decreasing in catalytic activity. However, all the synthesized catalysts, the amount of Ti^{3+} species are related to the catalytic activity as shown in Figure 4.4.
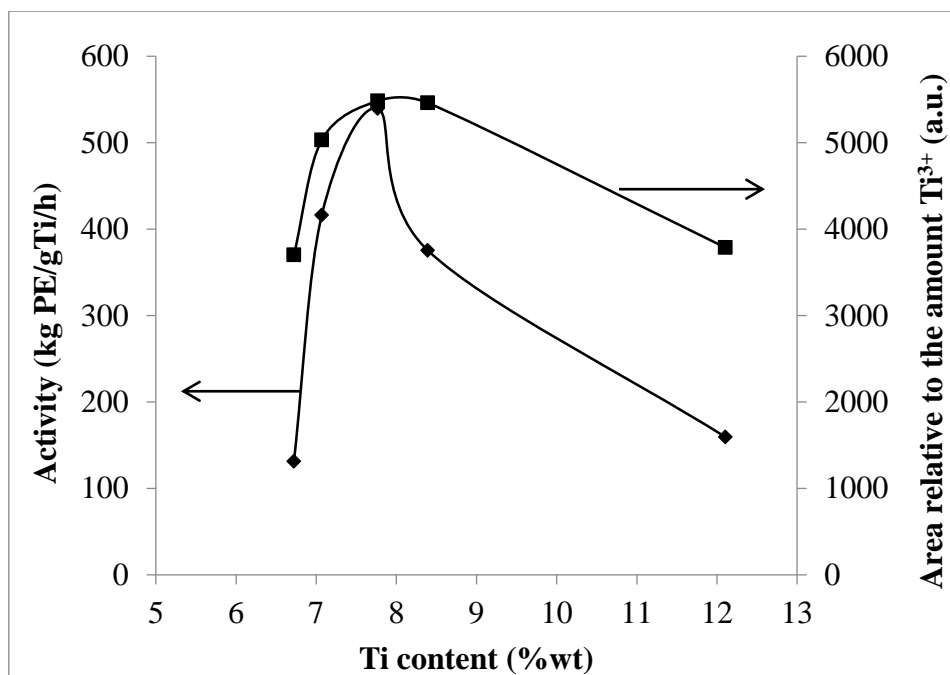
Figure 4.4 Effect of titanium content on catalytic activity in the series of catalysts was synthesized using different molar ratio of DEAC/MgCl$_2$

Table 4.4 Effect of different molar ratio of DEAC/MgCl$_2$ on catalytic activity

DEAC/MgCl$_2$	Ti	Area of ESR peak[a]		Yield	Time[b]	Activity[c]
		no react TEA	react TEA			
(molar ratio)	(%wt)	(a.u.)	(a.u.)	g PE	(h)	(kg PE/g Ti/h)
2.0	6.72	883	3703	153	2.44	131
2.5	7.07	757	5031	151	0.76	416
2.7	7.77	907	5484	150	0.58	540
3.0	8.39	826	5461	149	0.71	375
3.3	12.11	3727	3788	153	2.00	160

[a] Relation with amount of Ti^{3+} (condition: catalyst = 0.0005 mmolTi, measured at room temp., reaction with TEA with Al/Ti = 100)

[b] Time of ethylene polymerization reaction

[c] Polymerization condition: Al/Ti = 100, catalyst = 0.01 mmolTi, Temp. = 80 °C, H$_2$ = 2.5 bar, C$_2$H$_4$ = 8 bar

4.2.2 Effect of different molar ratio of $TiCl_4/MgCl_2$ in the synthesized catalyst

This experiment, the catalysts were synthesized with the difference of Ti content using different molar ratio of $TiCl_4/MgCl_2$. The molar ratio of $DEAC/MgCl_2$ was fixed as 3.0. The results of element content from ICP were showed in Table 4.5. It was found that Ti content was increased with an increase of $TiCl_4/MgCl_2$ molar ratio led to an increase in the Ti/Mg ratio, which similar in case of using different molar ratio of $DEAC/MgCl_2$. This is because a partial of $TiCl_4$ reacted with remaining EtOH in prepared support and another partial $TiCl_4$ impregnated on catalyst to activate. So, larger amount of $TiCl_4$ led to a higher Ti content. The other researches also discussed that the ethanol in final adducts could reduce with the amount of $TiCl_4$ and present high surface area [10, 43].

Table 4.5 Effect of different molar ratio of $DEAC/MgCl_2$ on element content

Catalyst[a]	$TiCl_4/MgCl_2$ (molar ratio)	Element content (%wt)			Ti/Mg (mol/mol)	Surface area (m^2/g)
		Ti	Mg	Al		
TMC-300314	0.87	6.48	13.23	2.49	0.25	28
TMC-240214	1.73	7.52	13.42	1.10	0.28	203
TMC-151213	2.60	8.12	13.20	0.93	0.31	260
TMC-271113	3.50	8.39	13.51	1.07	0.32	220
TMC-140214	4.33	8.56	12.07	0.83	0.36	369

[a] TMC refers to Titanium Magnesium Catalyst, where the six numbers presents the order of the day, month and year in the synthesis

The effect of Ti content on the catalytic activity of catalysts in ethylene polymerization system was indicated in Figure 4.4 and Table 4.6. It can be seen that an increase of $TiCl_4/MgCl_2$ molar ratio from 0.87 to 1.73, the activity was increased with an increase of Ti content. However, increasing greater of the molar ratio of

$TiCl_4/MgCl_2$ found that caused decrease in the catalytic activity. It means that the Ti species were not all active.

The results from ESR to characterize the Ti^{3+} species when the catalyst reacted with TEA showed in Table 4.6. It was also found that the amount of Ti^{3+} species is related to the catalytic activity except for molar ratio of $TiCl_4/MgCl_2$ as 4.33. This may be due to the effect of different Ti^{2+}.
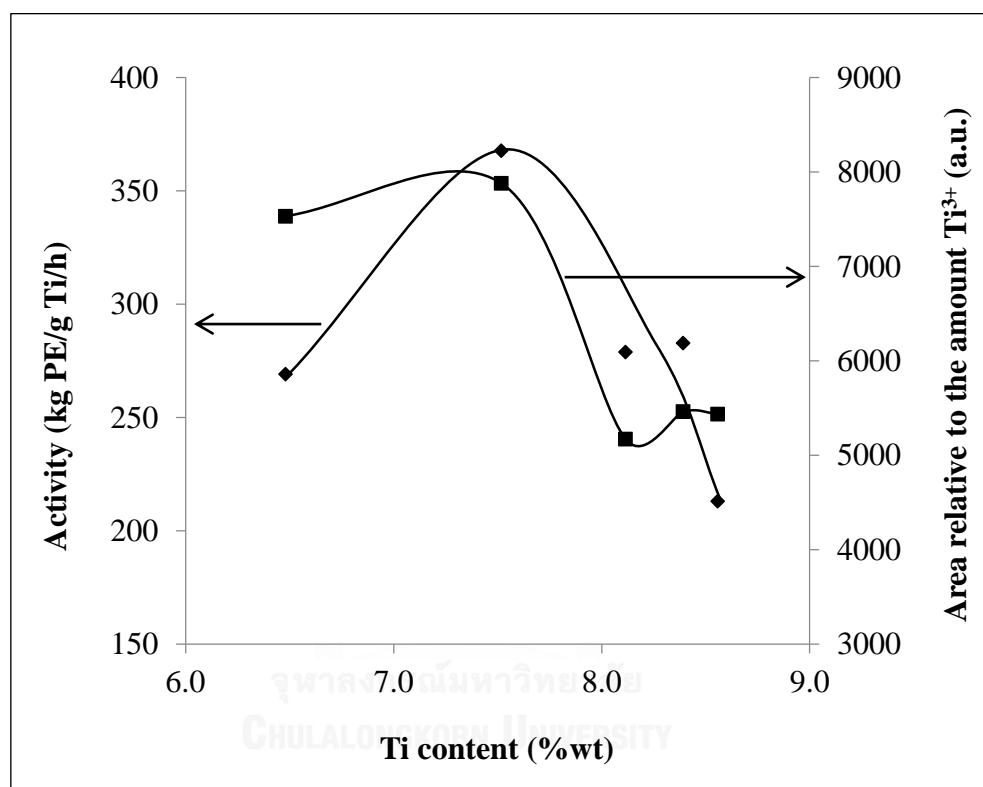
Figure 4.5 Effect of titanium content on catalytic activity in the series of catalysts was synthesized using different molar ratio of $TiCl_4/MgCl_2$

Table 4.6 Element content of the synthesis catalyst on effect of molar ratio of $TiCl_4/MgCl_2$

$TiCl_4/MgCl_2$ (molar ratio)	Ti (%wt)	Area of ESR peak[a] (a.u.)	Yield (g PE)	Time[b] (h)	Activity[c] (kg PE/g Ti/h)
0.87	6.48	7532	155	1.00	269
1.73	7.52	7878	152	0.72	368
2.60	8.12	5169	154	0.96	279
3.50	8.39	5461	155	0.95	283
4.33	8.56	5434	155	1.26	213

[a] Relation with amount of Ti^{3+} (condition: catalyst = 0.0005 mmolTi, measured at room temp., reaction with TEA with Al/Ti = 100)

[b] Time of ethylene polymerization reaction

[c] Polymerization condition: Al/Ti = 100, catalyst = 0.012 mmolTi, Temp. = 80 °C, H_2 = 2.5 bar, C_2H_4 = 8 bar

4.2.3 Comparison between the different molar ratio of $TiCl_4/MgCl_2$ and $DEAC/MgCl_2$

Compared between the synthesis of catalyst using different molar ratio of $DEAC/MgCl_2$ and $TiCl_4/MgCl_2$, it was observed that the catalyst with Ti content around 7.5 – 7.8 %wt exhibited the highest catalytic activity. This is because the suitable elimination of the ethanol or Lewis base from adducts can provide a good support. This affected the crystal structure leading to very active in the polymerization catalysis [6, 48]. The results are also consistent with Hadian et al. [6], which studied the thermal dealcoholation in $MgCl_2 \cdot 3.3EtOH$ adduct in order to the different molar ratio of $EtOH/MgCl_2$ in the range of 2.1 – 3.3 and the different Ti content as 0.824 – 1.402 %wt. The highest catalytic activity for the propylene polymerization reaction showed Ti content about 0.9 %wt. Moreover, Huang et al. [49] also found that the treatment alkylaluminum for $MgCl_2$/alcohol complex may be related to distribution of active titanium in ZN catalyst preparation. With lower concentration of TEA treatment, the distribution of Ti both on surface and in body of catalyst was quite

uniform. While with higher concentration of TEA treatment, the distribution of Ti found on the surface over, the distribution became to be non-uniform.

The example of the synthesized catalyst was also selected to characterize by XRD technique as shown in Figure 4.6 and Figure 4.7 which represent of the results using different molar ratio of DEAC/$MgCl_2$ and $TiCl_4$/$MgCl_2$, respectively. The XRD patterns show the reduction of intensity in all peak of α-$MgCl_2$. This is probably due to the interaction between Mg^{2+} and alcoholic oxygen. As a result, the insertion of alcohol between the Cl–Mg–Cl triple layers leads to an increase in the interplanar distance or decrease in 2θ value [9], meaning that the formation of a crystal is low. It was also observed that the final catalysts show the position of board peak of δ-$MgCl_2$, which active for polymerization.
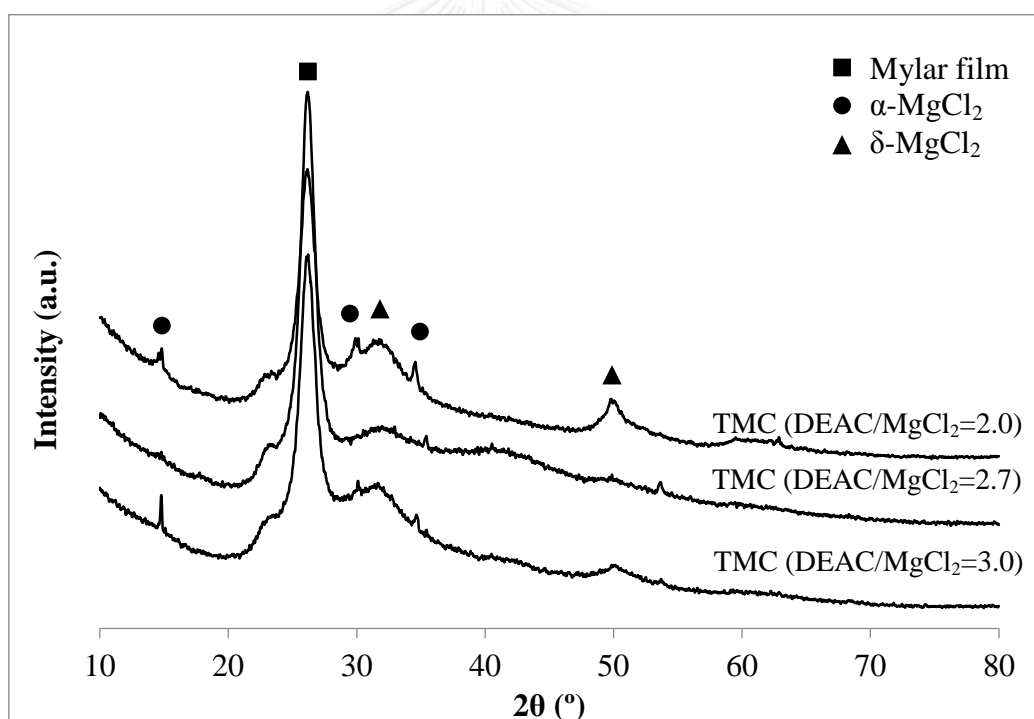
Figure 4.6 The XRD patterns of the synthesized catalyst using different molar ratio of DEAC/$MgCl_2$
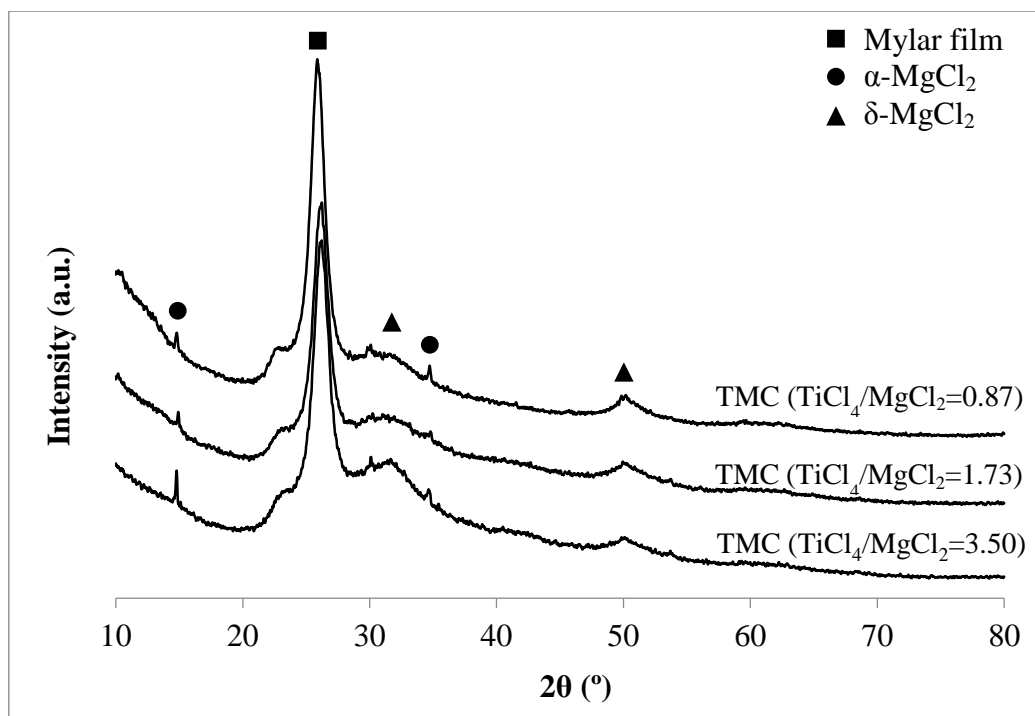
Figure 4.7 The XRD patterns of the synthesized catalyst using different molar ratio of
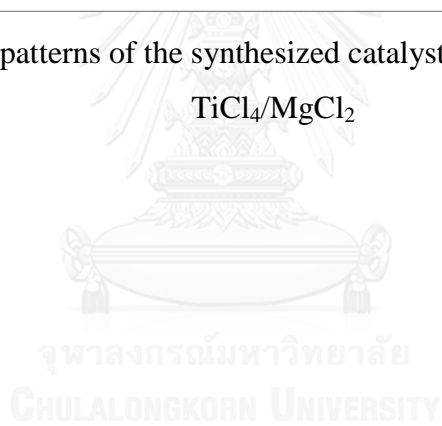
TiCl$_4$/MgCl$_2$

4.2.4 The polymer properties of using the different molar ratio of DEAC/MgCl$_2$ and TiCl$_4$/MgCl$_2$

The polymer properties both are using the different molar ratio of DEAC/MgCl$_2$ and TiCl$_4$/MgCl$_2$ in synthesis of catalyst as shown in Table 4.7 and Table 4.8. It showed that these parameters affected for MI. In general, low value of melt flow index relates to high molecular weight polymers, while and high melt flow index value relates to low molecular weight polymers [66, 67]. For the degree of crystallinity (χ_c) and the melting temperature (T_m) of polyethylene, it does not found any significant change.

Table 4.7 Effect of different molar ratio of DEAC/MgCl$_2$ on polymer properties

DEAC/MgCl$_2$ (molar ratio)	MI (2.16) (g/10min)	T_m °C	χ_c %
2.0	0.799	138	65
2.5	1.108	135	64
2.7	1.526	136	63
3.0	1.900	136	62
3.3	2.001	138	63

Table 4.8 Effect of different molar ratio of TiCl$_4$/MgCl$_2$ on polymer properties

TiCl$_4$/MgCl$_2$ (molar ratio)	MI (2.16) (g/10min)	T_m °C	χ_c %
0.87	4.164	136	69
1.73	3.877	136	71
2.60	2.353	135	72
3.50	2.088	136	68
4.33	1.619	137	69

Figure 4.8 and Figure 4.9 shows the surface and porosity of the synthesized catalysts using different molar ratio of $DEAC/MgCl_2$ and $TiCl_4/MgCl_2$, respectively. It observed that, the rough surface and porosity of the catalysts were increased compared with $MgCl_2 \cdot EtOH$ adduct. However, the influence of different molar ratio of $DEAC/MgCl_2$ and $TiCl_4/MgCl_2$ on does not effect on the surface, porosity and particle size of catalysts.
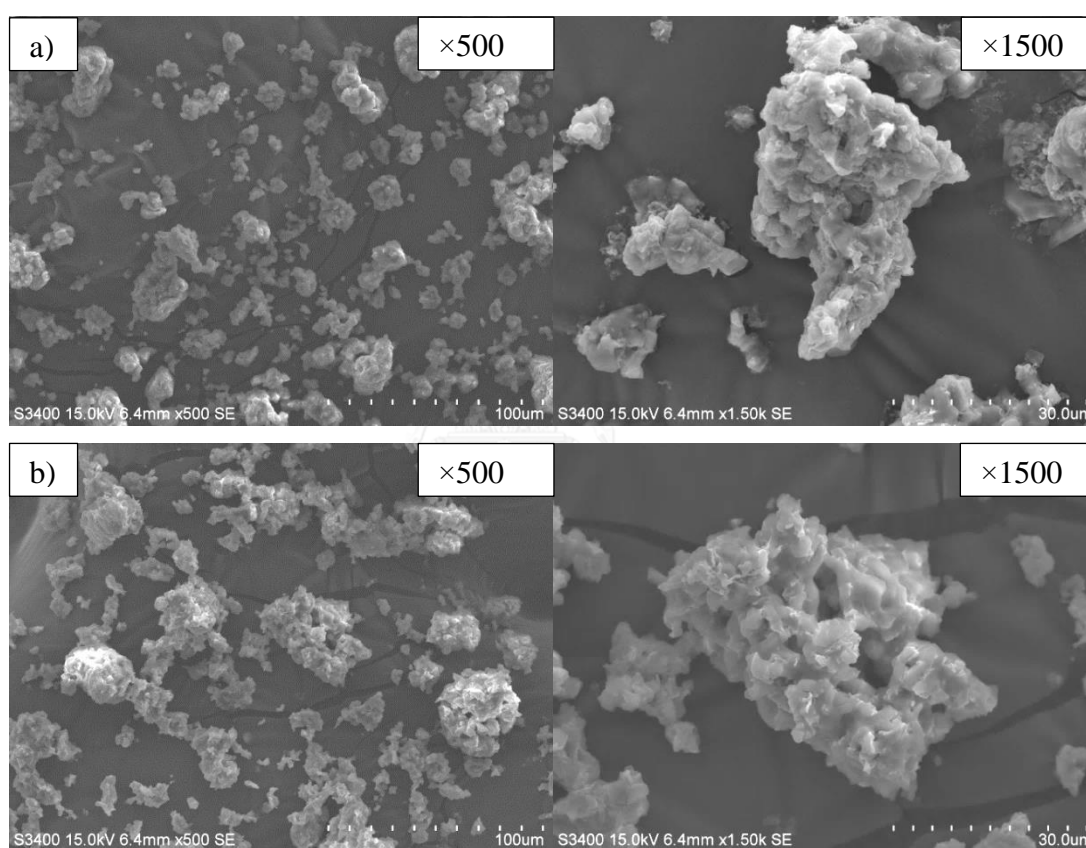
Figure 4.8 The morphology of catalysts with different molar ratio of $DEAC/MgCl_2$ is a) 2.0, b) 2.5, c) 2.7, d) 3.0 and e) 3.3

Figure 4.8 (cont.) The morphology of catalysts with different molar ratio of DEAC/MgCl$_2$ is a) 2.0, b) 2.5, c) 2.7, d) 3.0 and e) 3.3

Figure 4.9 The morphology of catalysts with different molar ratio of $TiCl_4/MgCl_2$;

a) 0.87, b) 1.73, c) 2.60, d) 3.50 and e) 4.33
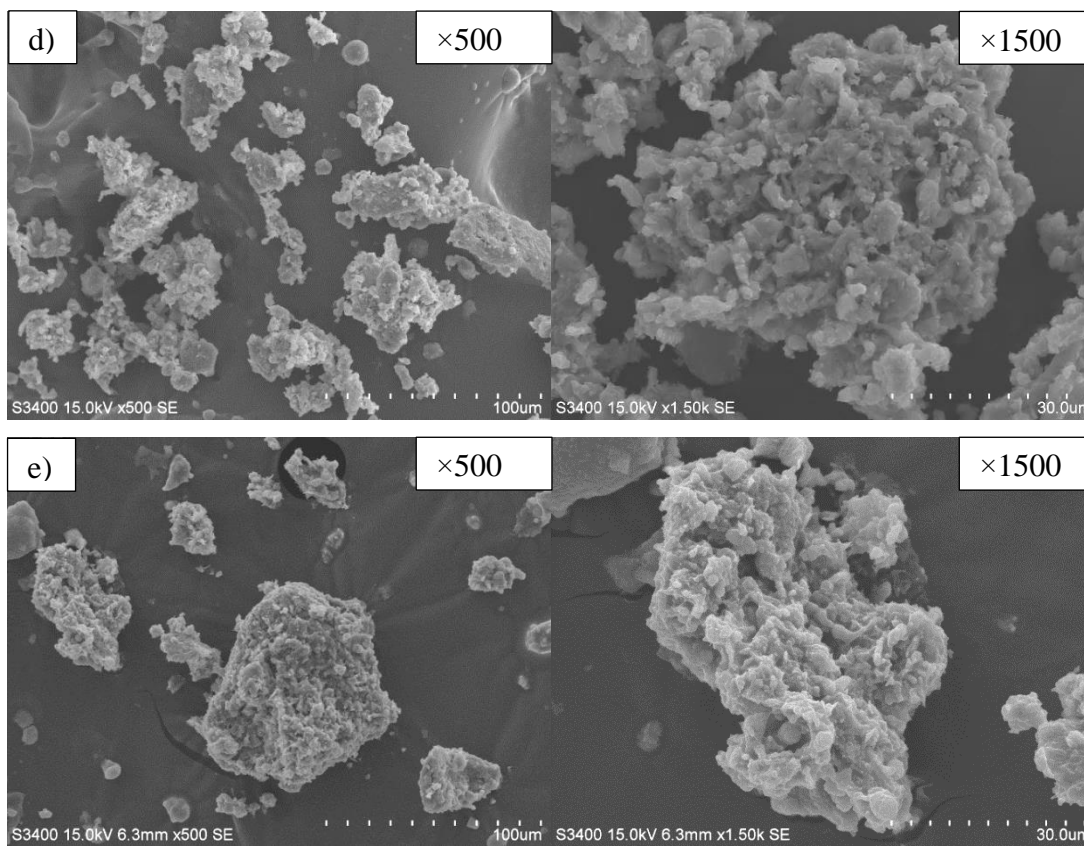
Figure 4.9 (cont.) The morphology of catalysts with different molar ratio of
TiCl$_4$/MgCl$_2$; a) 0.87, b) 1.73, c) 2.60, d) 3.50 and e) 4.33
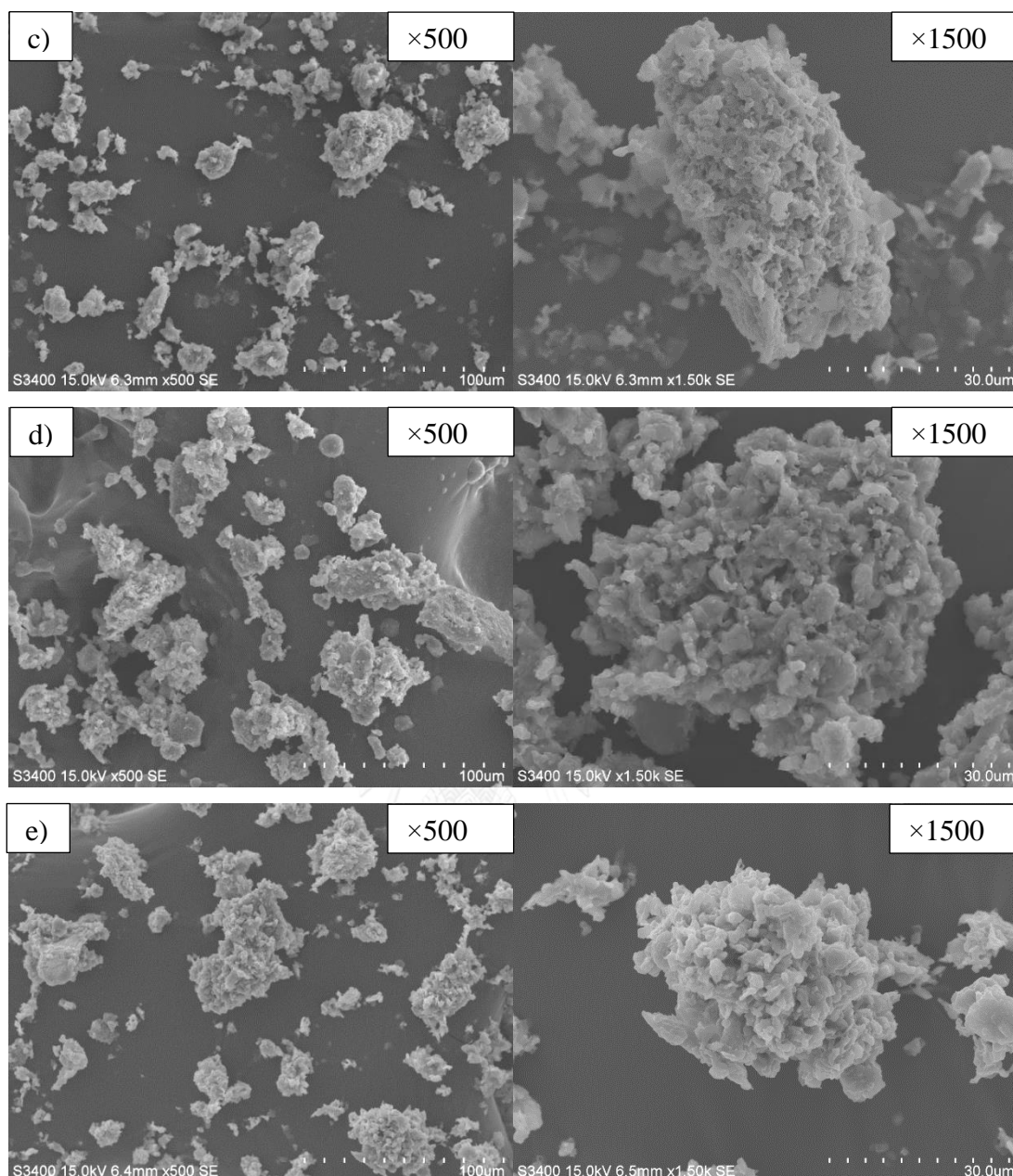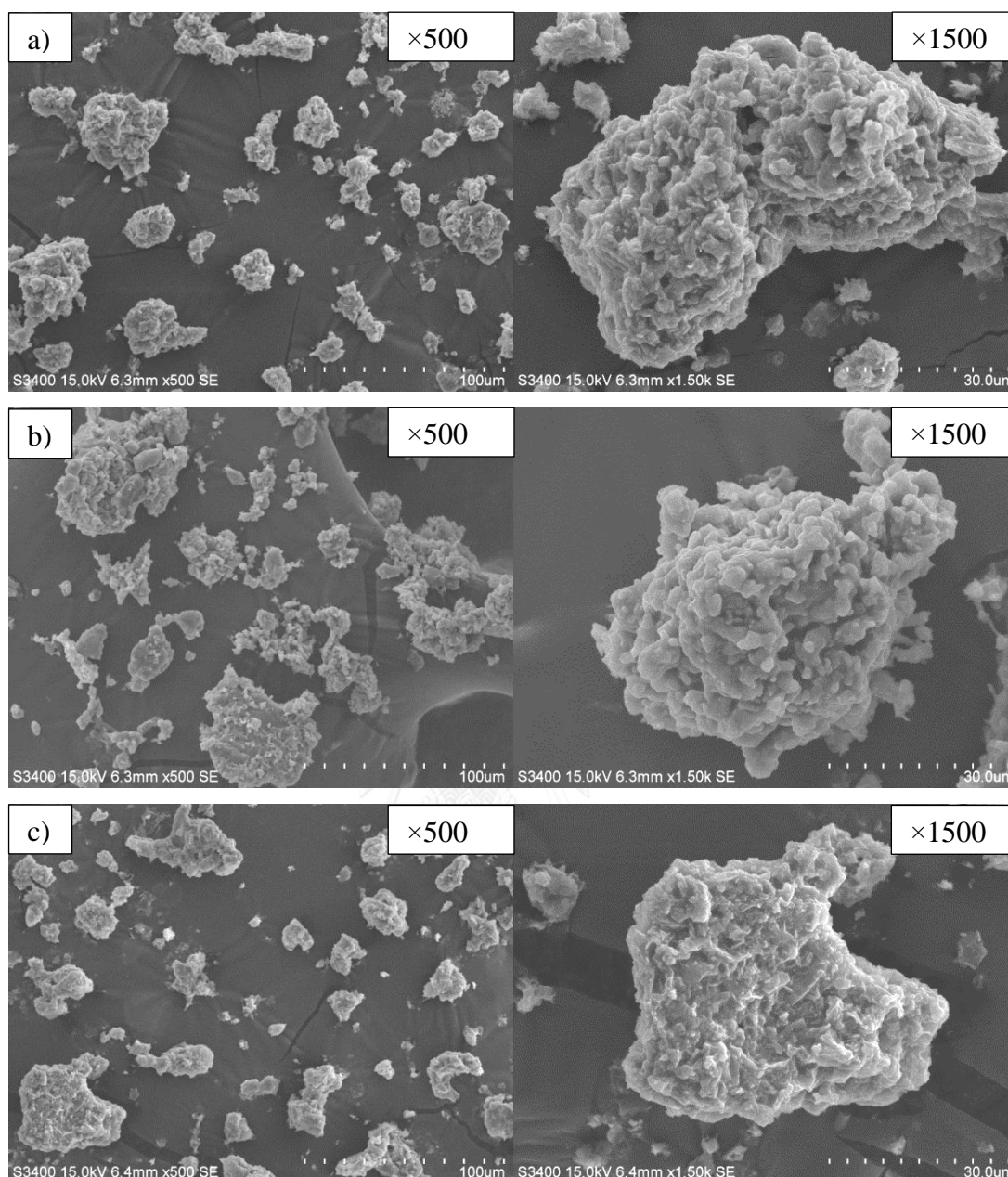
4.2.5 Effect of different molar ratio of DEAC/EADC mixture in the synthesized catalyst

Among the alkylaluminium chlorides employed as Lewis acids, in this part, EADC was chosen due to its low reduction power compared with other alkylaluminium chlorides [15, 68]. This is to avoiding the over-reduction of titanium species. For this experiment, the effect of DEAC/EADC mixture on Ti content and the catalytic activity was also studied.

The reaction of a mixture of DEAC and EADC with the monochloro and dichloro derivatives compound, respectively, as follows Reaction 4.2 [69]:

$$(C_2H_5)_2AlCl + C_2H_5AlCl_2 \rightarrow (C_2H_5)_3Al_2Cl_3 \qquad (4.2)$$
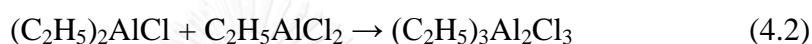
Data in Table 4.9 shows the result of catalysts which was synthesized using different molar ratio of DEAC/ EADC mixture. It was found that Ti content decreased with the increase of EADC molar ratio, whereas the molar ratio of DEAC decreased. On the other hand, Mg content was also increased led to a decrease in the Ti/Mg ratio. This is because DEAC can react with ethanol in structure of $MgCl_2$/EtOH adducts stronger than EADC. Therefore, it maked Ti content decreases when reduce the amount of DEAC. Huang et al. [49] also studied the removal of alcohol in the $MgCl_2$/alcohol complexes using two different types of alkylaluminum such as TEA and DEAC and found that TEA treatment showed the Ti content higher than DEAC treatment. The reason for this is because the reduction or alkylation power of alkylaluminum affects the removal of alcohol. The reduction and alkylation power is in the order of $R_3Al > R_2AlCl > RAlCl_2$ or $Al(C_2H_5)_3 > Al(C_2H_5)_2Cl > Al(C_2H_5)Cl_2$ or TEA > DEAC > EADC [42, 70]. However, the surface areas of all the catalyst were slightly different.

In the comparative study with types of alkylaluminium chloride compounds, DEAC and EADC were used to remove the ethanol in preparation of catalysts. The using of DEAC indicated the catalytic activity higher than using of EADC, as shown in Table 4.10 This phenomenon could be explained that Ti content in case DEAC is higher than in case EADC. Therefore, the higher Ti content leads to the higher activity.

Table 4.9 Effect of different molar ratio of DEAC/EADC mixture on element content

Catalyst[a]	DEAC/EADC (molar ratio)	Element content in bulk (%wt)			Ti/Mg (mol/mol)	Surface area (m²/g)
		Ti	Mg	Al		
TMC-130414	3.00/0.00	7.92	13.47	1.07	0.30	206
TMC-130714	2.25/0.75	7.59	13.30	1.27	0.29	188
TMC-300614	1.50/1.50	6.21	13.99	0.96	0.23	196
TMC-120714	0.75/2.25	5.71	14.64	1.67	0.20	194
TMC-030414	0.00/3.00	5.07	17.86	0.87	0.14	187

[a] TMC refers to Titanium Magnesium Catalyst, where the six numbers presents the order of the day, month and year in the synthesis

For in case of DEAC and EADC mixed with different molar ratio, the results become surprising. It was found that the activity is not increased by increasing the Ti content, but at molar ratio of DEAC/EADC = 0.75/2.25 showed the high activity. At molar ratio of DEAC/EADC = 2.25/0.75, the activity was lowest. The results from ESR to characterize the Ti^{3+} species when the catalyst reacted with TEA showed in Table 4.10 and Figure 4.10. It was also found that the amount of Ti^{3+} species related to the catalytic activity.

The Ti/Mg on surface of catalyst was also approximated by EDX technique to compare with Ti/Mg from ICP technique, as shown in Table 4.11. The results showed that at molar ratio of DEAC/EADC = 0.75/2.25 catalyst exhibited the highest of Ti/Mg content, whereas at molar ratio of DEAC/EADC = 0.00/3.00 catalyst showed the lowest of Ti/Mg. This may mean the different type of alkylaluminum chloride and its mixture affected the dispersion of Ti species. Comparison the results from EDX and ICP, in case using DEAC/EADC mixture, it was noticed that the higher catalytic activity is related to the increase of Ti/Mg on surface though the total Ti/Mg in bulk was lower.
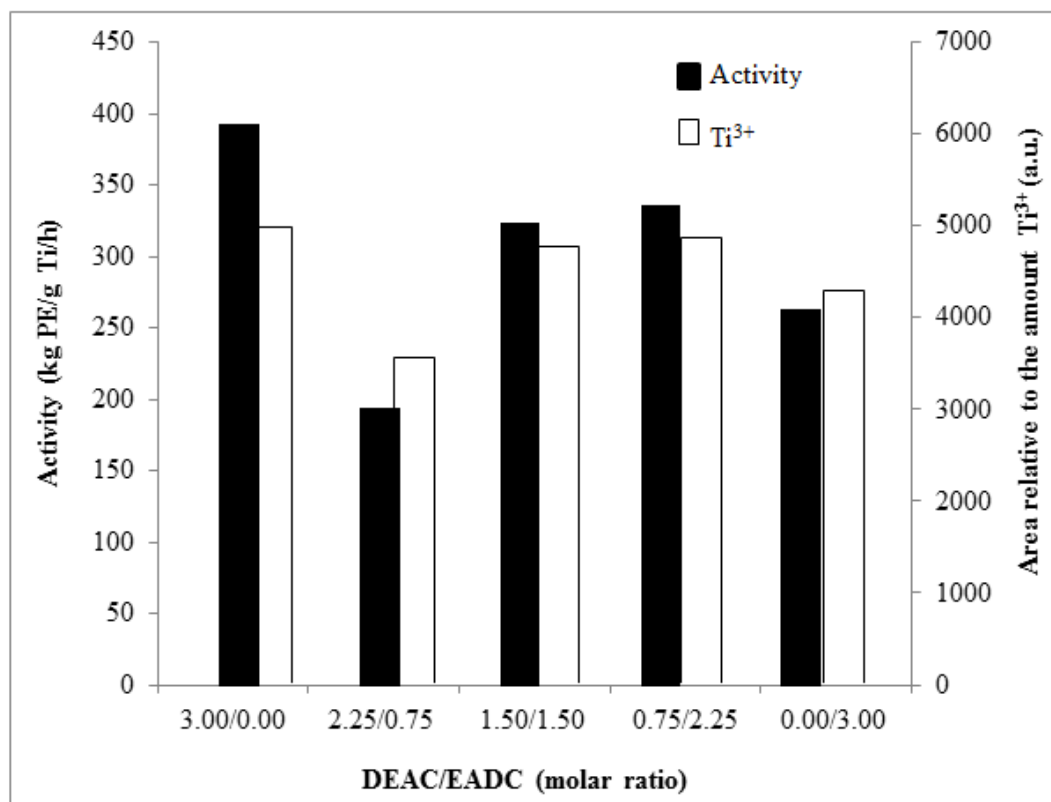
Figure 4.10 Effect of titanium content on catalytic activity in the series of catalysts was synthesized using different molar ratio of DEAC/EADC

Table 4.10 Element content of the synthesis catalyst on effect of molar ratio of $TiCl_4/MgCl_2$

DEAC/EADC (molar ratio)	Ti (%wt)	Area of ESR peak[a] (a.u.)	Yield (g PE)	Time[b] (h)	Activity[c] (kg PE/g Ti/h)
3.00/0.00	7.92	5325	129	1.11	404
2.25/0.75	7.59	3807	131	2.31	198
1.50/1.50	6.21	5091	130	1.37	330
0.75/2.25	5.71	5211	129	1.31	342
0.00/3.00	5.07	4580	135	1.75	268

[a] Relation with amount of Ti^{3+} (condition: catalyst = 0.0005 mmolTi, measured at room temp., reaction with TEA with Al/Ti = 100)

[b] Time of ethylene polymerization reaction

[c] Polymerization condition: Al/Ti = 100, catalyst = 0.012 mmolTi, Temp. = 80 °C, H_2 = 2.5 bar, C_2H_4 = 8 bar

Table 4.11 Comparison of element content in bulk and on surface

DEAC/EADC (molar ratio)	Ti/Mg in bulk[a]	Element content[b] (%wt)		Ti/Mg on surface[b]
		Ti	Mg	
3.00/0.00	0.30	10.98	22.96	0.24
2.25/0.75	0.29	8.76	27.35	0.16
1.50/1.50	0.23	10.66	19.48	0.28
0.75/2.25	0.20	12.71	17.58	0.37
0.00/3.00	0.14	5.43	24.76	0.11

[a] Results from ICP

[b] Results from EDX

$$H_3C\diagdown Al \diagup CH_3$$
$$\underset{Cl}{|}$$

$$\underset{Cl\diagup}{\overset{Cl}{|}} Al \diagdown CH_3$$

Diethylaluminum chloride (DEAC)   Ethylaluminum dichloride (EADC)
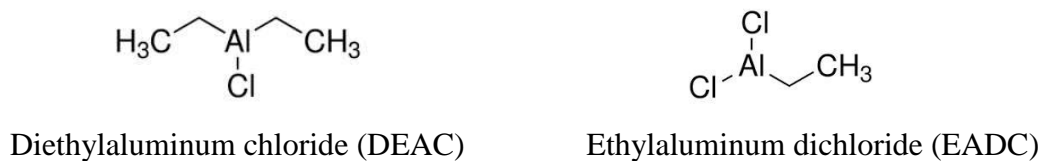
Figure 4.11 Structures of DEAC and EADC

Considering the structure of DEAC and EADC are shown in Figure 4.11, it was found the difference in number of ethyl and chloride ligands coordinates to the Lewis acidic aluminum center. In general, the replacement alkyl group by chloride reduces the mobile nature of the remaining alkyl groups. On the other hand, the Lewis acidity of aluminum is more enhanced by halide substitution than by alkyl substitution [41]. A combination of DEAC and EADC with suitable molar ratio may affect the crystal structure of $MgCl_2$ support leads to the suitable dispersion of Ti species and the active catalyst. However, using of single DEAC showed the highest catalytic activity. Almeida et al. [53] discussed in his work and reported that the presence of chlorine atoms in the structure of chlorotrimethylsilane $Cl(CH_3)_3Si$ and dichlorodimethylsilane $Cl_2(CH_3)_2Si$ affect in $MgCl_2$ surface defects.

Figure 4.12 shows surface and porosity of the synthesized catalysts using different molar ratio of DEAC/EADC from SEM characterization. It was presented that effect of different molar ratio of DEAC/EADC on surface, porosity and particle size of catalysts was not significantly.
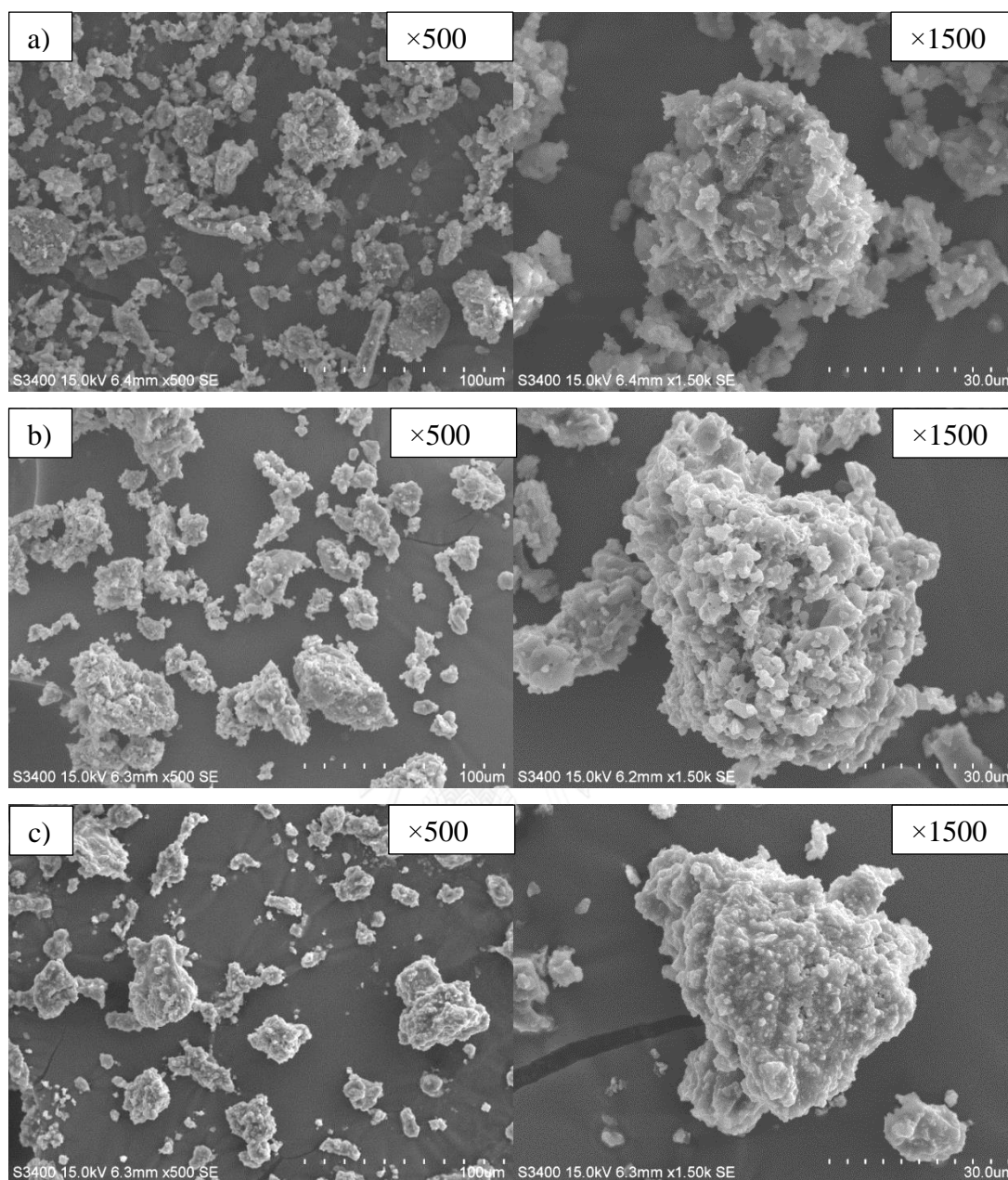
Figure 4.12 The morphology of catalysts with different molar ratio of DEAC/EADC
mixture; a) 3.00/0.00, b) 2.25/0.75, c) 1.50/1.50, d) 0.75/2.25 and e) 0.00/3.00

Figure 4.12 (cont.) The morphology of catalysts with different molar ratio of
DEAC/EADC mixture; a) 3.00/0.00, b) 2.25/0.75, c) 1.50/1.50, d) 0.75/2.25 and
e) 0.00/3.00

4.3 The TiCl$_4$/MgCl$_2$/THF catalytic systems

In this part, THF is the type of Lewis base, which was used in the preparation step to form molecular adduct to improve the surface of MgCl$_2$ support before treatment with an excess of TiCl$_4$. In the current, although alcohol is used as Lewis base greater, there are many researchers reported that the use of THF is easy to low cost, can control of polymer morphology 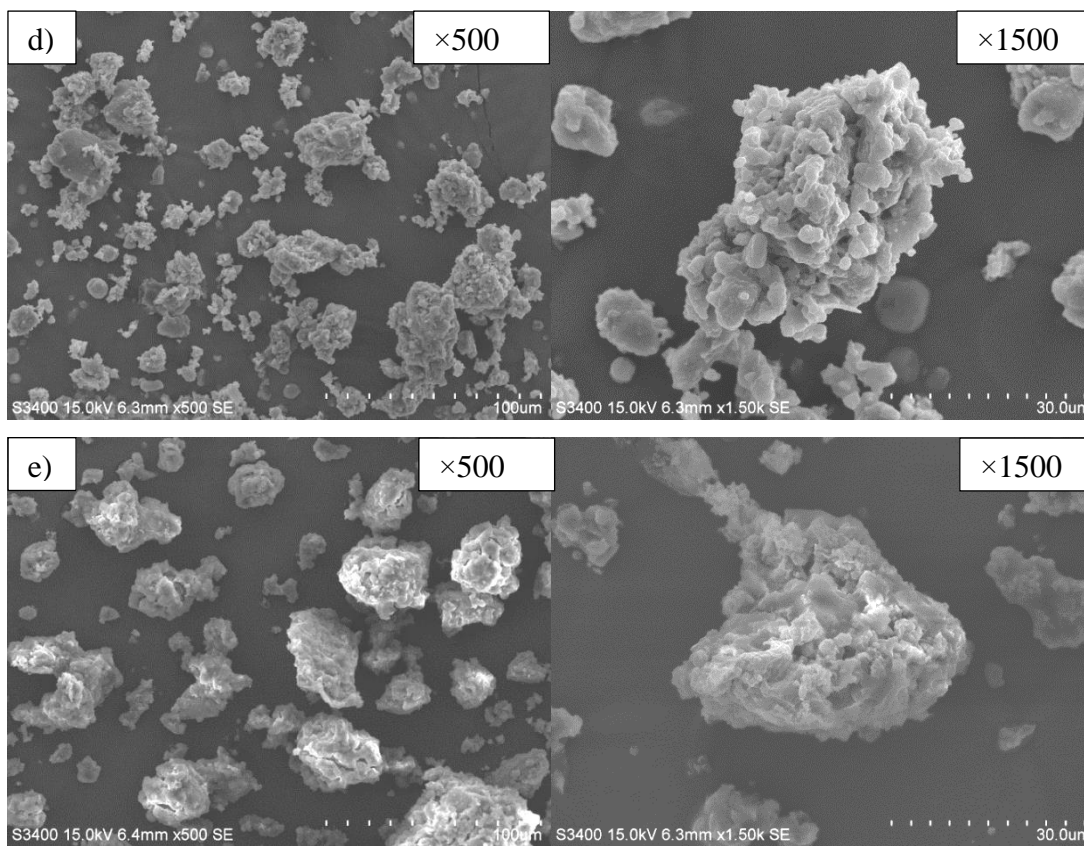and show good hydrogen response ability [71, 72]. Moreover, there are many researches that studied to improve the TiCl$_4$/MgCl$_2$/THF catalytic system [44, 73]. So, the TiCl$_4$/MgCl$_2$/THF catalytic system is one of the important ZN catalysts for the production of polyethylene. However, the remaining THF in the final catalyst leads to a decrease in catalytic activity because the excess of THF may poison the catalyst sites [15]. So, the removal of THF is very crucial for preparation of the catalyst.

In our previous research, the addition of mixed metal chlorides (Lewis acid) such as ZnCl$_2$/SiCl$_4$ could remove the THF in catalyst better than the single metal chloride. Thus, it leads to remarkably enhance the catalytic activity both in homo- and co- polymerization [50, 51]. Therefore, in this part, we focused on the removal of THF in MgCl$_2$·THF structure with various metal chlorides (CaCl$_2$, FeCl$_2$ and ZnCl$_2$) used in combination with AlCl$_3$. Since the presence of AlCl$_3$ in the TiCl$_4$/MgCl$_2$ could change the active center distribution resulting in the formation of more active center leading to an influence on performance of the catalyst and polymer properties [74, 75].

The abbreviations of synthesized catalysts were listed in Table 4.12.

Table 4.12 The abbreviation of catalyst

Catalysts	Abbreviation
TiCl$_4$/MgCl$_2$/THF [50]	None
TiCl$_4$/MgCl$_2$/THF/AlCl$_3$	None-Al
TiCl$_4$/MgCl$_2$/THF/AlCl$_3$+CaCl$_2$	Ca-Al
TiCl$_4$/MgCl$_2$/THF/AlCl$_3$+FeCl$_2$	Fe-Al
TiCl$_4$/MgCl$_2$/THF/AlCl$_3$+ZnCl$_2$	Zn-Al

The total element content in catalysts such as Ti, Mg, Ca, Fe, Zn and Al upon various mixed metal chlorides is listed in Table 4.13. The external surface compositions of all catalyst were approximated by EDX technique, as shown in Table 4.13. The results showed that None-Al exhibited the highest of Ti content on surface because $AlCl_3$ can provide small particle size, high surface area, high porosity and high disorder structure of $MgCl_2$ [76]. The Fe-Al catalyst exhibited the highest of Ti content for various mixed metal chloride. Comparison with ICP technique, it was observed that the Ti content in the bulk for Fe-Al is the lowest suggesting that Fe-Al catalyst is mostly contained Ti atoms located on the catalyst surface. Conversely, in the Zn-Al catalyst, most Ti atoms were located in the catalyst pores. However, None-Al showed the highest Ti atoms located on the catalyst surface.

Table 4.13 The element content and catalytic activity of catalysts

Catalysts	Element content in bulk[a] (wt %)				Ti on surface[c]
	Ti	Mg	Mx[b]	Al	(wt %)
None-Al	3.82	5.13	-	0.17	13.05
Ca-Al	3.70	6.09	0.92	0.55	10.26
Fe-Al	3.44	3.26	3.74	0.58	11.17
Zn-Al	4.28	6.12	1.43	0.59	9.51

[a] Results from ICP

[b] Mx refer to Ca, Fe and Zn

[c] Results from EDX

From our previous research [50], the XRD patterns of the $TiCl_4/MgCl_2/THF$ system shows peak of the $MgCl_2/THF$ complex at $2\theta = 10.4$, 20.2 and 32.3°, the $TiCl_4/THF$ complex at $2\theta = 11.1$ and 13.2°, and $TiCl_3/THF$ complexes at $2\theta = 12.2$, 16.7, and 16.9°. Moreover, $TiCl_4/MgCl_2/THF$ complex shows peaks around $2\theta = 11.5$ and 18.3°. Figure 4.13 shows the XRD patterns of catalysts with different addition of mixed metal chlorides. It was found that for the Fe-Al catalyst, the intensity of XRD patterns involving with structure of THF complex apparently decreased indicating that the THF in the structure of $TiCl_4/MgCl_2/THF$ complex could be better removed by

adding the Fe-Al. However, the XRD cannot detect the metal in catalyst due to its crystallite sizes are smaller than 3 nm.
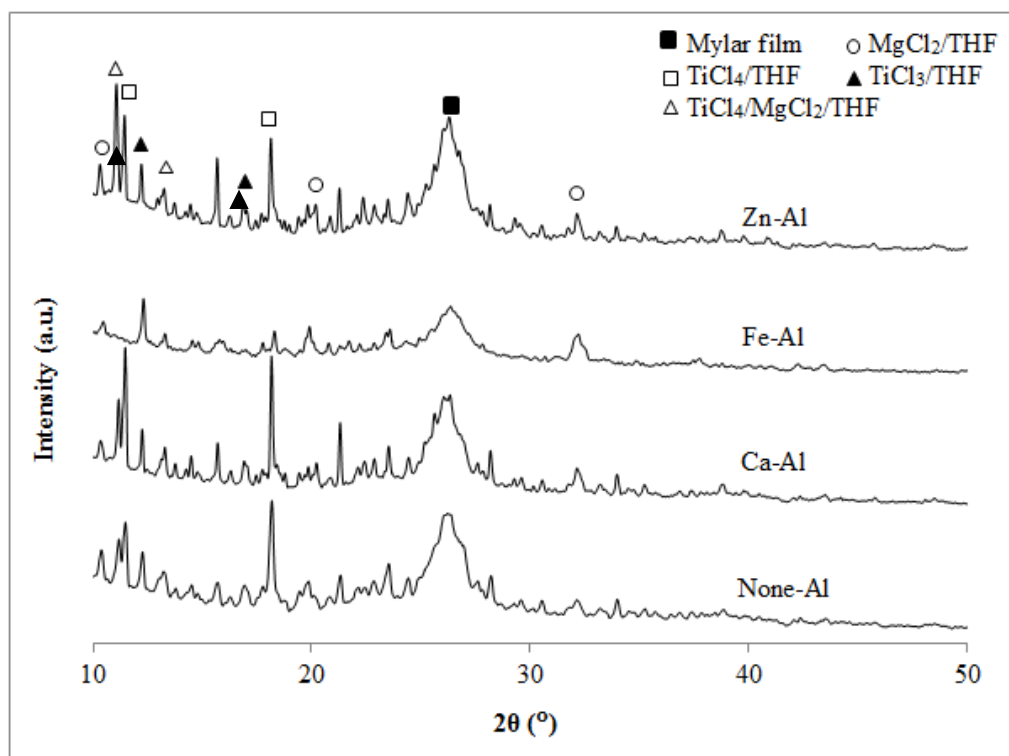
Figure 4.13 The XRD patterns of Ca-Al, Fe-Al and Zn-Al catalysts.

Figure 4.14 shows the absorption bands of THF examined by FT-IR technique. In general, a symmetrical and an asymmetrical C–O–C stretching band of THF is around 913 cm^{-1} and 1071 cm^{-1}, respectively [77, 78]. However, after mixed metal chloride was introduced into the catalyst, the IR peaks of the C–O–C stretching bands of THF were slightly shifted from 913 cm^{-1} to 872 cm^{-1} and from 1071 cm^{-1} to 1020 cm^{-1} as a result of the strong Lewis acidity of Ti and Mg [77]. These results are also similar with those reported by Chu et al. [78], Kim [77], Pirinen et al. [72] and Phiwkliang et al. [51]. The FT-IR results were corresponding to the XRD results which indicated that THF was partially removed from the structure of MgCl$_2$/THF complex by the modification of mixed metal chlorides. It is clear that the Fe-Al catalyst displays the most efficiency in removal of THF, while in the Ca-Al catalyst, the removal of THF is the lowest.
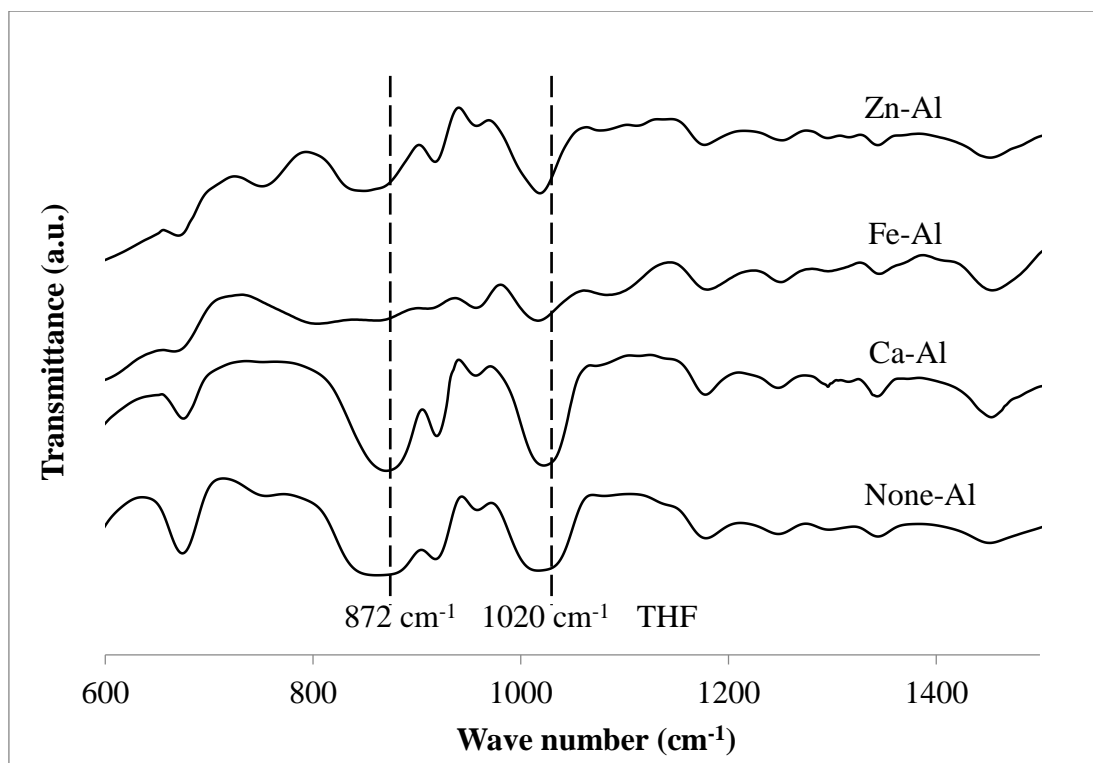
Figure 4.14 The FT-IR patterns of Ca-Al, Fe-Al and Zn-Al catalyst

The catalytic activity for ethylene polymerization with various mixed metal chlorides in $TiCl_4/MgCl_2/THF$ catalysts is shown in Table 4.15. The results show that the catalytic activity increases in order of Fe-Al > Zn-Al > Ca-Al > None-Al. All catalysts provide the higher activity than the unmodified one from our previous research [50]. The modification of $AlCl_3$ and $FeCl_2$ in $TiCl_4/MgCl_2/THF$ catalyst provides the highest activity because Fe-Al had an efficiency to remove higher amount of THF, which can be confirmed by XRD and FT-IR. Comparison for electronegativity (EN) values of Ca, Fe and Zn, they are 1.04, 1.64 and 1.66, respectively. Although EN values of Fe is as high as Zn, the radius of Fe^{2+} (0.61 Å) is closer to Mg^{2+} (0.65 Å) than Zn^{2+} (0.74 Å) and Ca^{2+} (0.99 Å). Therefore, the compatibility efficiency of $FeCl_2$ with $MgCl_2$ could be better than of $ZnCl_2$ or $CaCl_2$ with $MgCl_2$. This reason suggested the co-addition of $AlCl_3$ and $FeCl_2$ resulting in higher THF removal. These results also accord with work of Jiang et al., the selection between LiCl and NaCl to doping in $MgCl_2$. LiCl was selected as a doping agent because the radius of Li^+ (0.60 Å) is closer to Mg^{2+} (0.65 Å) than Na^+ (0.95 Å). Therefore, the compatibility of LiCl and $MgCl_2$ could be better than that of NaCl and

MgCl$_2$ [25]. However, the Ca-Al catalyst provides the lowest activity because the remaining THF may poison the catalyst sites which leads to the catalyst deactivation [15].

Table 4.14 The effect of mixed metal chlorides on catalytic activity for ethylene polymerization and polymer properties

Catalysts	Activity	Polymer properties	
	(kg PE/mol Ti h)	T$_m$ (°C)	%χ$_c$[a]
None [50]	406	134	53
None-Al	903	132	55
Ca-Al	979	131	54
Fe-Al	1476	132	54
Zn-Al	1009	130	52

[a] $\chi_c = [\Delta H/(\Delta H°)] \times 100$ [51]

The melting point (T$_m$), percentage of crystallinity (%χ$_c$) and density of polyethylene obtained were analyzed by DSC techniques as shown in Table 4.14. It shows that these properties are similar. Therefore, the modification of TiCl$_4$/MgCl$_2$/THF catalyst system with various metal chlorides did not significantly affect the thermal behavior of polyethylene. The morphology of catalyst was also showed in Figure 4.15.
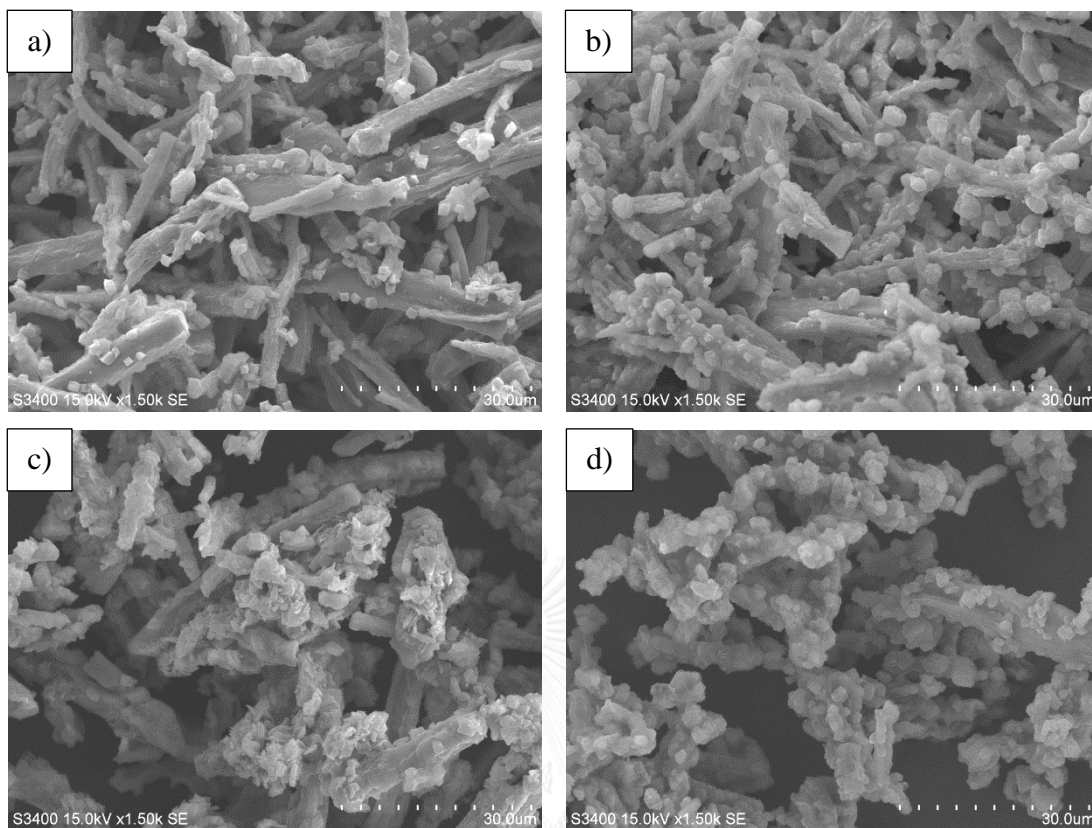
Figure 4.15 The morphology of catalyst in TiCl$_4$/MgCl$_2$/THF system;

a) None-Al,   b) Ca-Al, c) Fe-Al and d) Zn-Al

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 The TiCl$_4$/MgCl$_2$/EtOH catalytic systems

In this part, ethanol is the type of Lewis base which was used to prepare MgCl$_2$·6EtOH adduct. The results indicated that ethanol destroyed structure of layers of MgCl$_2$ led to the rough surface and an increase of surface area. An alkylaluminum chloride compound such as DEAC, EADC and its mixture were used to remove of ethanol in the adduct structure before impregnation with TiCl$_4$. The molar ratio of DEAC/MgCl$_2$ in range from 2.0 to 3.3 was studied. Increasing the amount of DEAC led to reaction between DEAC and ethanol is more; makes removal of ethanol is greater. Thus, Ti content was increased with an increase of DEAC/MgCl$_2$ molar ratio. However, the surface areas in the catalyst became decreased due to the strong reaction of TiCl$_4$ and the remaining ethanol with highly exothermic reaction at 80 °C. For polymerization of ethylene, it showed that an increase of DEAC/MgCl$_2$ molar ratio from 2.0 to 2.7, the activity was increased with an increase of Ti content. But when the molar ratio of DEAC/MgCl$_2$ was 3.0 or more, it was found that the activity decreased because Ti species were reduced with the large amount of DEAC and over-reduction when it reacted with TEA. The results of the amount of Ti^{3+} species that was approximated from ESR, also related to the catalytic activity.

The synthesis of catalysts with different molar ratio of TiCl$_4$/MgCl$_2$ in range of 0.87 to 4.44 was also studied. In experiment, the molar ratio of DEAC/MgCl$_2$ was fixed as 3.0, it was found that Ti content was increased with an increase of TiCl$_4$/MgCl$_2$ molar ratio This is because a partial of TiCl$_4$ would react with remaining EtOH in the prepared support and another partial TiCl$_4$ would impregnate on catalyst in order to active phase. For polymerization of ethylene, an increase of TiCl$_4$/MgCl$_2$ molar ratio from 0.87 to 1.73, the activity was increased with an increase of Ti content. However, increasing greater of the molar ratio of TiCl$_4$/MgCl$_2$, it was found that the catalytic activity was decrease. It means that the Ti species were not all active. It was also found that the amount of Ti^{3+} species related to the catalytic

activity except for molar ratio of TiCl$_4$/MgCl$_2$ as 4.33. This may be due to the effect of different Ti^{2+}.

In comparison between using different molar ratio of DEAC/MgCl$_2$ and TiCl$_4$/MgCl$_2$, it was observed that the catalyst with Ti content around 7.5 − 7.8 %wt exhibited the highest catalytic activity. This is due to the suitable elimination of the ethanol or Lewis base from adducts can provide a good support and affect the crystal structure leading to very active in the polymerization catalysis

For the effect of different molar ratio of DEAC/EADC mixture, it was found that Ti content decreased with the increase of EADC molar ratio This is because DEAC can react with ethanol in structure of MgCl$_2$/EtOH adducts stronger than EADC. The using of single DEAC indicated the catalytic activity higher than using of single EADC due to the higher Ti content of using of single DEAC. For in case of DEAC and EADC, it were mixed with different molar ratio, the result become a surprising. It was found that the activity is not increased by increasing the Ti content. But at molar ratio of DEAC/EADC = 0.75/2.25, the activity was high, while at molar ratio of DEAC/EADC = 2.25/0.75 the activity was lowest. However, the amount of Ti^{3+} species also related to the catalytic activity. A combination of DEAC and EADC with suitable molar ratio may affect the crystal structure of MgCl$_2$ support leads to the suitable dispersion of Ti species and the active catalyst.

In addition, the polyethylene properties which different Lewis base and molar ratio affect the melt index but did not affect the thermal behavior of polyethylene.

5.1.2 The TiCl$_4$/MgCl$_2$/THF catalytic systems

In this part, THF is type of Lewis base which was used to prepare the MgCl$_2$/THF adduct. However, the remaining THF in the final catalyst led to decrease in catalytic activity because the excess THF may poison the catalyst sites. So, the removal of THF is very crucial for preparation of the catalyst. Therefore, in this part, we focused on the removal of THF in MgCl$_2$·THF structure with various metal chlorides such as AlCl$_3$, CaCl$_2$, FeCl$_2$ and ZnCl$_2$. The results showed that None-Al exhibited the highest of Ti content on surface because AlCl$_3$ can provide small particle size, high surface area, high porosity and high disorder structure of MgCl$_2$. For in case of mixed metal chlorides, the results from EDX showed that Fe-Al

catalyst exhibited the highest of Ti content on surface. Comparison with ICP technique, it was observed that the Ti content in the bulk is the lowest suggesting that Fe-Al catalyst is mostly contained Ti atoms located on the catalyst surface. For the catalytic activity for ethylene polymerization, it showed that the catalytic activity increased in order of Fe-Al > Zn-Al > Ca-Al > None-Al. The modification of $AlCl_3$ and $FeCl_2$ provides the highest activity because Fe-Al had an efficiency to remove higher amount of THF, which can be confirmed by XRD and FT-IR. This may be due to high electronegativity values of Fe and the radius of Fe^{2+} (0.61 Å) is which close to Mg^{2+} (0.65 Å) than Zn^{2+} (0.74 Å) and Ca^{2+} (0.99 Å). Moreover, the modification did not affect the thermal behavior of polyethylene.

5.2 Recommendations

1. The dispersion of surface Ti species in catalyst is one of the important factors that affect the catalytic activity. The dispersion of $TiCl_4$ by the different Ti content in the catalyst, where the lower Ti content leads to more isolated Ti species (each Ti species existed on the $MgCl_2$ surface in single Ti active center manner), whereas the higher Ti content gives more aggregated Ti species (the Ti-Ti interaction) which some called as clustered Ti species. [79-81]. Moreover, the isolated Ti species relate to an aspecific species, while the clustered Ti species relate to an isospecific species in propylene polymerization [82]. In work of Taniike et al. [81], the aggregation of the Ti species significantly reduced in ethylene polymerization activities, and was identified as one of the major deactivation mechanisms. However, it is difficult to clearly explain because both Ti^{3+} and Ti^{2+} affect the catalytic activity of ethylene polymerization. To confirm these effects, it should be characterized or studied to compare in the propylene polymerization.

2. The activity from the effect of different DEAC/EADC molar ratio is still open discuss and should be taken into consideration later.

3. The modification of metal chloride may as guidelines to study to improve for the $TiCl_4/MgCl_2$/alcohol catalyst system.

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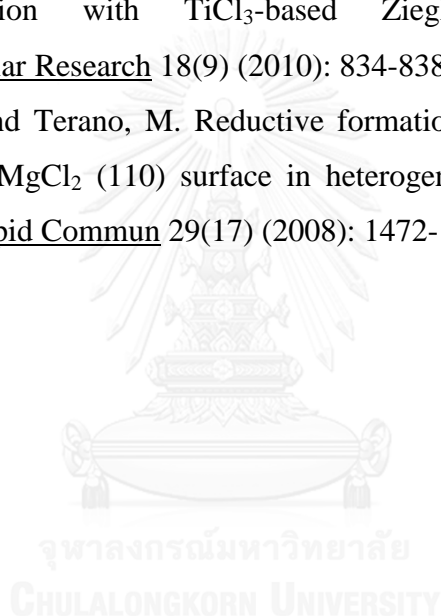
APPENDIX

APPENDIX A

THE RESULTS RFOM ESR

The ESR was used to characterize the amount of Ti^{3+} species in the synthesized catalyst. Figure A.1 showed peaks of ESR in case of catalyst not reacted with TEA. At molar ratio of $DEAC/MgCl_2$ as 3.3 presented the highest peak because it was reduced with the large amount of DEAC.

When the catalyst reacted with TEA (Figure A.2 – A.4), it can be seen that the amount of Ti^{3+} species exhibited peak with relative g value equal to 1.965 and 1.956 in all catalysts. It was noted that several g-values of Ti^{3+} species indicated heterogeneity of catalyst sites (multiple active site catalysts) [15]. The g values equal to 1.965 are assigned to the tetrahedral coordination of Ti^{3+} [64].
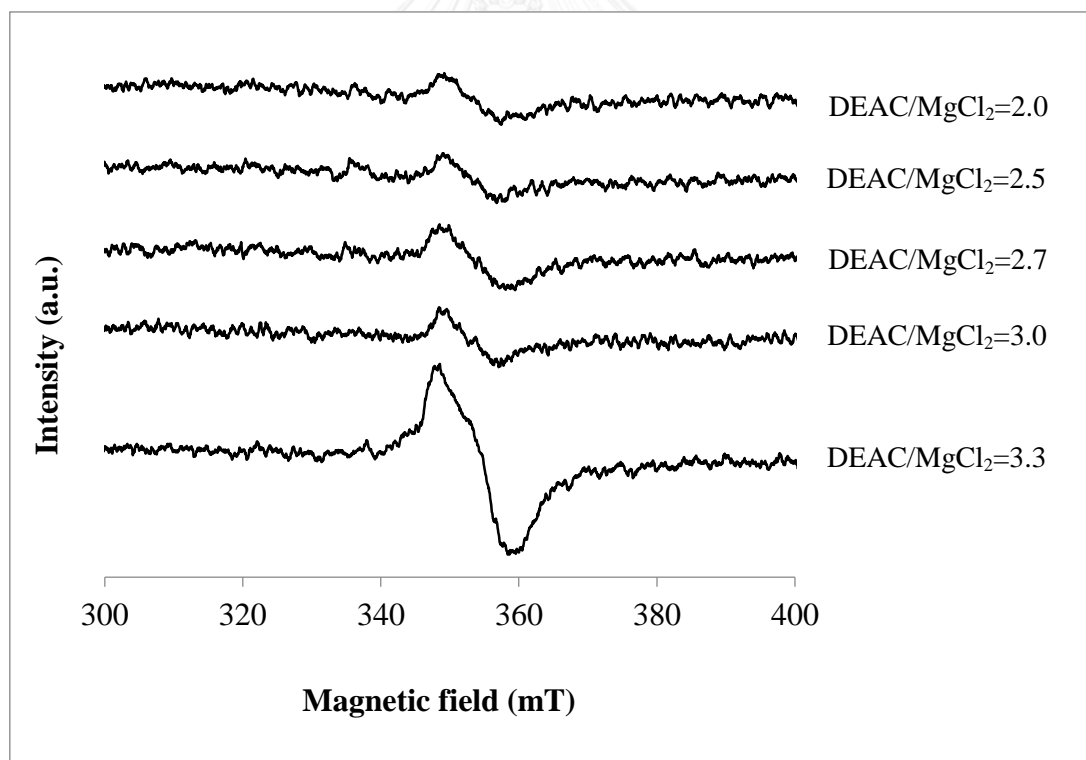

Figure A.1 The effect of Ti^{3+} before catalysts (vary the $DEAC/TiCl_4$) react with TEA
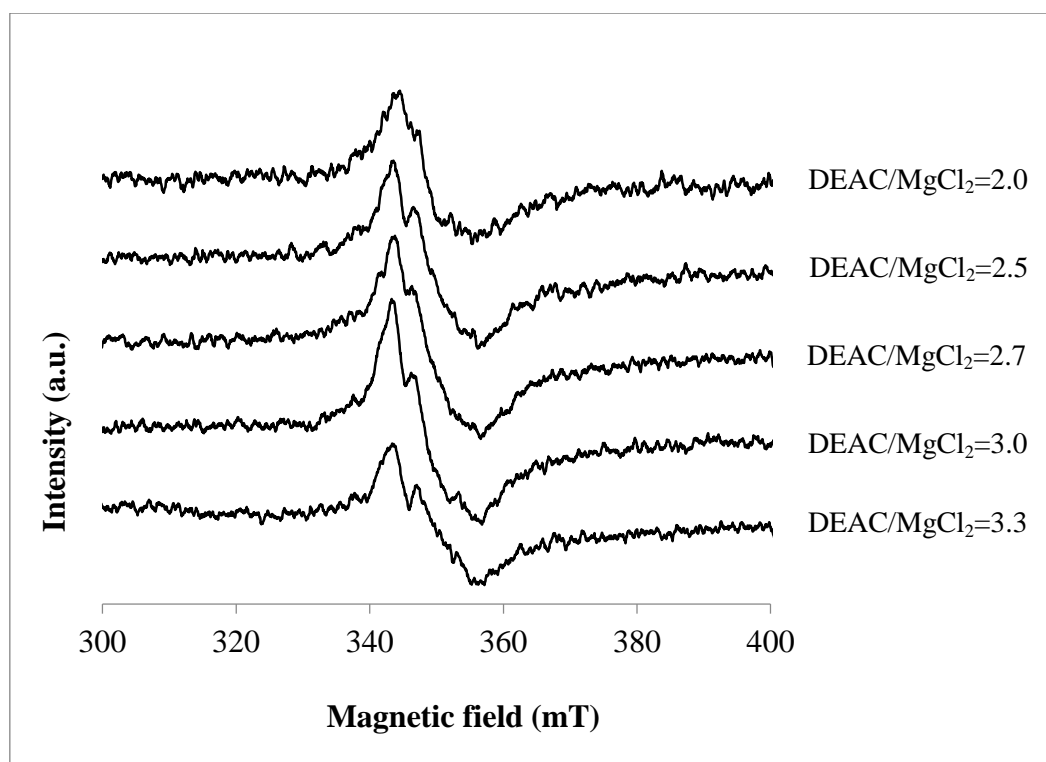
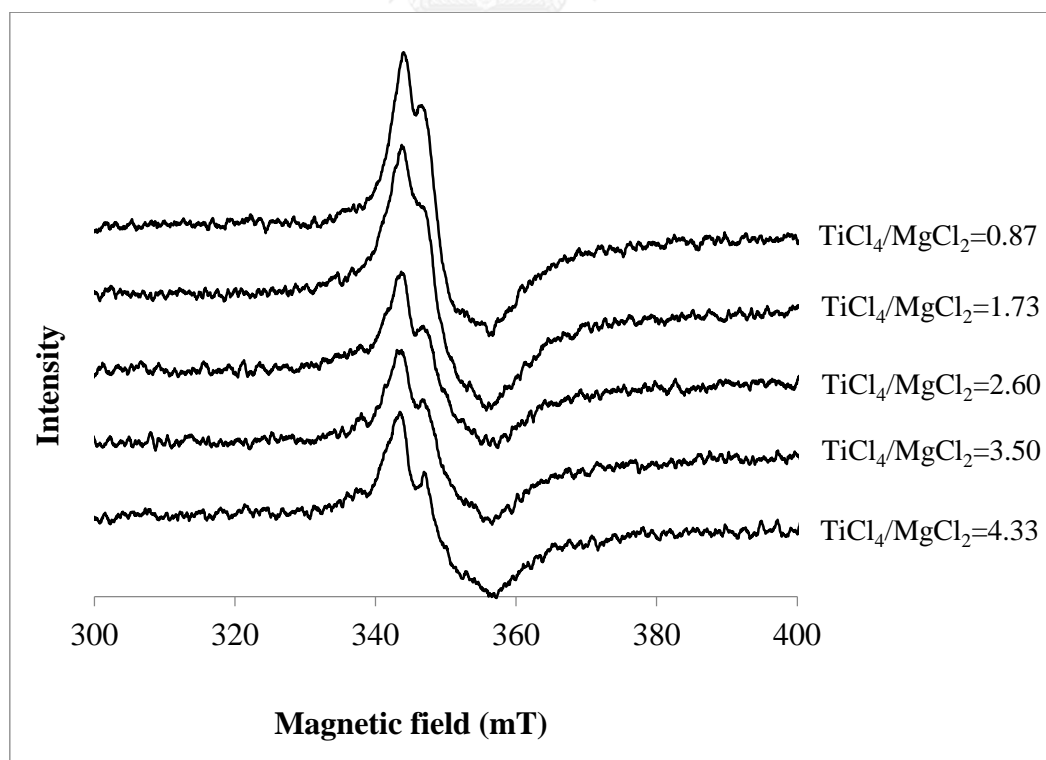**Figure A.2** The effect of Ti^{3+} after catalysts (vary the $DEAC/MgCl_2$) react with TEA

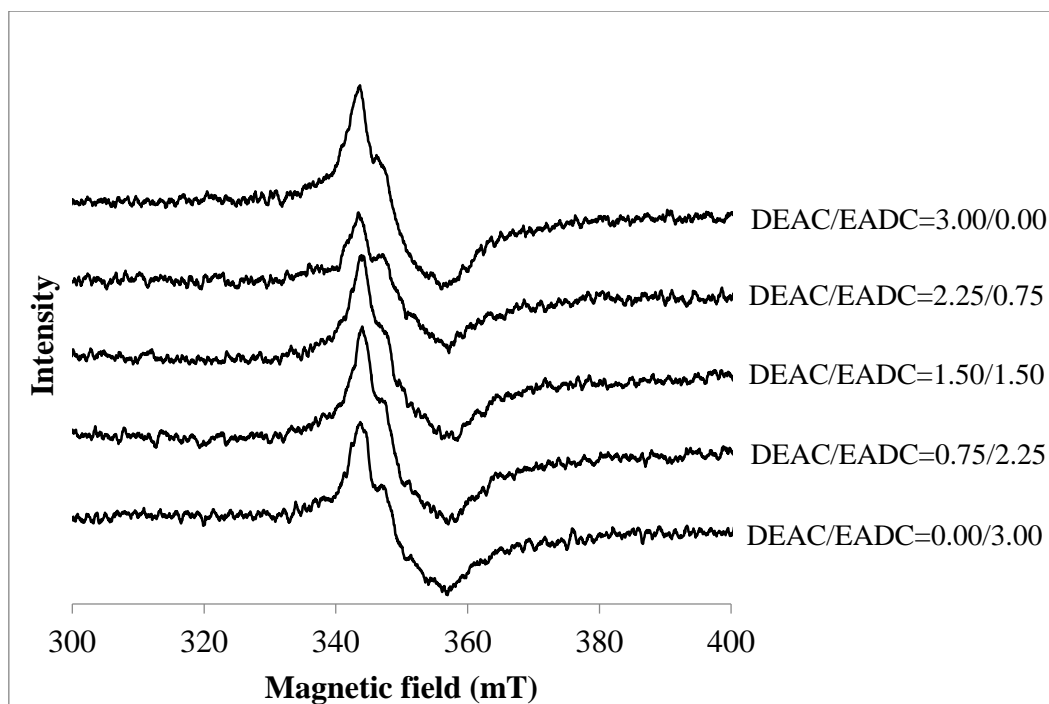**Figure A.3** The effect of Ti^{3+} after catalysts (vary the $TiCl_4/MgCl_2$) react with TEA

Figure A.4 The effect of Ti^{3+} after catalysts (vary the DEAC/EADC) react with TEA

The calculation of ESR peak

Simpson's rule is a method for numerical integration, the numerical approximation of definite integrals. It was applied to find the area under the graph from ESR results, the example as shown in Figure D.1.

$$\int_a^b f(x)dx \approx \frac{h}{3}\left[f(x_0)+4f(x_1)+2f(x_2)+4f(x_3)+f(x_4)+...+4f(x_{4-1})+f(x_n)\right]$$

where $h = \dfrac{b-a}{n}$, $x_0 = a$ and $x_n = b$

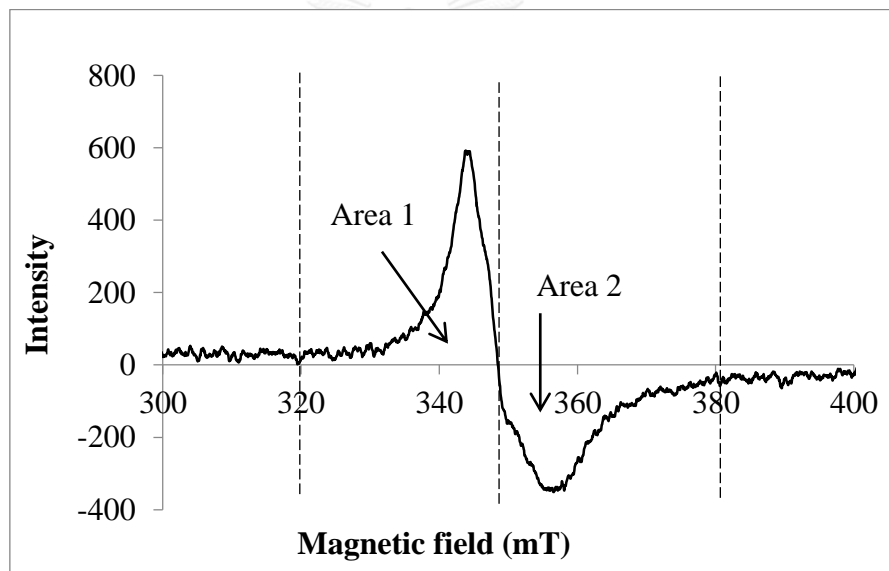Area = Area 1 + Area 2

Figure A.5 The graph from ESR result

APPENDIX B

THE RESULTS OF EFFECT OF DIFFERENT DEAC/EADC MOLAR RATIO

The results from XRD

The synthesized catalyst was characterized by XRD technique as shown in Figure B.1. It was observed that the final catalysts show the position of board peak of δ-MgCl$_2$, meaning the formation of a crystal is low.
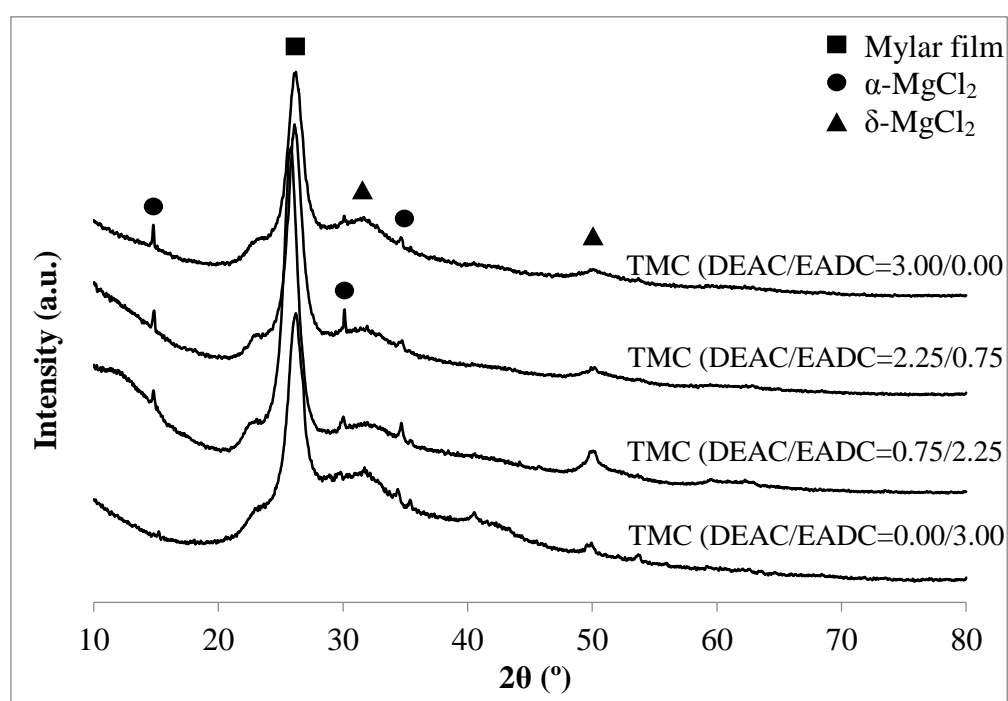

Figure B.1 The XRD patterns of the synthesized catalyst using different molar ratio of DEAC/EADC

The effect of different molar ratio of DEAC/EADC on polymer properties

The polymer properties of using the different molar ratio of DEAC/EADC in synthesis of catalyst were showed in Table B.2. It showed that slightly affected for MI except in molar ratio of DEAC/EADC = 2.25/0.75 which showed the highest MI. For density and degree of crystallinity (χ_c), it does not observe any significant change. While the melting temperature (T_m) was slightly change.

Table B.1 Effect of different molar ratio of DEAC/EADC on polymer properties

DEAC/EADC (molar ratio)	MI (2.16) (g/10min)	T_m °C	χ_c %
3.00/0.00	0.965	136	69
2.25/0.75	1.804	137	64
1.50/1.50	0.873	135	61
0.75/2.25	1.110	136	63
0.00/3.00	1.186	135	53

APPENDIX C
LIST OF PUBLICATIONS

Poster: <u>Nittaya Sudsong</u>, Wanna Phiwkliang and Piyasan Praserthdam "Effects of various mixed metal chlorides-$AlCl_3$ in Ziegler-Natta catalyst for ethylene polymerization". Asian Polyolefin Workshop 2013 (APO 2013), Beijing, China, October 15-19, 2013.

VITA

Miss Nittaya Sudsong was born on June 26, 1989 in Nakhon Si Thammarat, Thailand. She graduated with a Bachelor's degree on the major of Chemical Engineering, Faculty of Engineering from Srinakharinwirot University with GPA 3.23 in June, 2012. Afterward she has continued her study in Master's degree, majoring in Chemical Engineering at Chulalongkorn University and joined the Center of Excellence on Catalysis and Catalytic Reaction Engineering in October, 2012.