

ตัวเร่งปฏิกิริยาเอโฟโอบนตัวรองรับแมกนีเซียมคลอไรด์ที่ถูกกระตุ้นด้วยทีเอ็มเอสำหรับพอลิเมอร์ไรเซชันของเอทีลิน

นางสาวธัญพร พงษ์จันทร์



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)

เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

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คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2559

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

MgCl₂-
SUPPORTED FI CATALYST ACTIVATED WITH TMA FOR ETHYLENE POLYMERIZATION

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2016

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Thesis Title MgCl₂-SUPPORTED FI CATALYST ACTIVATED WITH
TMA FOR ETHYLENE POLYMERIZATION
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Field of Study Chemical Engineering
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ฉันทพร พงษ์จันทร์ : ตัวเร่งปฏิกิริยาเอพไออบนตัวรองรับแมกนีเซียมคลอไรด์ที่ถูกกระตุ้นด้วยทีเอ็มเอสำหรับพอลิเมอร์ไรเซชันของเอทิลีน (MgCl₂-SUPPORTED FI CATALYST ACTIVATED WITH TMA FOR ETHYLENE POLYMERIZATION) อ.ที่ปรึกษาวิทยานิพนธ์
หลัก: ศ. ดร.บรรเจิด จงสมจิตร, 101 หน้า.

ในวิทยานิพนธ์ฉบับนี้ได้ทำการศึกษาเกี่ยวกับการสังเคราะห์ของตัวเร่งปฏิกิริยาแบบมีตัวรองรับ ซึ่งสามารถทำปฏิกิริยากับไตรเมทิลอะลูมิเนียม (ทีเอ็มเอ) ที่กระจายตัวอยู่บนแมกนีเซียมคลอไรด์เอทานอลแอตดัก (หมู่แอลกอฮอล์) เป็นสิ่งสำคัญสำหรับการปรับปรุงค่าความว่องไวจากการพอลิเมอร์ไรเซชันของเอทิลีน ดังนั้นในการศึกษานี้อัตราส่วนที่เหมาะสมของทีเอ็มเอและแมกนีเซียมคลอไรด์เอทานอลแอตดักได้รับการยืนยันเพื่อผลิตพอลิเอทิลีนมวลโมเลกุลสูง โดยใช้ตัวเร่งปฏิกิริยาฟีนอกซีอิมินที่มีองค์ประกอบของไทเทเนียม (ตัวเร่งปฏิกิริยาเอพไอ) นำมาใช้กับตัวเร่งปฏิกิริยาร่วมคือ ทีเอ็มเอ สำหรับส่วนที่หนึ่ง อัตราส่วนที่เหมาะสมของแมกนีเซียมคลอไรด์ต่อเอทานอลคือ 1:6 อย่างไรก็ตามปริมาณของทีเอ็มเอในหลายอัตราส่วนได้รับการศึกษาและพบว่าอัตราส่วนของแมกนีเซียมคลอไรด์ต่อเอทานอลต่อทีเอ็มเอที่เหมาะสมคือ 1:6:6.3 ซึ่งมีค่าความว่องไวสูงที่สุด จึงนำอัตราส่วนของแมกนีเซียมคลอไรด์ต่อเอทานอลต่อทีเอ็มเอที่ดีที่สุดมาใช้ในส่วนถัดไป ในส่วนที่สอง ศึกษาเกี่ยวกับการเติมของสารทำให้เกิดการเชื่อมโยง (คลอสลิงกิ้งเอเจนต์) ถูกศึกษาเพื่อปรับปรุงคุณสมบัติแมกนีเซียมคลอไรด์ที่ถูกรองรับด้วยตัวเร่งปฏิกิริยาเอพไอ พบว่าการเติมกลีเซอรอลสามารถควบคุมมวลโมเลกุลของพอลิเมอร์ได้เป็นพอลิเอทิลีนมวลโมเลกุลสูง ซึ่งใกล้เคียงกับการใช้ตัวเร่งปฏิกิริยาเอพไอเพียงอย่างเดียว แต่อย่างไรก็ตามการเติมคลอสลิงกิ้งเอเจนต์มีค่าความว่องไวสูงกว่าตัวเร่งปฏิกิริยาเอพไอที่ปราศจากตัวคลอสลิงกิ้งเอเจนต์

ภาควิชา วิศวกรรมเคมี

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ปีการศึกษา 2559

5870166121 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: MAGNESIUM CHLORIDE, TMA, ETHYLENE POLYMERIZATION, FI CATALYST, CROSS-LINKING AGENTS

THANYAPORN PONGCHAN: MgCl₂-SUPPORTED FI CATALYST ACTIVATED WITH TMA FOR ETHYLENE POLYMERIZATION. ADVISOR: PROF.BUNJERD JONGSOMJIT, Ph.D., 101 pp.

In this study, the synthesis of heterogeneous catalyst, which can react with trimethylaluminum (TMA) dispersed on the MgCl₂:EtOH adduct (-OH group) is crucial to improve the ethylene polymerization activity. Therefore, in this study the proper molar ratios of TMA and MgCl₂:EtOH adduct was investigated to produce high molecular weight polyethylene (HMWPE). The phenoxy-imine Ti-based catalyst (FI catalyst) was employed using TMA as cocatalyst precursor. In the first part, the suitable molar ratios of MgCl₂/EtOH is 1:6. However, the amounts of TMA were varied and found properly at MgCl₂/EtOH/TMA ratio of 1:6:6.3 to obtain the highest activity. The optimum mole ratio of MgCl₂/EtOH/TMA was used in the next section. In the second part, the addition of cross-linking agents was studied to improve the MgCl₂-supported FI catalyst properties. It can be found that adding glycerol could control molecular weight of polymer to obtain HMWPE, which is similar to with only FI catalyst. However, it exhibited higher catalytic activity than the FI catalyst without cross-linking agent addition.

Department: Chemical Engineering Student's Signature

Field of Study: Chemical Engineering Advisor's Signature

Academic Year: 2016

ACKNOWLEDGEMENTS

First of all, I would like to be pleased a great consultant to my lovely advisor, Professor Dr. Bunjerd Jongsomjit, who accept me a welcome to be part in the member in the Ziegler-Natta and Metallocene group, give the best suggestion and useful help in every step. Moreover, I would like to sincere thank Professor Dr. Piyasan Prasertthdam for teaching about all in laboratory.

Next, I would also be sincere to Assistant Professor Dr. Suphot Phantasri as the chairman, Dr. Chutimon Satirapipathkul, Dr. Sasiradee Jantasee for serving as the committee members. I sincerely thanks to Dr. Supaporn Khubunsongserm from PTT public Co., Ltd. for the valuable helping and kindly guidance the knowledge for more understanding in the synthesis of supported catalysts and ethylene polymerization throughout my research.

Furthermore, the author gratefully acknowledge all experimental support by PTT Research and Technology Institute (PTT RTI) during I studied this research.

Many thanks for all members in Ziegler-Natta and Metallocene group and all my friend in Center of Excellent on Catalysis and Catalytic reaction Engineering for relationship, and helpful to me during the research.

Finally, I would like to greatly thank to my beloved family for supporting and encouragement in my life all the time.

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CHAPTER 1

INTRODUCTION

1.1 General introduction

Polyethylene can be produced through ethylene polymerization by using the suitable catalyst. For olefin polymerization process, there are many types of catalyst. Mostly they are three types of catalyst used, including Ziegler-Natta, metallocene, and post-metallocene catalysts [1]. One of them is the FI (Fujita Inventor) catalyst that can be used for olefins polymerization. It was found by Fujita et al [2-7]., they have successfully published highly active Ti/Zr catalyst using various phenoxy-imine ligands, Ti-, Zr-, V-based FI catalyst [8-10]. Furthermore, the FI catalyst is developed to increase performance by adding co-catalyst for changing oxidation state of metal in active form. FI catalyst with co-catalysts can improve the quality and properties of polymer which are into species of polymer types such as ultra-high molecular weight polyethylene (UHMWPE) and high molecular weight polyethylene (HMWPE). From the above, this process is named “homogeneous system”. The use of FI catalyst on homogeneous system without support is very easy to synthesize the catalyst because it is not required to use support and impregnation. However, the problem of homogeneous system is on the polymer morphology that always appears as fine particles and it has much fouling around stirrer.

Generally, the ethylene polymerization is preferred in heterogeneous systems by adding the support into the FI catalyst to improve morphology and prevent fouling. This process, which is added supported catalyst, is called that “heterogeneous system”. This approach leads to use of support and the most common support as a single-site catalyst immobilization is silica. However, several groups have investigated the use of $MgCl_2$ support [11]. In previous study, $MgCl_2$ is used as a support, which can improve the poor polymer morphology and control particle size, porosity and fouling. However, using $MgCl_2$ support is famous among industries. So, in the new suitable way,

we can use the supported catalyst for the purpose of the control of polymer morphology. We must choose suitable co-catalyst with catalyst as well. The types of co-catalyst are important factors in polymerization process. Each co-catalyst has a different property that is based on cost and application such as combination of FI catalyst with methylaluminoxane (MAO) is expensive, but it gives a high performance [12]. Other example is co-catalysts such as trimethylaluminum (TMA), triethylaluminum (TEA), can also activate Zr-, Ti- based FI catalyst, but activity is relatively low. Almost, FI catalyst activated with MAO exhibits high efficiency, but it is expensive. In addition, Soga et al. [13, 14] have used $MgCl_2$ with a zirconocene catalyst for combination and AlR_3 to obtain polyolefins with suitable high polydispersity. More recently, Kissin et al. [13] used mixtures of MgR_2 to generate $MgCl_2$ and AlR_3 as co-catalyst components for olefin polymerization using various metallocenes. Thus, the alternative approach for good dispersion of $MgCl_2$ support involves in catalyst immobilization method such as adducts of $MgCl_2$ and ethanol. In previous study, Z. Guan et al. [14] investigated the spherical $MgCl_2$ -supported MAO pre-catalysts, which were prepared by using $MgCl_2 \cdot nEtOH$ adducts as support that obtained the polymers with spherical morphology having high bulk density. Therefore, the preparation of $MgCl_2 \cdot nEtOH$ adducts, which have -OH group by using trimethylaluminum (TMA) instead of MAO as co-catalyst is interesting because TMA reacts with -OH group and transforms into $MgCl_2 \cdot EtOH$ with MAO [15].

In this research, we purpose to develop effective methods for immobilizing the Ti-based FI catalyst on $MgCl_2$ support. The activated solid catalyst is tested in ethylene polymerization by immobilizing of FI catalyst onto $MgCl_2$ with high bulk density [8, 16]. Moreover, modification of $MgCl_2$ adduct is also investigated in order to control the quantity of the Ti- based FI catalyst adsorbed on $MgCl_2$ support and modified $MgCl_2$ using different adduct ratios and spacer groups, which are crosslinking-agents such as glycol, glycerol or triethanolamine.

1.2 Research objective

- 1) To investigate the characteristics and ethylene polymerization behaviors of synthesized Ti-based catalyst-supported on MgCl_2 .
- 2) To study the effect of $\text{MgCl}_2/\text{EtOH}/\text{TMA}$ ratios on catalytic properties and to increase the amount of FI catalyst adsorbed on MgCl_2 support using cross-linking agent.

1.3 Research scopes

- 1) Synthesis of FI catalyst supported on MgCl_2 by varying TMA at 1:6:6, 1:6:6.3 and 1:6:6.6 ($\text{MgCl}_2/\text{EtOH}/\text{TMA}$).
- 2) Perform ethylene polymerization: pressure of ethylene gas 1 bar, 450 rpm, time 30 minutes at 55 °C.
- 3) Determining the most suitable $\text{MgCl}_2/\text{EtOH}/\text{TMA}$ ratio with various temperatures of polymerization at 35, 45, 55, 65 and 75 °C.
- 4) Modification of the most suitable $\text{MgCl}_2/\text{EtOH}/\text{TMA}$ ratio, which gives the highest polyethylene yield, for adding cross-linking agents including glycol, glycerol and triethanolamine.
- 5) Perform ethylene polymerization: pressure of ethylene gas 1 bar, 450 rpm, time 30 minutes at 55 °C.
- 6) Characterization of the MgCl_2 and MgCl_2 -supported FI catalyst before polymerization of ethylene by the following methods;
 - Fourier transform infrared spectroscopy (FTIR)
 - Inductively coupled plasma (ICP)
 - Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

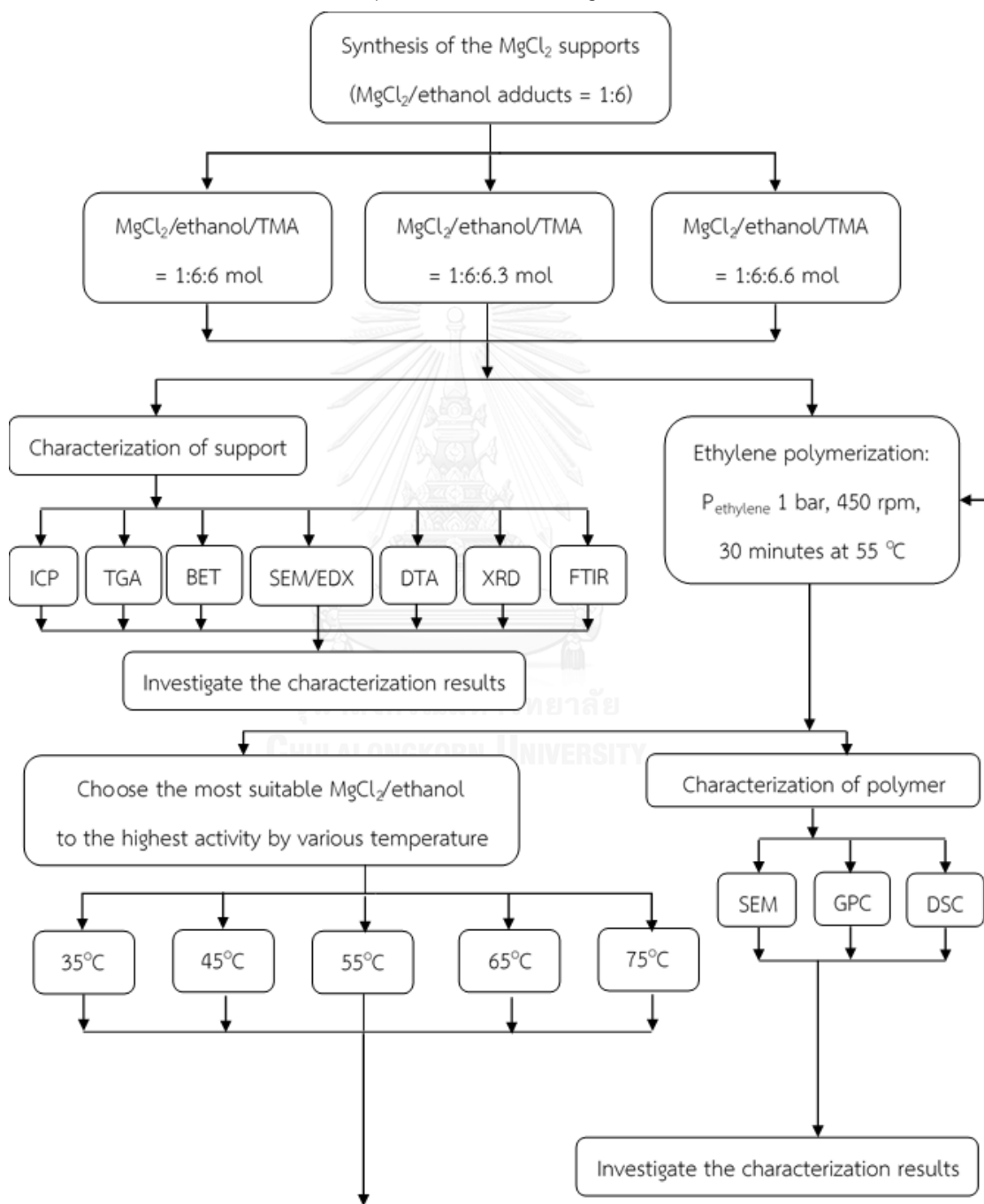
- N₂ physisorption
 - Thermo gravimetric analysis (TGA)
 - X-ray diffraction (XRD)
 - Differential Thermal Analysis (DTA)
 - Nuclear magnetic resonance spectroscopy (NMR)
- 7) Characterization of polymer by the following methods;
- Differential scanning calorimeter (DSC)
 - Gel permeable chromatography (GPC)
 - Scanning electron microscopy (SEM)



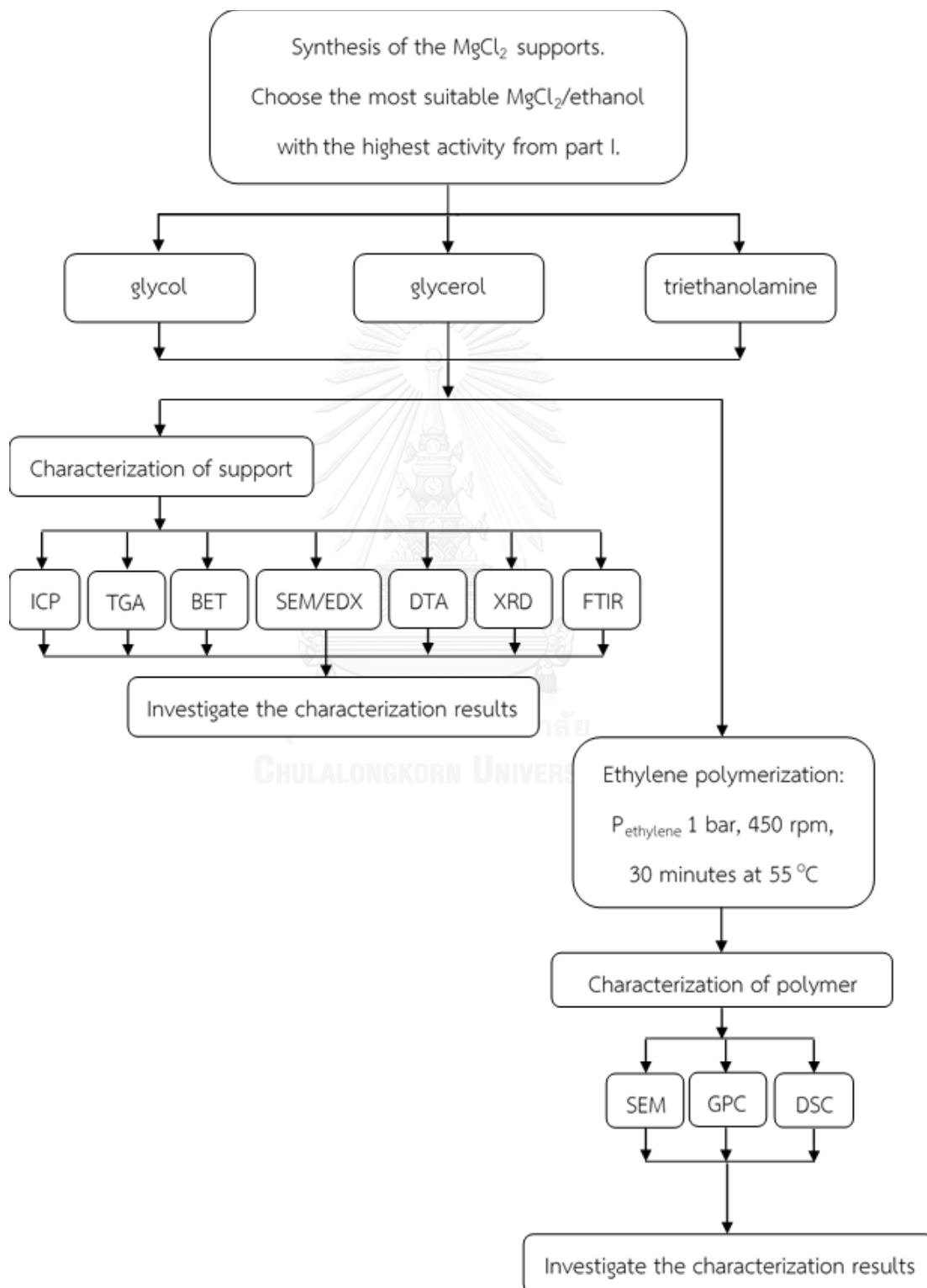
1.4 Research methodology

Research methodology is as shown below;

Part I: Immobilization of FI catalyst onto various MgCl_2 :EtOH:TMA ratios.



Part II: Modification of $\text{MgCl}_2\text{:EtOH}$ adducts with cross-linking agents on prior to immobilization.



CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Polyethylene

2.1.1 History of polyethylene

In 1933, Eric Fawcett and Reginald Gibson, who worked in ICI chemist produced ethylene with benzaldehyde at extremely high pressure and temperature, but they obtained a small residue is called “polyethylene”. From this reaction, using oxygen resulted to difficult reproduction.

In 1935, ICI chemist Michael Perrin succeeded to developed for producing industrial low density polyethylene (LDPE), which it occurred radical polymerization [17]. Among World War II, Phillips Petroleum Chemist investigated way for utilized products of refining process, propylene and ethylene.

In 1951, Hogan and Banks observed new chromium catalyst could produce linear high density polyethylene (HDPE). Furthermore, using silica supported developed new catalytic process at mild temperatures and pressures.

In 1953, Karl Ziegler of the Max Planck Institute reveal that binary mixture of metal alkyls, usually an aluminum alkyl, and transition metal component, usually either titanium or vanadium, could catalyze the production of linear high density polyethylene (HDPE) without using high pressure and temperature as previous practical.

By the end of the 1950s both the Ziegler-type and Phillips- catalysts were used for HDPE.

In 1963, Ziegler and Natta discovered catalyst for development polyethylene obtained, which were awarded the Nobel Prize.

In the 1970s, the incorporation of $MgCl_2$ improved the Ziegler system. Catalytic systems depended on soluble catalysts.

In the late 1970s, Sinn and Kaminsky reacted homogeneous titanocene dichloride (known as Metallocene) with aluminum alkyl as cocatalysts, inserted water into a reaction resulting to an extremely active ethylene polymerization. This situation leading to the discovery and application of methylaluminoxane (MAO) with metallocene, which gave the olefin polymerization [18].

2.1.2 Classify of polyethylene

Polyethylene is the one of the most important polyolefins which commonly produces in various plastic products. Generally, there are several different polyethylene types depend on mechanical and density properties.

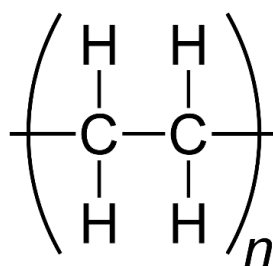


Figure 2.1 Structure of polyethylene

The American Society for Testing and Materials (ASTM) has also classified various types of polyethylene which are shown in **Table 2.1**

Table 2.1 Density of polyethylene classification by ASTM [19]

Polymer types	Density (g/cm^3)
Ultra-high molecular weight polyethylene (UHMWPE)	>0.960
High density polyethylene (HDPE)	0.941-0.960
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

From **Table 2.1**, they presented these classifications in the industry, such as molecular weight or co-monomer employed, were investigated. Typically, polyethylene in industry is high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE), as described below.

- *High density polyethylene (HDPE)*

Using Ziegler-Natta, Metallocene and supported chromium Phillips catalysts reacted to ethylene polymerization. HDPE density has in the range of 0.94-0.97 g/cm³. HDPE commonly used closely pack structure, which is stronger intermolecular forces, tensile strength but less flexible than LDPE. And, because of high crystalline structure, HDPE cannot match the clarity of LDPE or LLDPE film. For HDPE application, it is widely used to create material, such as gas pipe, fertilizer bag, bottles for bleach, car gas tanks, etc.

- *Linear Low density polyethylene (LLDPE)*

This type could produce ethylene copolymerization, which using Ziegler-Natta react α -olefins with 1-butene, 1-hexene, or 1-octene. Like HDPE, LLDPE cannot produce by free radical polymerization. LLDPE density has in the range of 0.915-0.930 g/cm³, giving its natural milky color, translucent with high impact strength. Because of comonomers, LLDPE has short chain branches, higher crystalline, and heterogeneous composition distribution resulting to film product which is not as clear as LDPE. Other applications are shopping bag, stretch wrap, toys, etc.

- *Low density polyethylene (LDPE)*

LDPE is produced only by radical polymerization at high pressure and temperature. LDPE density has in the range of 0.915-0.930 g/cm³, but the structure is highly branched and high amorphous content resulting to greatly flexible plastic, high impact strength and conspicuous film. LDPE apply to produce a plastic wrap, wire, sheathing, waterproof membrane and plastic film for food packaging that is a major application.

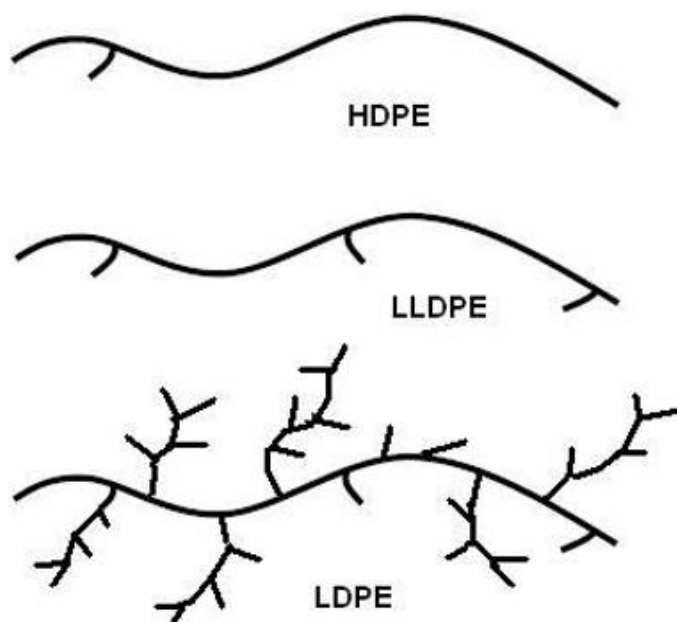


Figure 2.2 Molecular structures of various types of polyethylene

2.2 Post-metallocene catalyst

A post-metallocene catalyst is an activated for the olefin polymerization and in industry production of the most common plastics. "Post-metallocene" is homogeneous catalysts. This catalyst can produce polyethylene, polypropylene, and related copolymers is large. Many polymerize alkenes methods still are used to produce the bulk of polyethylene, including the routes using Philips catalyst and heterogeneous Ziegler-Natta catalysts. [20]

2.2.1 General introduction to post-metallocene catalyst (FI catalyst) [21]

FI catalyst is one of the new catalyst families for use in olefin polymerization, and include transition metal, which almost use 4B groups and normally use titanium (Ti), zirconium (Zr) and hafnium (Hf). The molecular structures of group 4 metal FI catalyst [(phenoxy-imine)₂ MCl₂ (M = Ti, Zr, Hf) in **Figure.2.3**. The FI catalyst was also known as "phenoxy-imine". It is important for group 4 metal FI catalyst commonly exhibit fluxional character in solution, which can bring about to unique polymerization

catalysis such as can controlled multimodal polymerization. Besides, the nature of FI catalyst activated with an MAO system to the highest activity and turnover frequency (TOF) value (64,900 /s/atm).

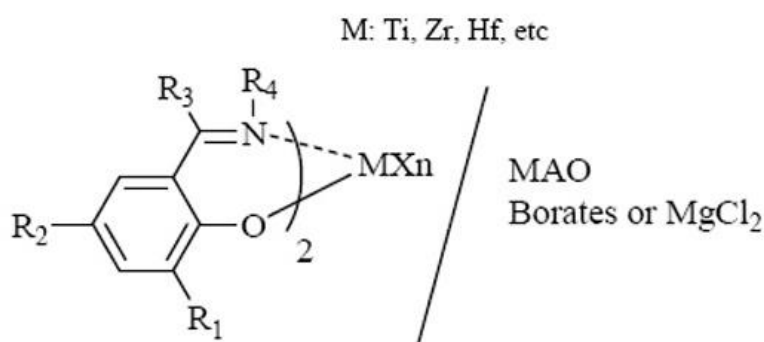


Figure 2.3 the basic structure of FI catalyst.

Marzena B. and Anna P., (2009) [15] used salen type as ligands of catalyst and V and Ti complexes as metal in ethylene polymerization with moderate activity. Such complex of V is more active activation with EtAlCl_2 and produce HDPE. In the part of Ti catalyst represent the highest activity in conjunction with Et_2AlCl , and inferior activity in conjunction with MAO.

Rieko F. et al., (2005) [21] showed effect of group 4 metal FI catalyst in ethylene polymerization. Zr catalyst displays the highest activity followed by Hf catalyst and Ti catalyst. The molecular weights (Mw) of the products concluded Ti catalyst > Hf catalyst > Zr catalyst. In view of the fairly narrow molecular weight distribution (Mw/Mn) of 1.61 obtained with 1/MAO in combination with the facts mentioned above, we postulated that a Ti catalyst might have potential and become good catalyst as a catalyst for living ethylene polymerization.

2.3 Magnesium Dichloride (MgCl_2)

Magnesium dichloride, widely used support in Ziegler-Natta catalysts. Reaction of dibutylmagnesium by tert-butyl chloride in a diisoamyl ether-hexane mixture produces MgCl_2 with very narrow particle size distribution. Dealcoholysis of a $\text{MgCl}_2 \cdot 3\text{EtOH}$ adduct was prepared for good disperse of MgCl_2 and alcohol lead to highly porous MgCl_2 . The Cp_2TiCl_2 -MAO- MgCl_2 catalysts as using supported catalyst exhibits higher activity in the xylene slurry polymerization of ethylene than does the homogeneous catalyst. Cp_2ZrCl_2 - MgCl_2 adduct (supported catalyst) is more active in ethylene polymerization (heptane slurry) if reacted with a trialkylaluminum (TMA). The number of active sites is only about 20% of those in the homogeneous catalyst. [22]

The using MgCl_2 alcohol adduct are interesting for the support catalysts. Over years, many researchers have studied to effective immobilization, activation of catalyst and develop the catalyst. These researchers are shown as follows;

Han S. C. and Wha Y. L., (2003) [23] studied the preparation of MgCl_2 -alcohol adduct from the metallocene catalysts impregnation. The supported catalysts were characterized by XRD, TGA. This result to be concluded that anhydrous MgCl_2 showed a strong XRD pattern at $2\theta = 15, 35$ and 50° . However, MgCl_2 adduct was found that peak intensities were weaker than anhydrous MgCl_2 . Then, using TGA shows that MgCl_2 adduct desorbed at around 110, 140 and 250°C .

Smit M. et al., (2006) [24] showed that the reaction of AlR_3 with MgCl_2 -ethanol adduct obtained $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$, which have higher activity than using SiO_2 . The develop the support catalyst by using borate immobilization immobilized on MgCl_2 . This research studied the compare between MgCl_2 and SiO_2 in propylene and ethylene polymerization. The results are MgCl_2 -based support has higher activities than SiO_2 -based support. The molecular weight distribution (MWD) of polymer was also narrower

using MgCl_2 -based support, the results indicating effective single-site of the catalyst in retention. The morphology of polymer particle showed MgCl_2 -derived polymer has spherical having more porous on surface.

Damavandi S. et al., (2012) [25] investigated MgCl_2 was used as an activator for the bis(phenoxy-imine)Ti complexes that these complexes possess O and N heteroatoms in the ligands. Thus, they determined developing these complexes lead to high performance catalysts.

The modification of catalyst was made by the use of carrier in catalysts for polymerization. The carriers commonly use SiO_2 and MgCl_2 for post-metallocene catalysts with using thermal dealcoholizing of adduct of MgCl_2 and alcohol or reacting with an alkylaluminium compound.

2.4 The role of co-catalysts

FI catalyst have to work with a co-catalyst or activator which cannot work by itself. The co-catalysts are the key to the activity of FI catalyst in olefins polymerization. Besides, it still helps to be inserted ethylene provides active form. For the co-catalyst, which is the most commercial popular in polymerization are called “spacer groups” such as methylaluminoxane.

The cocatalysts for bis(phenoxy-imine)Zr and Ti complexes are generally MAO, or MgCl_2 -based activators. There has been some alkylaluminums, such as triethylaluminum (Et_3Al), trihexylaluminum (He_3Al), or trimethylaluminum (Me_3Al), could activate bis(phenoxy-imine)Zr and Ti complexes for ethylene polymerization without MAO. [9]

2.4.1 Methylaluminoxane (MAO) [18]

Methylaluminoxane (MAO), which the co-catalyst is an important activity of metallocene catalyst and FI catalyst that is mostly used and is synthesized by the hydrolysis of trimethylaluminum (TMA).

Akzo N., (1998) [26] presented the invention of non-hydrolysis route process by using TMA with an easily available organic compounds which has a carbon-to-oxygen bond such as, an alcohol, ketone, carboxylic acid, or carbon dioxide. These oxygen containing compounds can be methylated by an alkylaluminum moiety, into a catalytically useful aluminoxane. Moreover, the amount of free TMA remaining in the aluminoxane composition may be adjusted from very low levels to over 50% by controlling the stoichiometry and reactions in the process.

Obrey et al., (2001) [27] studied that to derive between TMA and metal hydroxides (Ph_3SnOH and Ph_3PbOH) into MAO. The reaction was operated at room temperature by yield MAO, which was guaranteed by ^1H NMR spectroscopy was used to determine a broad resonance between 0.5 and -0.5 ppm. The results are the reaction of Ph_3EOH or Ph_3PbOH and TMA have a yield MAO, but Ph_3EOH (E= C, Si, Ge) did not have. They show that produce an alkane instead of hydroxide exchange, normally for alcohols. These results can describe in terms of relative acidity of the hydroxide that occur with the group 4A metal. More acidic hydroxides undergo alkane elimination, whereas the more basic hydroxides undergo hydroxide exchange. Moreover, the low temperatures can inhibit alkane elimination resulting in the ability for the formation MAO via hydroxide/alkyl exchange reaction by using Ph_3COH in **Figure 2.4**.

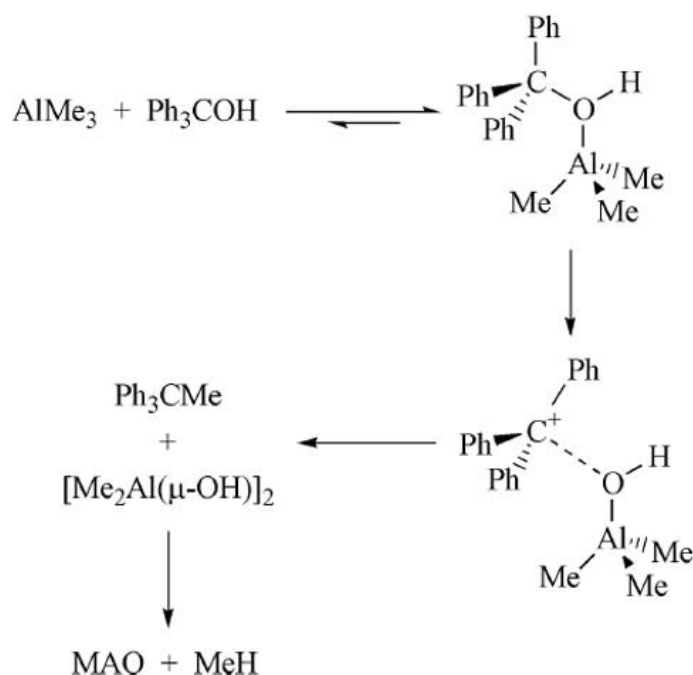


Figure 2.4 The reaction of AlMe₃ with Ph₃COH at low temperature

2.4.2 Synthetic routes of MAO by hydrolysis route

MAO is synthesized from the reaction of trimethylaluminum (TMA) with water, which is hydrolysis route.

MAO is conventionally prepared by controlled hydrolysis of TMA. Several sources of water have been employed in the manufacture of MAO such as direct water, solid ice, emulsified water vapor, water-saturated nitrogen vapor, etc. [27, 28]. This route quite endangers because it is highly exothermic nature between TMA and water that may cause runaway reaction, thus it must be carefully under controlled.

Korneev et al., (1993) [27] investigated the change of products of the interaction between TMA and H₂O during the reaction by using ²⁷Al and ¹H NMR and proposed the transformations, which are the most probable occurrence in **Figure 2.5**.

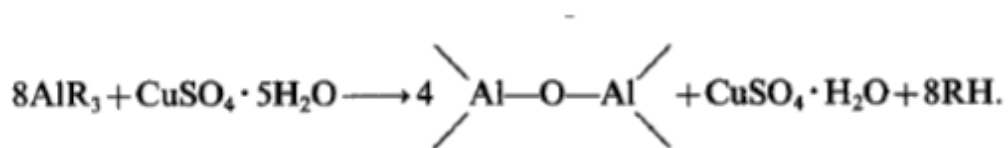


Figure 2.6 The reaction of organoaluminum compounds with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

2.4.3 Trimethylaluminum (TMA)

This research interests TMA as cocatalysts due to MAO has more expensive price than TMA and TMA react with -OH group can transform MAO.

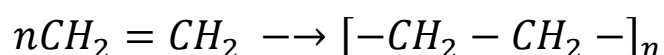
Marzena B. and Anna P., (2009) [15] have the results that effect of activators changes in the following: $\text{MAO} > \text{Me}_3\text{Al} > \text{Et}_3\text{Al} > \text{Et}_2\text{AlCl} > \text{EtAlCl}_2$, while the last two of all have negligible yields of polymer only. In the part, the immobilization of Ti complexes on MgCl_2 support with higher activity than without support are more active after activated with MAO than with Et_2AlCl .

Liu D. et al., (2006) [9] studied the comparing Et_3Al , He_3Al , Me_3Al with MAO (methylaluminoxane) for bis(phenoxy-imine)zirconium complexes, the activity of 1 with Et_3Al is the similar to MAO at the same molar ratio Al/Zr, whereas the activity of 1 with He_3Al or Me_3Al is lower than with MAO. The result of effect the activator trialkylaluminums to complexes efficiency: $\text{Et}_3\text{Al} > \text{Me}_3\text{Al} > \text{He}_3\text{Al}$.

The cocatalysts for bis(phenoxy-imine)Ti and Zr complexes are generally MAO, MgCl_2 -based activators. There is some report on common alkylaluminums as cocatalysts for bis(phenoxy-imine)Ti and Zr complexes system, for example, triethylaluminum (Et_3Al), trimethylaluminum (Me_3Al) or trihexylaluminum (He_3Al), could activate bis(phenoxy-imine)Ti and Zr complexes for ethylene polymerization without MAO. It is found that the alkylaluminum can activate catalyst except using *i*- Bu_3Al or Et_2AlCl as cocatalysts. FI catalyst produce Mw of polyethylene with MAO, which is lower than those produced with Et_3Al , Me_3Al , or He_3Al . Also MWD (Mw/Mn) of polyethylene produced by FI catalyst with MAO is lower than with trialkylaluminums [25].

2.5 Ethylene polymerization

The mechanism of the ethylene polymerization was formed by a free radical addition reaction. It happened during thousands of ethylene molecules join continue in the polymerization to make polyethylene.



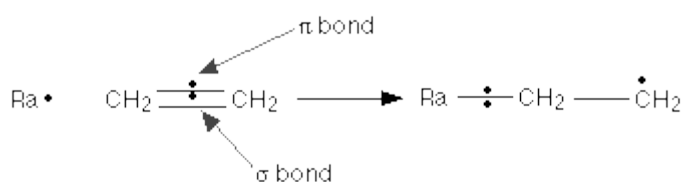
For ethylene polymerization, the overall process is known as *free radical addition*. There are 3 steps as shown below: initiation, termination and propagation [30].

Step 1: Chain Initiation

Chain initiation explains about giving free radicals [i.e. Cl^*] to occurs from homolytic cleavage of relatively weak bonds like Cl-Cl. All of free radical begins to react from step by step where it is produced, and this initial step is called initiation.

Step 2: Chain Propagation

$CH_2=CH_2$, which has the structure of an ethylene molecule, has electrons two pairs which make up the double bond aren't the same. One pair is carried securely on the line between two carbon radicals in a bond called "sigma bond". The other pair is much slackly carried in an orbital above and below the plane of the molecule known as a π bond.



The sigma bond between the carbon atoms isn't affected by any of this. $Ra \cdot$ as free radical carries one of the electrons in the π bond to produce a new bond between the left-hand carbon atom and itself. The other electron converts to the right-hand carbon. Showing this using "curved arrow" mark if you want to:



The π bond which is broken is weaker than this is forcefully worth doing for the new bond between carbon and radical. When the new bond is made more than was used to break the old one, you would get more energy out that is given out are cause of more stable system becomes. If they have to get a bigger free radical-lengthened by CH_2CH_2 , they can react the similar way with another ethylene molecule:

This way take the methyl radical, and there has been no net change in the number of free radicals, so this is still a “propagation”.



Step 3: Chain Termination

That immediately stops the growth of two chains and produces one of the final molecules in the polyethylene. That here, the number of free radical decreases from 2 to zero. This is called “**termination**”.



The polymerization of olefins which are used FI catalyst system have two processes as the following: gas-phase process and slurry process which as heterogeneous system. In case of homogeneous system is not as popular, although, this system provides high activity but happens finer particle into fouling on the wall of reactor and the stirrer. Hence, we used heterogeneous system, which are as follows

For the ethylene polymerization via FI catalyst system, these can be controlled polymer properties by various catalyst concentration, type of co-catalyst, Al/Ti ratio. In addition, these also based on the polymerization factors which have polymerization time, reaction temperature, solvent, ethylene pressure and catalyst/co-catalyst molar ratio. That is all based on requisition and application of the tailor. [34]

2.6 Cross-linking agents

Zhe G. et al., (2002) [14] investigated the effect of adding some crosslinking-agents as glycol, glycerol and triethanolamine on the catalyst. The result from this study, using CAs content added to catalyst system increases, the Al content in catalyst increase. However, this research suggests that MAO impregnated through CAs. As a result, the most Al content do not have the highest activity, indicating that more addition of CA leads to decrease in catalyst activity due to uncompleted reaction. From among three CAs, glycerol shows the highest activity at the mole ratio of OH/Al is 0.2.



CHAPTER 3

EXPERIMENTAL

This chapter explains the research methodology including the synthesis of support on catalyst, the experimental for ethylene polymerization and the characterization of support, catalyst and polymer, respectively.

3.1 Chemicals

All chemicals and materials used in this research were specified details as following;

1. Anhydrous magnesium chloride was donated from PTT research& technology institute at PTT Co., Ltd.
2. Polymerization grade ethylene gas was supplied from PTT research& technology institute at PTT Co., Ltd.
3. Ultra-high purity nitrogen gas (99.9999%) was supplied from Linde (Thailand) PLC.
4. Ultra-high purity Argon gas (99.9999%) was purchased from Linde (Thailand) PLC.
5. Distillated n-heptane (99%) was supplied from PTT research& technology institute at PTT Co., Ltd. under argon atmosphere and molecular sieve 4Å for removal of impurity.
6. Distillated toluene (AR. Grade) was supplied from PTT research& technology institute at PTT Co., Ltd. under argon atmosphere and molecular sieve 4Å for removal of impurity.

7. Ethanol (AR. Grade) was purchased from RCI Labscan limited.
8. Trimethylaluminum (97% in toluene) was supplied from PTT research& technology institute at PTT Co., Ltd.
9. Propylene glycol was purchased from Carlo Erba Reagents.
10. Glycol was purchased from Carlo Erba Reagents.
11. Triethanolamine was purchased from Carlo Erba Reagents.
12. Bis[N-(3-tert-butylsalicylidene)cycloheptylamine] titanium dichloride, which is FI catalyst was synthesized by N-(3-tert-butylsalicylidene)cycloheptylamine and tetrahydrofuran (THF) mixtures [35]. As shown in **Figure 3.1**, it is the 3-tert-C7 structure.

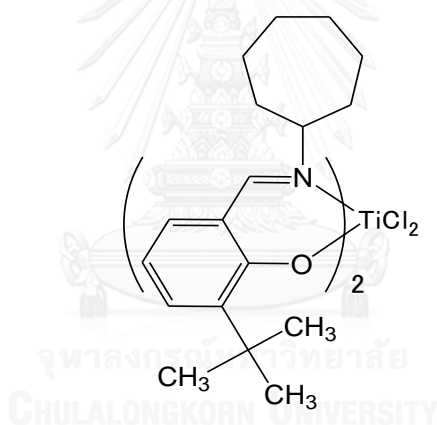


Figure 3.1 the structure of 3-tert-C7

3.2 Catalyst Preparation

3.2.1 Synthesis of MgCl_2 -supported FI catalysts

MgCl_2 -supported FI catalyst was prepared by immobilization of FI catalyst onto MgCl_2 under argon atmosphere. First, 5.72 g (1 mol) of anhydrous MgCl_2 was put into 500 ml three-neck flask with magnetic bar, which it was closed in glove box. Next, put approximately 100 ml of n-heptane with 6 mol of ethanol and stirred at 450 rpm for 1 hour. Then, added drop-wise of TMA in the range of 6, 6.3 and 6.6 mol into flask while cooled to 0°C with stirred. After TMA was added, the flask was held at room temperature and stirred overnight. Then, the FI catalyst was added into flask for 90 μmol and stirred 2 hours. After that, stirrer was stopped and filter solvent layer out. Finally, dried the solid mixture for 3 hours under vacuum recorded the weight of immobilized catalyst as shown in **Figure 3.2**. Besides, the nomenclatures used for all samples in this study are reported in **Figure 3.3**.

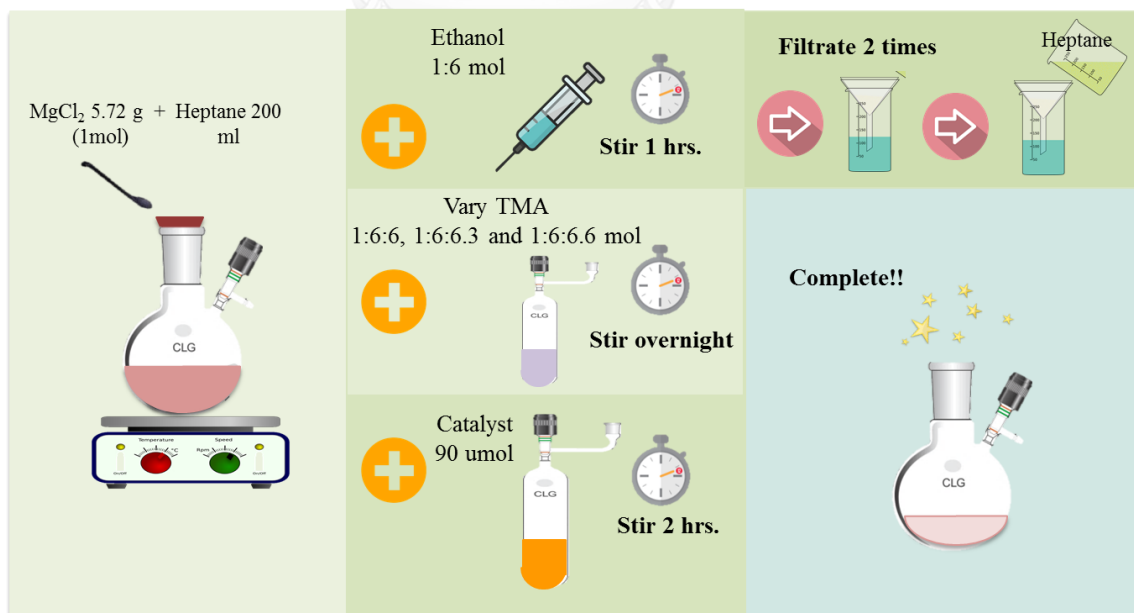


Figure 3.2 Synthesis of MgCl_2 -supported FI catalyst diagram

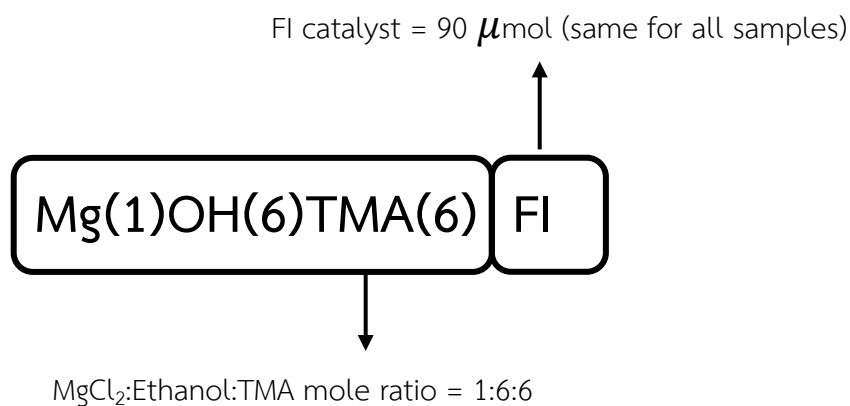


Figure 3.3 Nomenclatures for all samples

3.2.2 Synthesis of modified MgCl₂-supported FI catalyst with cross-linking agents

The modified MgCl₂-supports were prepared based on method of synthesis of MgCl₂ supports. First, 6 mol of ethanol was added into 5.72 g of anhydrous MgCl₂ with 100 ml of n-heptane and stirred at room temperature for 1 hour. Then, added 0.2 - OH/Al ratio of cross-linking agents such as glycol (gc), glycerol (gcr), and triethanolamine (trEtOH) into the solution and added drop-wise 6.3 mol of TMA. The catalyst was put into mixture solution. After the impregnation, the catalyst mixture was filled and evacuated until dried powder was obtained.

3.3 Ethylene polymerization

3.3.1 Effect of MgCl₂:EtOH:TMA molar ratios

Polymerization of ethylene was operated in a 500-ml borosilicate glass reactor as the lines of argon and ethylene gases were directly connected into the reactor. First, clean up and check the system that was closed system. The reactor was heated at 120°C under evacuate and purge by inert argon gas for 2 hours with stirred. Then, the system was cooled down to 55 °C, which was also controlled and filled n-heptane as

solvent 250 ml. After that, the argon gas was replaced by ethylene gas at 1 barg for 20 minutes and kept within the reactor at 1 barg. TMA and supported catalyst were prepared in glove box by syringe of 1 ml and 10 ml, respectively. Then, they were fed into the reactor. Due to the reactor was filled by ethylene gas, then, TMA and catalyst were injected into the reactor. Polymerization was continued for 30 minutes. Finally, the reactor was cooled down. The polymer was filtered and dried polymer at 60 °C under evacuation to remove solvent as shown in **Figure 3.4**.

3.3.2 Effect of ethylene polymerization temperature

This procedure was performed with similar to method as mentioned above. Differently, polymerization temperatures were varied in the range of 35, 45, 55, 65 and 75°C.

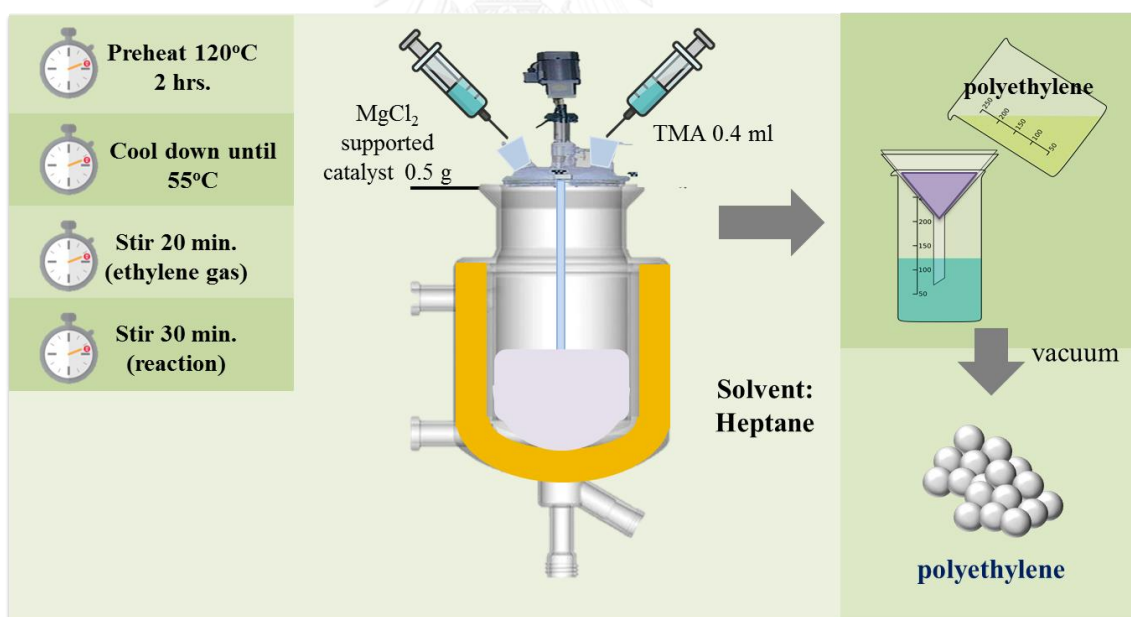


Figure 3.4 Ethylene polymerization method

3.4 Characterization of support and catalyst

3.4.1 Fourier transform infrared spectroscopy (FTIR)

Absorbance FT-IR spectra were recorded by a Nicolet 6700 FT-IR spectrometer with 100 scans at resolution of 4 cm^{-1} . The FT-IR spectra was analyzed under nitrogen in the scanning range of $4000\text{-}500\text{ cm}^{-1}$. The measurement was performed to identify functional groups on MgCl_2 surface. Changes of these functional groups and interaction between MgCl_2 adduct and TMA were investigated by Fourier-transform infrared spectroscopy (FT-IR).

3.4.2 Inductively coupled plasma (ICP)

The supported catalyst was measured by Perkin Elmer OPTIMA 2100™ instrument. The instrument used energy from inductive coupled plasma to stimulate the transition of atoms from ground state to excited state and collected the energy released when returning to ground state by DBI-CCD (Dual backside-illuminated charge-coupled device). The measurement was used to determine the element of the supported catalyst in bulk.

3.4.3 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

SEM-EDX were investigated by the SEM of Hitachi mode S-3400N and the EDX of Link Isis series 300 program. SEM-EDX showed morphology and the elemental distribution of MgCl_2 -supported catalyst. The samples were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

3.4.4 N_2 physisorption

The catalyst support was measured by Quantachome Autosorb 1 instrument. The instrument analyzed that pore size diameter, surface area of porous materials and

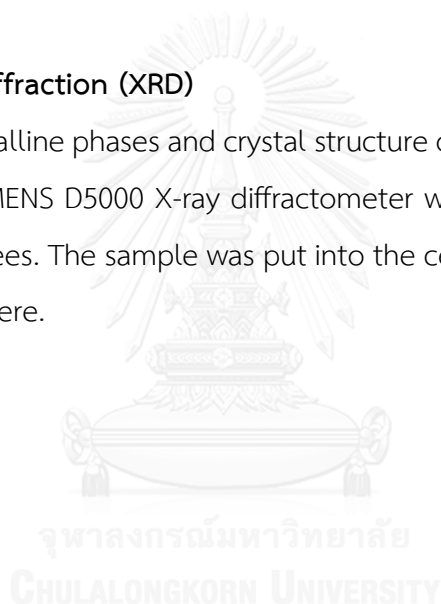
pore volume by vacuum volumetric technique. This process shows about adsorption (physisorption) /desorption of nitrogen gas at 77 K in replacing of materials' porous.

3.4.5 Thermal gravimetric analysis (TGA)

TGA determined composition, thermal stability and weight loss of the supported catalyst with changed temperatures. It was analyzed by TA Instrument model SDT Q 600 analyzer. The measurement was operated under nitrogen atmosphere in the range from room temperature to 600°C and heating rate of 10°C/min.

3.4.6 X-ray diffraction (XRD)

The bulk crystalline phases and crystal structure of the supported catalyst were analyzed using a SIEMENS D5000 X-ray diffractometer with the scanning in range of 2 theta = 10 to 70 degrees. The sample was put into the center holder and closed cover under argon atmosphere.



3.5 Characterization of polymer

3.5.1 Differential scanning calorimeter (DSC)

This instrument observes melting temperature (T_m). DSC measurement was investigated by TA instruments of SDT Q 600 V8.1 Build 99. The operation was performed at a heating rate at 10°C/min in room temperature to 600°C.

3.5.2 Gel permeable chromatography (GPC)

Molecular weight (M_w) and molecular weight distribution (MWD) of polyethylene were determined using GPC at 135 °C oil equipped with a viscometric detector. The measurement used 1,2,4-trichlorobenzene as a solvent at 160°C.

3.5.3 Scanning electron microscopy (SEM)

Morphology and elemental distribution of $MgCl_2$ supported catalyst were investigated by the SEM of Hitachi mode S-3400N.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter mentioned results and discussion of research. There are two parts. First, it explained about immobilization of FI catalyst on MgCl_2 adduct support by varying co-catalyst (TMA) ratios as fixed $\text{MgCl}_2/\text{EtOH}$ ratio constant. In the last part, it brought the best $\text{MgCl}_2/\text{EtOH}/\text{TMA}$ ratio in the first part to use in this part and modify it by addition of cross-linking agents. Both parts are discussed in more details.

4.1 Immobilization of FI catalyst onto various $\text{MgCl}_2/\text{EtOH}/\text{TMA}$ adducts

4.1.1 The characteristics of MgCl_2 -supported FI catalyst

In this topic, it explains the characteristics of the supported catalysts, which have the different TMA and ethanol ratios. Various characterization techniques such as ICP, SEM/EDX, N_2 physisorption (BET), XRD, FT-IR, TGA, and DTA were used. More details are discussed as follows;

4.1.1.1 Inductively Coupled Plasma (ICP)

Table 4.1 presents the elemental distribution and composition of MgCl_2 -supported FI catalysts using ICP technique. It shows that $\text{Mg}(1)\text{OH}(6)\text{TMA}(6)\text{FI}$ has the highest amount of %Ti at 80.32%. The ratios of Ti/Mg of all the supported catalysts were similar having the value of 0.37 to 0.43. It can be observed that the $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$ exhibited the lowest amount of Ti/Mg molar ratio. Thus, Ti species can be more dispersed when compared to other samples.

Table 4.1 the element of MgCl_2 supported FI catalyst^a

Catalysts	Elemental contents (wt%) ^a			Ti/Mg (mol/mol)
	%Ti	%Al	%Mg	
Mg(1)OH(6)TMA(6)FI	80.32	6.05	93.92	0.43
Mg(1)OH(6)TMA(6.3)FI	57.29	8.41	77.60	0.37
Mg(1)OH(6)TMA(6.6)FI	72.57	7.15	89.41	0.41

^a Obtained by ICP

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

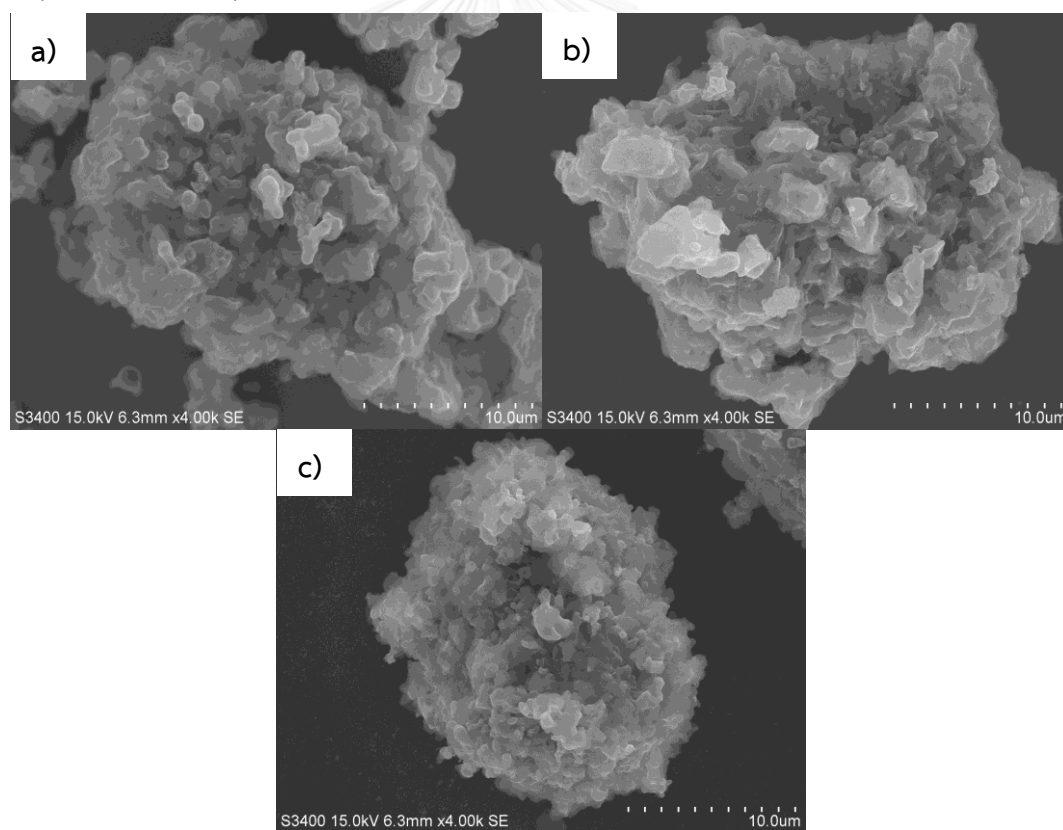


Figure 4.1 SEM micrographs of different MgCl_2 -supported FI catalyst at 4 kx magnification where: a) Mg(1)OH(6)TMA(6)FI, b) Mg(1)OH(6)TMA(6.3)FI and c) Mg(1)OH(6)TMA(6.6)FI

SEM images of different MgCl_2 supported FI catalysts are shown in **Figure 4.1**. It was observed that $\text{Mg}(1)\text{OH}(6)\text{TMA}(6)\text{FI}$, $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$ and $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.6)\text{FI}$ were almost similar with high porous on the external surface.

The EDX analysis shows distribution of Ti, Al and Mg on near surface as seen in **Table 4.2**. It was found that it has the similar elemental distribution among them. In addition, the Ti/Mg ratios of all supported catalysts were also similar at 0.03.

Table 4.2 Ti, Al and Mg distribution on near surface of different catalysts

Catalysts	Elemental contents (wt%) ^a			Ti/Mg (mol/mol)
	%Ti	%Al	%Mg	
$\text{Mg}(1)\text{OH}(6)\text{TMA}(6)\text{FI}$	3.35	38.80	57.85	0.03
$\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$	2.13	55.15	42.72	0.03
$\text{Mg}(1)\text{OH}(6)\text{TMA}(6.6)\text{FI}$	2.91	45.76	51.33	0.03

^a Determined by EDX

The comparison between ICP analysis as found in the supported catalyst in bulk and EDX analysis as seen on near surface can be seen that **Tables 4.1** and **4.2**, respectively. It was observed that mostly Ti species were distributed in bulk compared to surface. Ti species in bulk by ICP were in the range of 57-80% while the Ti species at near surface by EDX were only little amounts (2.1-3.3%).

4.1.1.3 N_2 physisorption (BET)

All supported catalysts were analyzed by N_2 -physisorption to determine the surface area, pore volume, and pore size.

Table 4.3 N₂-physisorption of MgCl₂ supported FI catalyst

Catalysts	Surface area ^a (m ² /g)	Pore volume ^a (cm ³ /g)	Pore size ^a (Å)
MgCl ₂	2.25	0.02	37.1
Mg(1)OH(6)TMA(6)FI	195	0.28	37.0
Mg(1)OH(6)TMA(6.3)FI	210	0.19	37.0
Mg(1)OH(6)TMA(6.6)FI	224	0.31	37.0

^a analyzed by Brunauer Emmett Teller (BET) and multipoint N₂ physisorption technique.

From **Table 4.3**, it can be seen that MgCl₂ has surface area only 2.25 m²/g confirmed by Zhe et al [14]. It was found that Mg(1)OH(6)TMA(6.6)FI exhibited the largest surface area as 224 m²/g, followed by Mg(1)OH(6)TMA(6.3)FI and Mg(1)OH(6)TMA(6)FI, which have surface area of 211 m²/g and 195 m²/g, respectively. In addition, pore volume of all supported catalysts is about 0.19-0.31 cm³/g, but their pore sizes were still similar (c.a. 37 Å) with in mesoporous range. This can be concluded that adding TMA or ethanol into MgCl₂ can result in increased surface area without significant change in pore size.

4.1.1.4 X-ray Diffraction (XRD)

The X-ray diffraction (XRD) patterns showed the crystalline structure of MgCl₂ and MgCl₂-supported FI catalysts. It indicated that MgCl₂ support, ethanol, and FI catalyst were highly dispersed (no sharp peaks were observed).

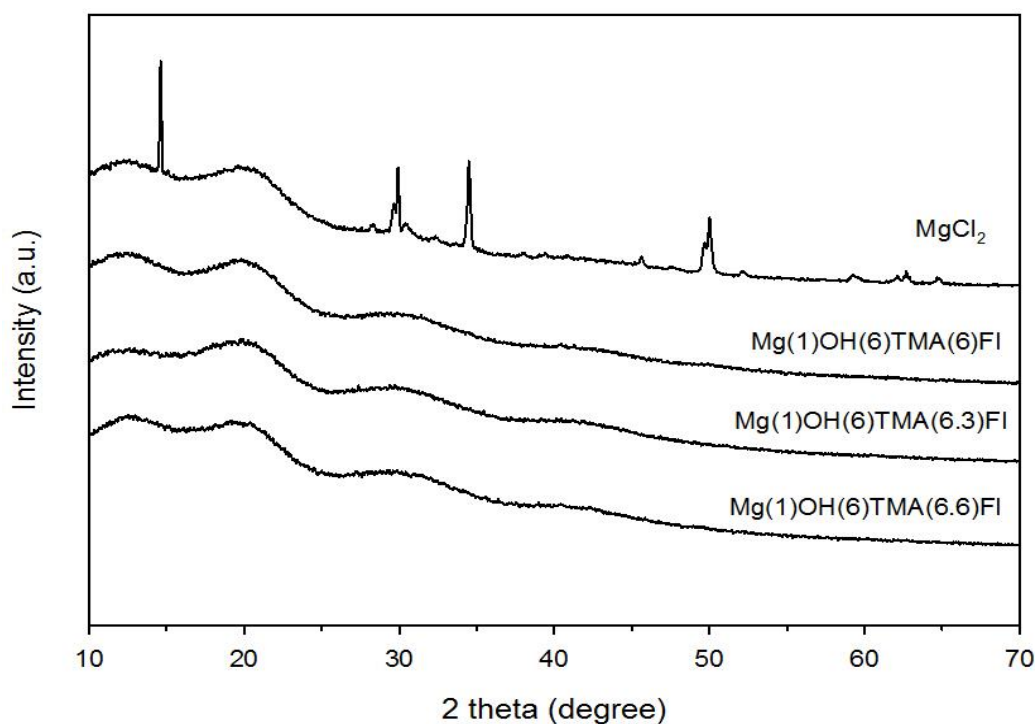


Figure 4.2 XRD patterns of MgCl_2 and MgCl_2 -supported FI catalysts

In more details, **Figure 4.2** showed XRD patterns of MgCl_2 and MgCl_2 -supported FI catalysts, which were collected in the range of 10 to 70 degree. The XRD peaks at $2\theta = 14.9^\circ$, 30.2° , 34.8° and 50.3° are assigned to α - MgCl_2 having high order or crystalline structure. The sharp peak of MgCl_2 at $2\theta = 14.9^\circ$ indicated the stacking of Cl-Mg-Cl triple layer. The others peaks, at $2\theta = 30.2^\circ$, 34.8° and 50.3° showed the triple layer as well. In addition, $\text{Mg(1)OH(6)TMA(6)FI}$, $\text{Mg(1)OH(6)TMA(6.3)FI}$, and $\text{Mg(1)OH(6)TMA(6.6)FI}$ are also presented in **Figure 4.2**. In the range of appeared MgCl_2 XRD peaks, it did not observe any peaks in case of alcohol adduct. It was found that the supported catalysts containing alcohol exhibited only broad peak. As a result, the interaction between Mg^{2+} and alcoholic oxygen forms adduct pattern. Both increasing in the planer distance and decreasing in 2θ value result from insertion of alcohol in between the Cl-Mg-Cl triple layers [36]. From the above, it indicated that those supported catalysts exhibited good dispersion of Ti species and TMA on the MgCl_2 -OH adduct. It suggests that $\text{MgCl}_2 \cdot n\text{C}_2\text{H}_5\text{OH}$ was formed during the MgCl_2 /ethanol adduct preparation by the recrystallization method [23].

4.1.1.5 Fourier Transform Infrared Spectroscopy (FTIR)

The IR spectra of all MgCl_2 supported FI catalysts and MgCl_2 support were obtained in the range of $4000\text{-}600\text{ cm}^{-1}$. It analyzed the functional groups in each wavenumber, as shown in **Figure 4.3**.

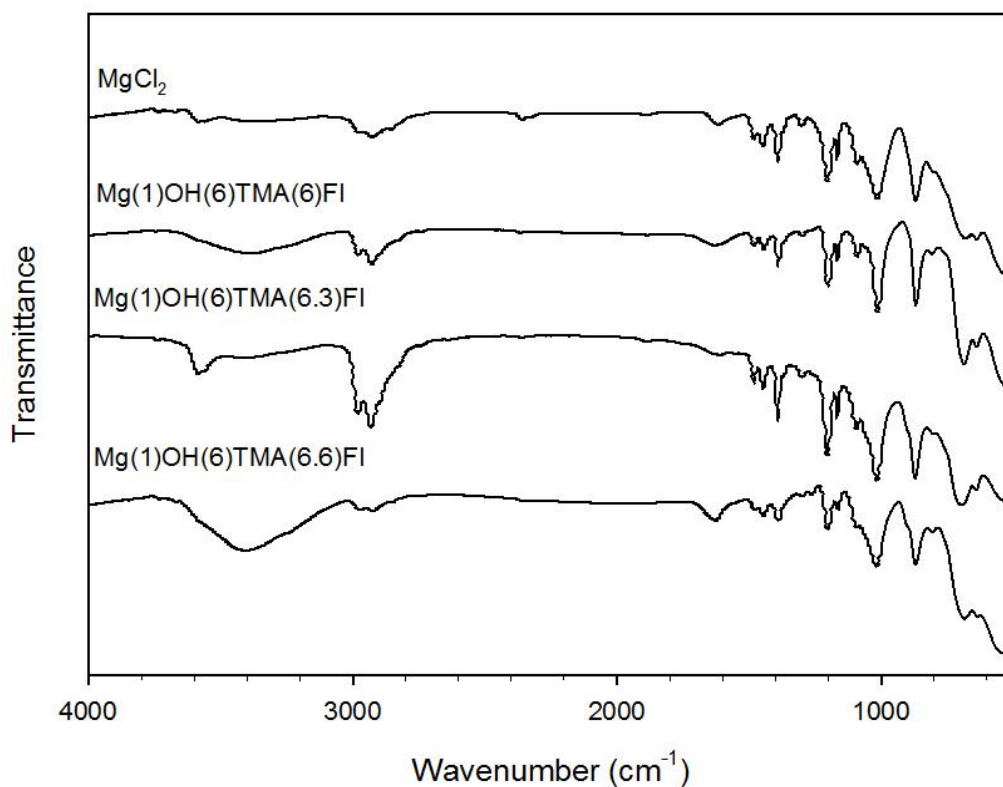


Figure 4.3 FTIR spectra of MgCl_2 and MgCl_2 supported FI catalysts

As shown in **Figure 4.3**, the analysis of IR spectra of all supported catalyst revealed that O-H stretching band at $3584.2\text{-}3386.8\text{ cm}^{-1}$ as ethanol, which is in supported catalyst. While $\text{Mg(1)OH(6)TMA(6.3)FI}$ peak still is a free peak of OH groups at 3600 cm^{-1} , suggesting that ethanol was not completely removed during immobilization, probably due to the entrapment within MgCl_2 structure. Some researchers reported that IR bands at 3400 cm^{-1} were assigned to alcoholic functional group, as O-H stretching. Zhe Guan et al. confirmed IR spectrum of MgCl_2 adduct indicates OH groups in ethanol appears a broad band at 3400 cm^{-1} and a feature peak at 1404 cm^{-1} , corresponding to alcoholate. [14, 16] The other peaks were

corresponding to the C-H stretching of these supported catalysts was found at 3000-2900 cm^{-1} (alkanes) and 1680-1620 cm^{-1} (alkenes), corresponding to C=C stretching in catalyst. The signal at 1100 cm^{-1} is strong indicating the presence of the C-O stretching. Finally, it is observed that a band at 870 cm^{-1} , which is clearly visible by the presence of MAO, can be assigned to the Al-O bond. [14, 16]

4.1.1.6 Thermal Gravimetric Analysis (TGA)

The thermal gravimetric analysis measures the amount of weight change of each supported catalyst with decreasing upon increasing temperatures. The weight loss patterns can indicate the supported catalyst composition upon decomposition with increased temperature.

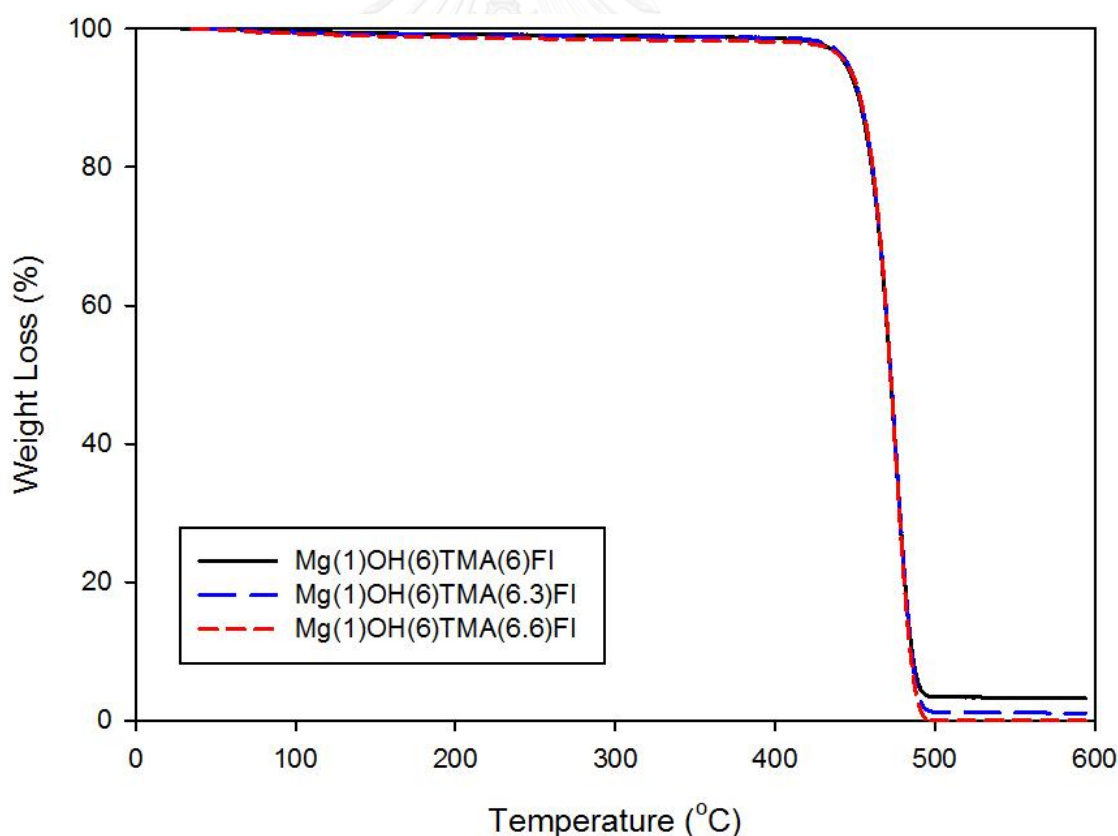


Figure 4.4 TGA profiles of MgCl₂-supported FI catalysts

From **Figure 4.4**, all TGA curves indicated a single degradation process. It can be seen that around 420°C, it began to drop down dramatically indicating the weight loss of hydrocarbon. Then, up to 500°C, it has almost 100% of weight loss. The TGA patterns of all supported catalysts showed that Mg(1)OH(6)TMA(6.6)FI has completely decomposed around 500°C. In addition, the Mg(1)OH(6)TMA(6.3)FI and Mg(1)OH(6)TMA(6)FI have 1%wt and 5%wt as residue, respectively. Furthermore, it was observed that TGA profile before 600°C confirms to be due to the decomposition of organic containing of carbon and hydrogen [37]. It can result that supported catalyst degrades absolutely indicating that variety of MgCl₂/EtOH/TMA ratios did not affect on the decomposition of supported catalysts.

4.1.1.7 Differential Thermal Analysis (DTA)

According to **Figure 4.5**, DTA analysis showed that differential thermal between supported catalysts and reference sample was transformed into exothermic or endothermic, due to enthalpic transition of supported catalyst.

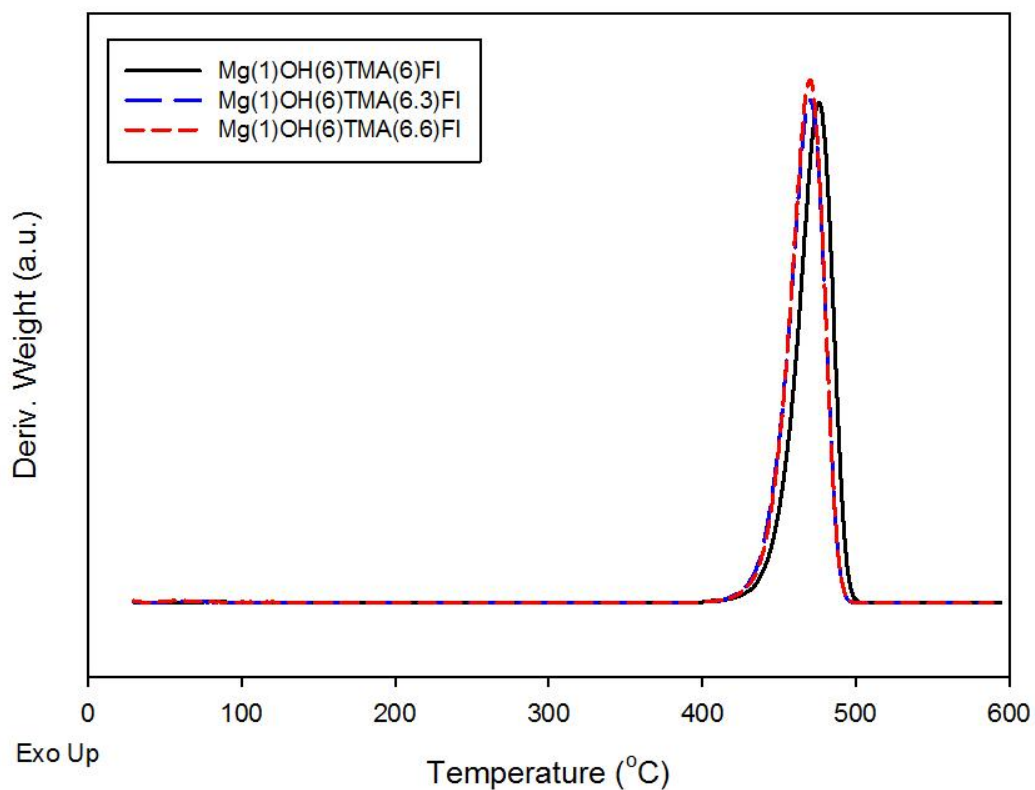


Figure 4.5 DTA profiles of MgCl₂ supported FI catalysts

The DTA profiles for all MgCl₂-supported FI catalysts were similar as shown in **Figure 4.5**. The loss of organic substances apparently occurred at 400-500°C. It can be seen that in the range of 230-490°C assigned to organic oxidation weight loss. These supported catalyst does not decompose before 105°C because they do not contact air and moisture. The result of this figure is consistency with **Figure 4.4**, which it began to decompose at 420°C as similar.

4.1.1.8 Nuclear magnetic resonance spectroscopy (NMR)

Mg(1)OH(6)TMA(6.3)FI was investigated by ^1H NMR in **Figure 4.6**. ^1H NMR presented the MgCl_2 -supported FI catalyst activation by hydrolytically prepared MAO [38, 39].

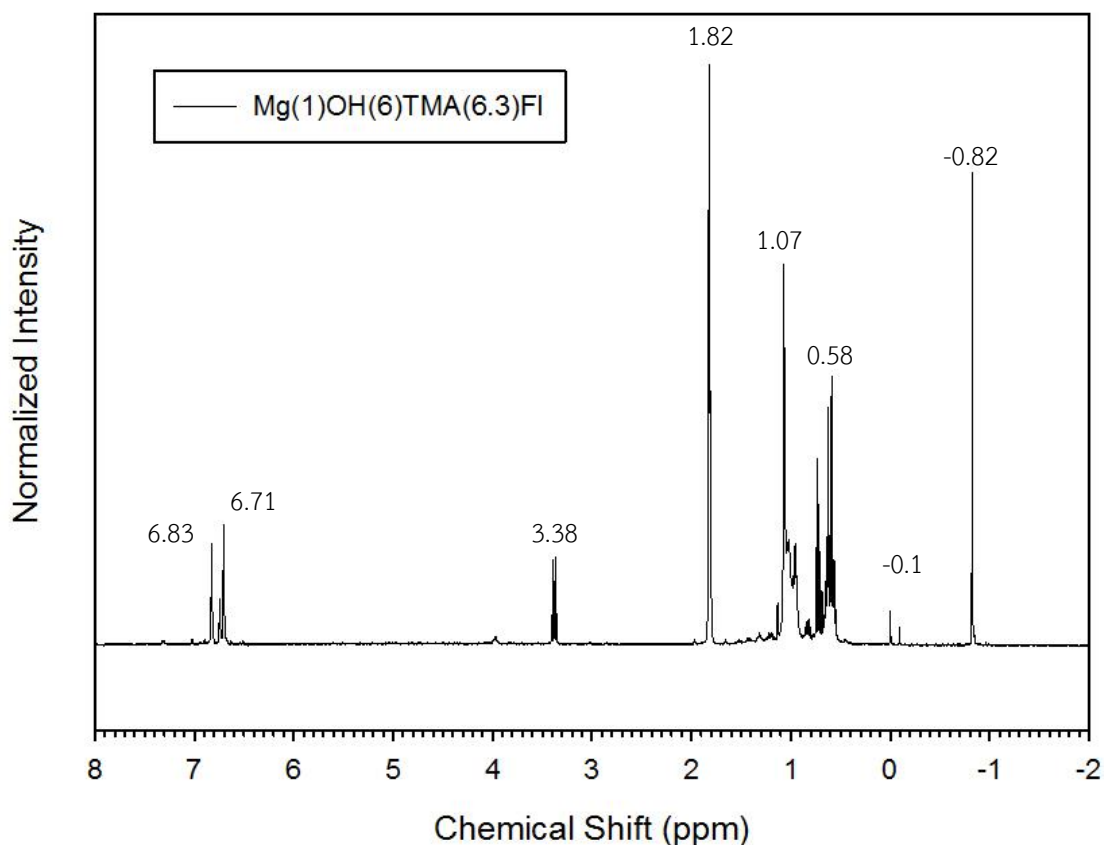


Figure 4.6 ^1H NMR of MAO solution of Mg(1)OH(6)TMA(6.3)FI

According to **Figure 4.6**, it displayed the spectrum of Mg(1)OH(6)TMA(6.3)FI in the range of 8 to -2 ppm to confirm the transformation of TMA to MAO. It shows that the peak (1.82 ppm) is attributed to $-\text{OAlMe}_2$ of MAO species and at -0.82 ppm as associated with TMA has been oxidized. Free TMA signal at -0.1 ppm [AlCH_3]₃ was detected very little and the residual TMA was found at 3.38 ppm [40]. Furthermore, at 6.71-6.83 ppm, it presented the aromatic proton in meta and para position. It confirmed the formation of MAO species and the forward reaction to produce MAO [33].

4.1.2 The catalytic activities of ethylene polymerization

4.1.2.1 Effect of TMA ratios

The FI catalyst was immobilized on $\text{MgCl}_2/\text{EtOH}$ adduct having mole ratio of 1:6 with 3 different amounts of TMA including 1:6:6, 1:6:6.3 and 1:6:6.6. The MgCl_2 -supported FI catalysts were brought to polymerize with ethylene gas to determine the yield of polyethylene and activity as shown in **Table 4.4**.

Table 4.4 Effect of TMA mole ratios on the ethylene polymerization

Catalysts	PE yield (g)	Activity ^a (kg PE/mmol cat .h)
FI (homogeneous)	3.40	1.51
Mg(1)OH(6)TMA(6)FI	14.10	5.16
Mg(1)OH(6)TMA(6.3)FI	16.67	7.03
Mg(1)OH(6)TMA(6.6)FI	13.58	5.06

^a Condition of ethylene polymerization using 0.5 g MgCl_2 -supported FI catalyst in 10 ml hexane, co-catalyst= TMA, reaction time= 30 mins, temperature= 55°C, stir= 450 rpm, $P_{\text{ethylene}} = 1$ barg

It was found that the Mg(1)OH(6)TMA(6.3)FI exhibited the highest PE yield up to 16.67 g with the highest activity of 7.03 kg PE/mmol cat. h. It revealed that $\text{MgCl}_2/\text{EtOH}/\text{TMA}$ ratios at 1:6:6.3 was suitable to hydrolyze TMA to MAO. It can be considered from **Table 4.1**, that the Ti/Mg ratio (ICP) of Mg(1)OH(6)TMA(6.3)FI was 0.37. Normally, high Ti/Mg ratio of catalyst can result in high activity due to Ti species are active sites. However, from **Table 4.4**, Mg(1)OH(6)TMA(6.3)FI exhibited the highest activity, although it had the lowest Ti/Mg ratio value. However, this is perhaps due to most of Ti species were present in the highly-dispersed form. On the other words, the highly-dispersed form is more isolated and being more active [41-43].

The result of the effect of TMA ratios obtained as shown in **Table 4.4** revealed that the catalytic activity of Mg(1)OH(6)TMA(6.3)FI was the highest. They might be the effect of homogeneous MAO, which was inefficiently immobilized on support, that also caused the formation fouling in the reactor. Thus, the morphology of polyethylene obtained from each catalyst must be determined using SEM.

4.1.2.2 Effect of polymerization temperature

From **Table 4.4**, the suitable of TMA mole ratios was found to obtain the highest activity of ethylene polymerization at this condition. The result from the previous section can be concluded that Mg(1)OH(6)TMA(6.3)FI exhibited the highest activity of 7.03 kg PE/mmol cat.h. In this part, Mg(1) OH(6)TMA(6.3)FI was used at various polymerization temperatures for ethylene polymerization including 35, 45, 55, 65, and 75°C.

Table 4.5 Effect of ethylene polymerization temperatures

Temperature (°C)	Yield (g)	Activity ^a (kg PE/mmol cat .h)
35	8.92	3.78
45	12.20	5.08
55	16.67	7.03
65	13.92	5.90
75	13.04	5.50

^a condition of ethylene polymerization using 0.5 g MgCl₂-supported FI catalysts in 10 ml hexane from Mg(1)OH(6)TMA(6.3)FI, co-catalyst= TMA, reaction time= 30 mins, stir= 450 rpm, P_{ethylene}= 1 barg

As seen from **Table 4.5**, it shows that at 55°C of ethylene polymerization temperature, it has PE yield up to 16.67 g and the highest activity of 7.03 kg PE/mmol cat.h. It was found that the yield of polyethylene increased progressively when starting the polymerization at 35°C and raising up to 55°C. At 55°C of ethylene polymerization temperature, it exhibited the highest yield and activity of polyethylene. After that, beyond 55°C of ethylene polymerization temperature, it decreased the PE yield. This is perhaps due to catalyst deactivation with increased temperatures.

On the other words, the trend of ethylene polymerization temperature on catalytic activity increased with increased temperature up to 55°C and went down with temperature higher than 55°C. Therefore, it can be concluded that at 55°C is the optimal temperature for ethylene polymerization in this study.



4.1.3 The characterization of polyethylene

In this part, polyethylene from ethylene polymerization of the different TMA moles ratios of supported catalyst was characterized by SEM, DSC, and GPC.

4.1.3.1 Scanning Electron Microscopy (SEM)

The morphology of the polyethylene surface is presented in **Figure 4.7**.

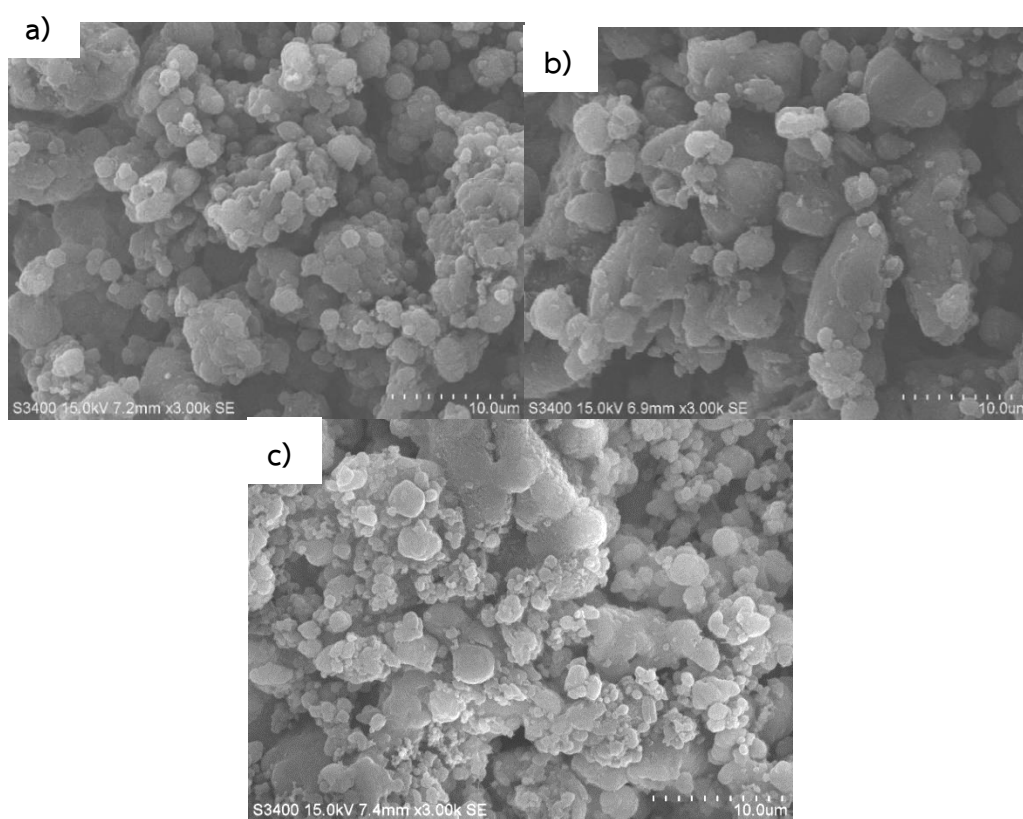


Figure 4.7 SEM micrographs of the polyethylene at 3 kx magnification
a) Mg(1)OH(6)TMA(6)FI b) Mg(1)OH(6)TMA(6.3)FI and c) Mg(1)OH(6)TMA(6.6)FI

As shown in **Figure 4.7**, it referred to morphology of polymer obtained from using the MgCl_2 -supported FI catalyst for polymerization of ethylene. It can be seen that all of this polyethylene were also spheroidal lump. While the other polymers have both mixed large and small spherical shape, the polymer from $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$ has only large spheroidal shape. Therefore, $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$ polymer have suitable polymer, probably due to well distribution of active sites on the MgCl_2 support that makes less small polymer (from the leaching of active sites).

4.1.3.2 Gel Permeable Chromatography (GPC) and Differential Scanning Calorimeter (DSC)

The molecular weight and molecular weight distribution of polyethylene were widely characterized by gel permeable chromatography (GPC). Besides, melting temperature of polyethylene was analyzed by differential scanning calorimeter (DSC). All of these are presented in **Table 4.6**.

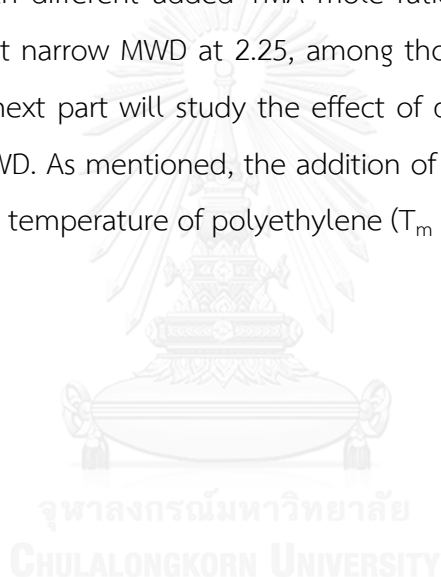
Table 4.6 Influence of various TMA ratios and ethanol ratios on polyethylene properties

catalysts	Mn ($\times 10^5$) ^a	Mw ($\times 10^5$) ^a	MWD ^a	T _m (°C) ^b
FI (homogeneous)	8.40	14.06	1.67	127.6
$\text{Mg}(1)\text{OH}(6)\text{TMA}(6)\text{FI}$	4.19	12.16	2.98	127.2
$\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$	5.86	13.21	2.25	126.3
$\text{Mg}(1)\text{OH}(6)\text{TMA}(6.6)\text{FI}$	5.21	12.87	2.47	126.4

^a Determined by GPC

^b Determined by DSC

From **Table 4.6**, when compared between polyethylene obtained from the homogeneous system and polyethylene with the MgCl_2 -supported FI catalyst, $(\text{Mg}(1)\text{OH}(6)\text{TMA}(6)\text{FI})$, $(\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI})$, and $(\text{Mg}(1)\text{OH}(6)\text{TMA}(6.6)\text{FI})$, it revealed that the supported system had lower molecular weight (MW) than the polyethylene obtained from the homogeneous system. Moreover, they have broader molecular weight distribution (MWD) than the homogeneous system as well. In fact, polyethylene of only FI catalyst (homogeneous system) has a narrow MWD (1.67) and can be the high molecular weight polyethylene (HMWPE) [35]. For polymer of the supported catalyst, it can be HMWPE with different added TMA mole ratios. In case of $(\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI})$, it has the least narrow MWD at 2.25, among those polymer obtained from FI catalyst. Hence, the next part will study the effect of different types of cross-linking agents to improve MWD. As mentioned, the addition of different TMA mole ratios did not affect the melting temperature of polyethylene ($T_m = 126.3\text{-}127.6^\circ\text{C}$ which did not significantly change).



4.2 Modification of MgCl₂ with cross-linking agents prior to immobilization

In this part, it studied on the effect of different types of cross-linking agents by immobilization of MgCl₂-support FI catalyst using that Mg(1)OH(6)TMA(6.3)FI. The cross-linking agent was applied including glycol, glycerol, and triethanolamine to modify MgCl₂ support prior to react with FI catalyst and polyethylene obtained from polymerization of modified supported catalyst were investigated.

4.2.1 Characterization of modified MgCl₂-supported FI catalyst with cross-linking agents

After immobilization of modified supported catalyst with cross-linking agents, all samples were determined by ICP, SEM/EDX, BET, XRD, FT-IR, TGA, and DTA.

4.2.1.1 Inductively Coupled Plasma (ICP)

Ti content of all samples were determined by ICP. Mg(1)OH(6)TMA(6.3)FI_gcr has the highest %Ti content in bulk at 79.29% and the highest Ti/Mg molar ratio of modified supported catalyst as shown in **Table 4.7**.

Table 4.7 Elemental analysis of different cross-linking agents modified MgCl₂-supported FI catalysts

Catalysts	Elemental contents (wt%) ^a			Ti/Mg (mol/mol)
	%Ti	%Al	%Mg	
Mg(1)OH(6)TMA(6.3)FI_gc	64.59	11.17	88.46	0.37
Mg(1)OH(6)TMA(6.3)FI_gcr	79.29	7.01	91.75	0.44
Mg(1)OH(6)TMA(6.3)FI_trEtOH	69.12	7.76	93.71	0.37

^a Obtained by ICP

Mg(1)OH(6)TMA(6.3)FI_gc and Mg(1)OH(6)TMA(6.3)FI_trEtOH have the equal ratios of Ti/Mg at 0.37, while Mg(1)OH(6)TMA(6.3)FI_gcr has 0.44 of Ti/Mg molar ratio, which is highest active sites among the other samples. As a consequence, Mg(1)OH(6)TMA(6.3)FI_gcr has higher surface than Mg(1)OH(6)TMA(6.3)FI_gc and Mg(1)OH(6)TMA(6.3)FI_trEtOH.

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

The morphology of modified supported catalyst and dispersion of Ti on surface can be analyzed by SEM and EDX, respectively.

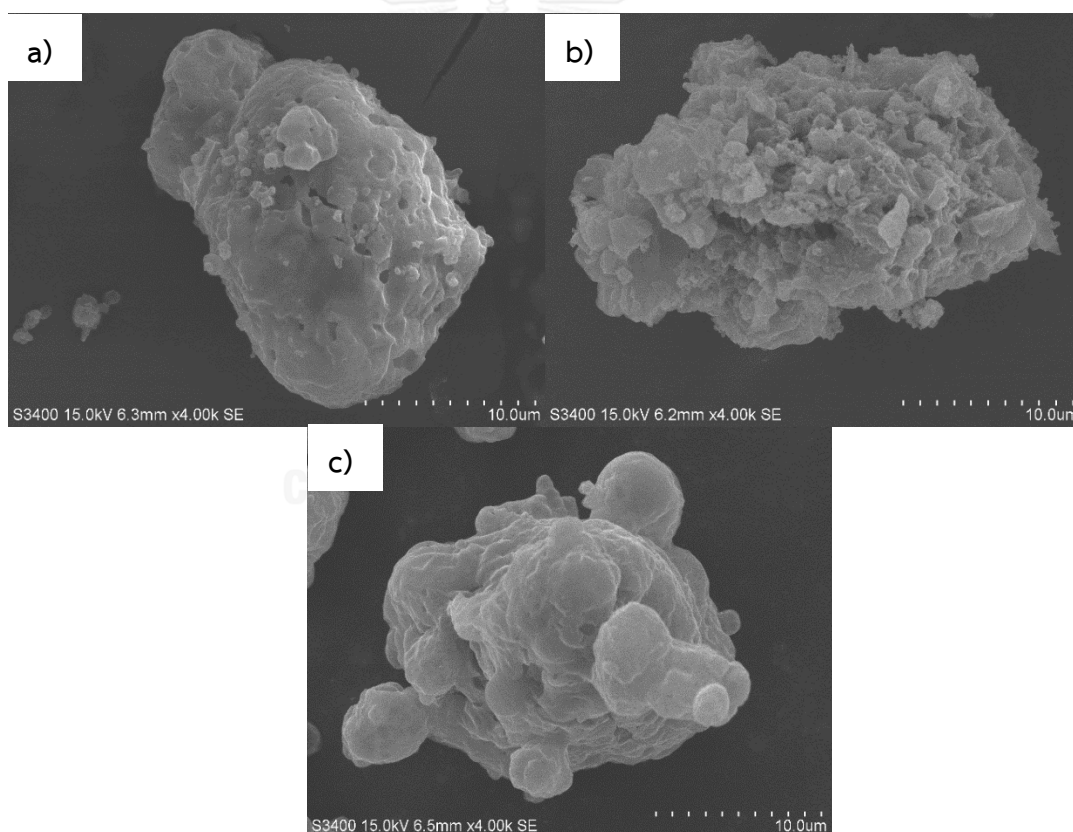


Figure 4.8 SEM micrographs of modified MgCl₂-supported catalyst at 4 kx magnification a) Mg(1)OH(6)TMA(6.3)FI_gc b) Mg(1)OH(6)TMA(6.3)FI_gcr and c) Mg(1)OH(6)TMA(6.3)FI_trEtOH

As represented in **Figure 4.8**, it can be observed that Mg(1)OH(6)TMA(6.3)FI_gcr, which has much porous on surface, has the morphology of well-defined particles resulting in high catalytic activity, while Mg(1)OH(6)TMA(6.3)FI_gc and Mg(1)OH(6)TMA(6.3)FI_trEtOH have smooth lump or less porous.

EDX analysis displays that the dispersion of Ti, Al, and Mg on surface catalyst.

Table 4.8 Ti, Al and Mg percentages dispersed on surface of catalyst

Catalysts	Elemental contents (wt%) ^a			Ti/Mg (mol/mol)
	%Ti	%Al	%Mg	
Mg(1)OH(6)TMA(6.3)FI_gc	3.17	61.15	35.69	0.05
Mg(1)OH(6)TMA(6.3)FI_gcr	3.75	48.84	47.41	0.04
Mg(1)OH(6)TMA(6.3)FI_trEtOH	4.44	48.66	46.90	0.05

^a Determined by EDX

From **Table 4.8**, the Ti/Mg molar ratios on surface of catalyst have nearly similar value (0.04-0.05). Mg(1)OH(6)TMA(6.3)FI_gc, and Mg(1)OH(6)TMA(6.3)FI_trEtOH were similar as 0.05, while Mg(1)OH(6)TMA(6.3)FI_gcr has Ti/Mg molar ratio only 0.04. Considering the well-known result, Ti/Mg molar ratio refers to effect to polymerization and is important factor for polymerization [44].

4.2.1.3 N₂ physisorption

The surface area, pore volume, and pore size of modified supported catalyst were analyzed by N₂ physisorption technique.

Table 4.9 N₂ physisorption after addition of cross-linking agents in MgCl₂-supported FI catalysts

Catalysts	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)
Mg(1)OH(6)TMA(6.3)FI_gc	88.6	0.01	36.3
Mg(1)OH(6)TMA(6.3)FI_gcr	47.8	0.06	36.7
Mg(1)OH(6)TMA(6.3)FI_trEtOH	98.6	0.15	37.0

^a analyzed by Brunauer Emmett Teller technique (BET)

According to **Table 4.9**, the BET surface areas into supported catalyst with cross-linking agent addition were ranged between 47.8-98.6 m²/g. The pore volume of modified supported catalyst was ranged between 0.01-0.15 cm³/g. The pore volume of Mg(1)OH(6)TMA(6.3)FI_trEtOH was higher than Mg(1)OH(6)TMA(6.3)FI_gcr and Mg(1)OH(6)TMA(6.3)FI_gc probably due to the pore blockage of glycol and glycerol on supported catalyst or the mixing of supported catalyst and cross-linking agents was not suitable. However, the pore size of modified supported catalysts is almost similar (c.a. 36 Å) within the mesoporous range. This can be concluded that addition of cross-linking agents can result in decreased surface area compared to result in **Table 4.3** of Mg(1)OH(6)TMA(6.3)FI, but they were without significant change in pore size.

4.2.1.4 X-ray Diffraction (XRD)

The structural features of the modified supported catalyst were studied by XRD analysis.

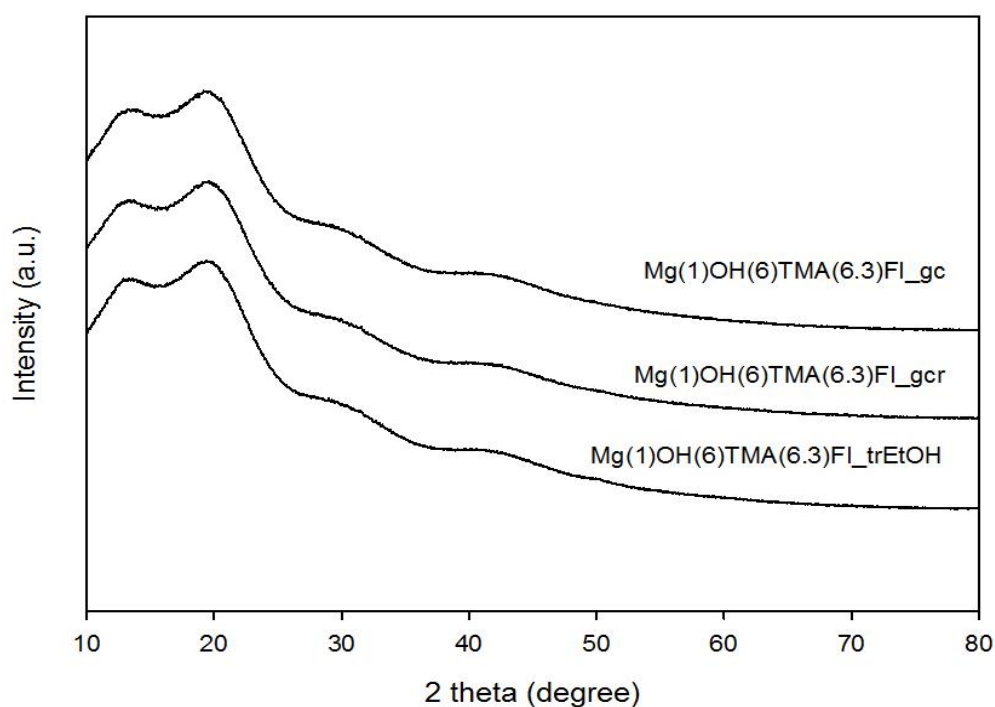


Figure 4.9 XRD patterns after addition of cross-linking agents in MgCl_2 -supported FI catalysts

As displayed in **Figure 4.9**, XRD patterns of modified MgCl_2 supported FI catalysts are showed in the range of 10 to 80 degree. It was found that $\text{Mg(1)OH(6)TMA(6.3)FI_gc}$, $\text{Mg(1)OH(6)TMA(6.3)FI_gcr}$, and $\text{Mg(1)OH(6)TMA(6.3)FI_trEtOH}$ exhibited broad reflections at $2\theta = 12\text{--}16^\circ$ representing a disordered structure of typical MgCl_2 such as $\delta\text{-MgCl}_2$ [45]. At $2\theta = 19.5^\circ$, 30° , and 42° , it showed $\gamma\text{-MgCl}_2$ peaks, which were probably due to using alcohol adduct. The result of disorder MgCl_2 is between ethanol and Mg^{2+} from MgCl_2 support which hold molecular forms resulting in increasing the distance of planer as board peak [36]. When compared **Figure 4.9** with $\text{Mg(1)OH(6)TMA(6.3)FI}$ from **Figure 4.2**, it can concluded that the trend of this graph was similar to that of $\text{Mg(1)OH(6)TMA(6.3)FI}$ structure because all of supported catalyst have the main composition as alcoholic groups.

4.2.1.5 Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra showed the functional groups of modified supported catalyst obtained in the range of 4000-500 cm^{-1} , as shown in **Figure 4.10**.

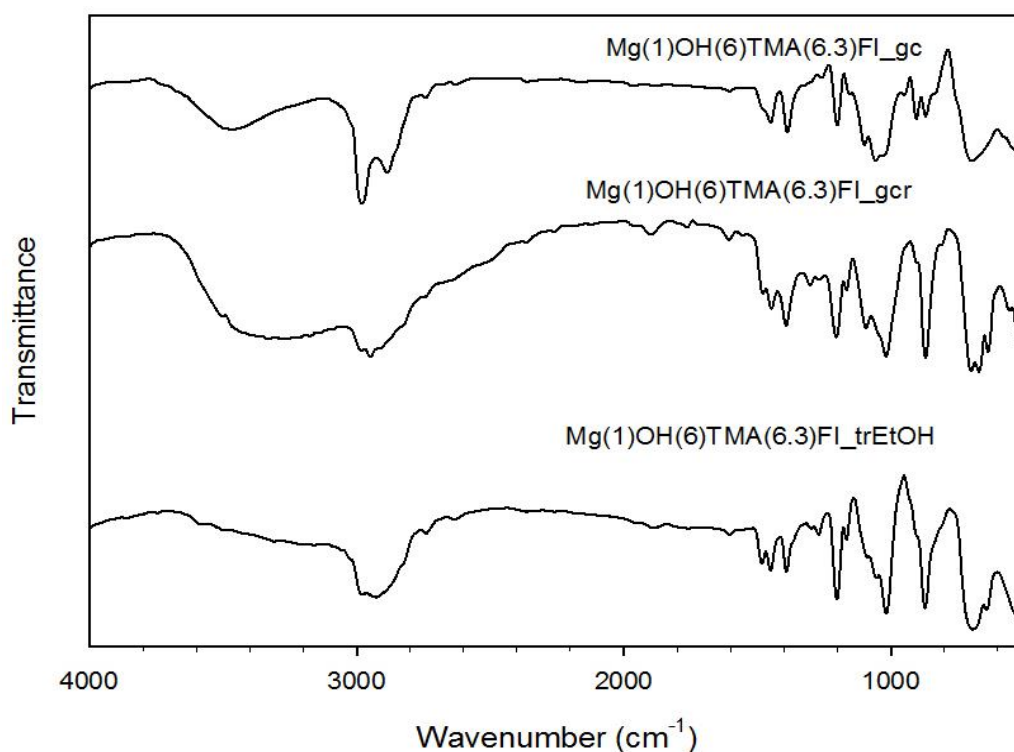


Figure 4.10 FTIR spectra after addition of cross-linking agents in MgCl_2 supported FI catalyst

From **Figure 4.10**, IR analysis of all modified supported catalyst demonstrated at 3467.6-3319.6 cm^{-1} presents the residual O-H stretching band [14], which is referred to ethanol in supported catalyst. The $\text{Mg(1)OH(6)TMA(6.3)FI_trEtOH}$ peak is medium broad at 3600-3300 cm^{-1} due to O-H stretching and at 3500-3300 cm^{-1} (N-H stretching), suggesting that the coating of triethanolamine was perfect where O-H and N-H peaks were merged together. The other signal of the supported catalyst was found with corresponding to C-H stretching at 2980.5-2926.1 cm^{-1} . Furthermore, the IR bands at 1465-1405 and 1395-1355 cm^{-1} were found assigned to C-H bending vibrations of cross-linking agents, which are CH_2 and CH_3 , respectively. At 1897.6 cm^{-1} , with corresponding

to C=O stretching vibration, it was only observed Mg(1)OH(6)TMA(6.3)FI_gcr, probably due to new bonding between catalyst and cross-linking agent. Finally, it is still observed that at 870 cm^{-1} , which is clearly visible by the presence of MAO, can be assigned to the Al-O bond [14, 16].

4.2.1.6 Thermal Gravimetric Analysis (TGA)

Thermal stability of the addition cross-linking agents in supported catalysts with %weight loss was investigated by TGA under nitrogen atmosphere.

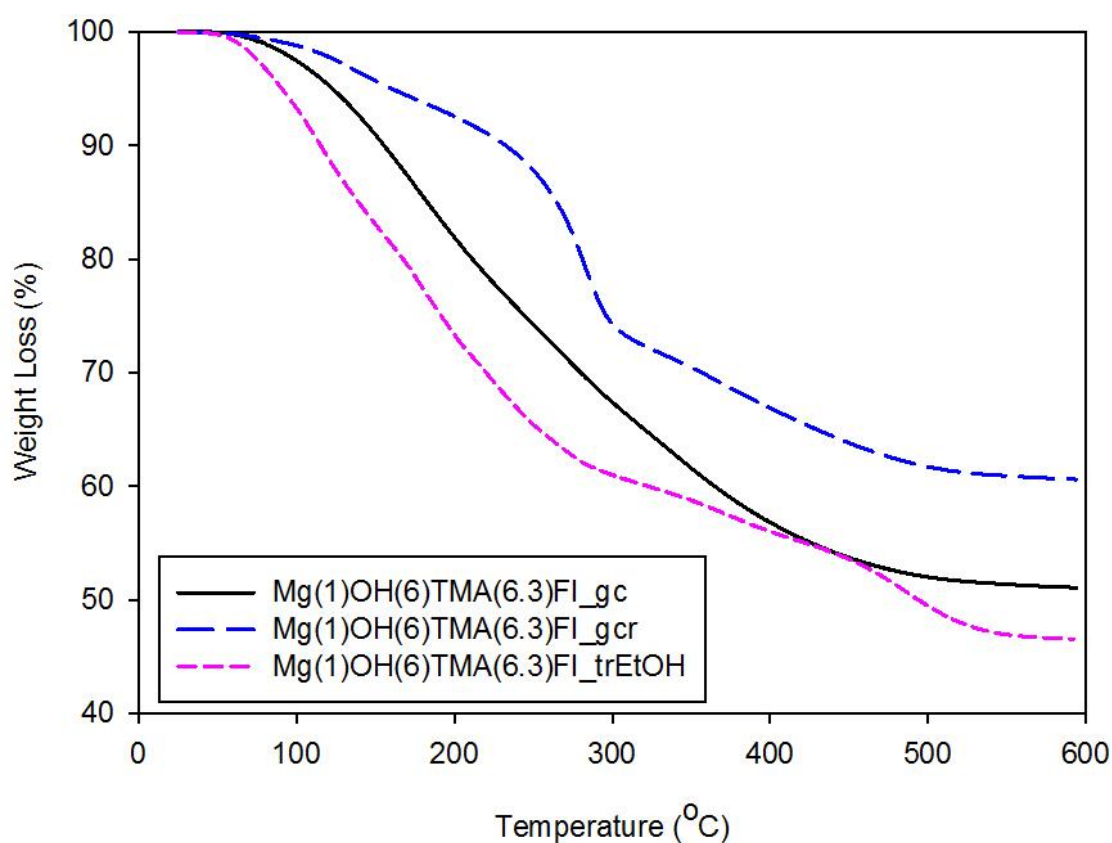


Figure 4.11 TGA profiles of MgCl_2 supported FI catalysts after addition cross-linking agents

As shown in **Figure 4.11**, it was found that compared to this curve, the weight loss of the addition cross-linking agents in supported catalysts with the different types of cross-linking agents decreased significantly and had the similar trend. It was observed that Mg(1)OH(6)TMA(6.3)FI_gcr has the least %weight loss at 38%, followed by Mg(1)OH(6)TMA(6.3)FI_gc and Mg(1)OH(6)TMA(6.3)FI_trEtOH, which have %weight loss at 48% and 54%, respectively. In all graphs, the first period of temperature before 105°C displayed the decomposition moisture. After that, modified supported catalyst decreased continuously as follow: volatile matter, and ash. And after 600°C, in the residues are fixed carbon. From above, the result of this figure indicated that Mg(1)OH(6)TMA(6.3)FI_trEtOH has the strongest thermal stability among all supported catalysts due to %weight loss of the addition cross-linking agents in supported catalysts still have much residue.

4.2.1.7 Differential Thermal Analysis (DTA)

DTA measurement presented the differential thermal analysis of all modified supported catalysts. It can be seen in **Figure 4.12**.

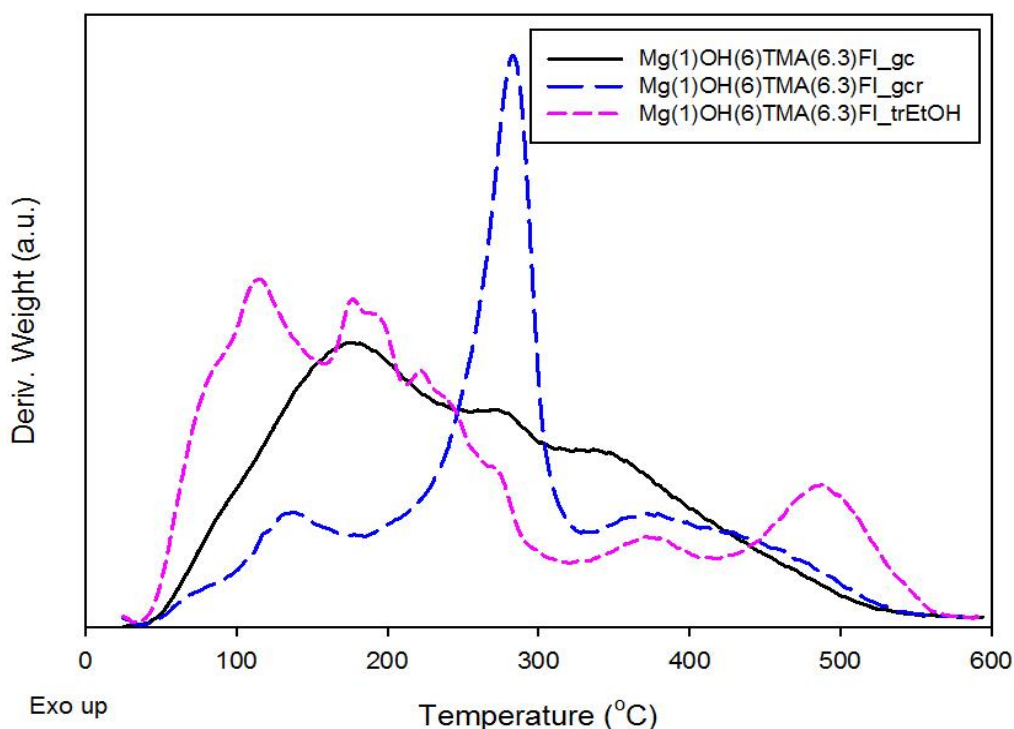


Figure 4.12 DTA profiles of MgCl_2 supported FI catalysts after addition of cross-linking agents

From **Figure 4.12**, DTA curves show that weight loss of modified supported catalysts decomposed in each range of temperatures. The dissociation of alcohol molecular starts from room temperature. First stage occurs quickly with broken of bond. It can be observed that first dissociation was assigned to the loss of O-H molecules as alcohol [36]. In fact, it showed peaks around 160-260°C. Next, the dissociation of second molecule occurred at 300-330°C. $\text{Mg(1)OH(6)TMA(6.3)FI_gc}$ and $\text{Mg(1)OH(6)TMA(6.3)FI_gcr}$ presented two peaks for exothermic desorption. In the part of $\text{Mg(1)OH(6)TMA(6.3)FI_trEtOH}$, it has three peaks displaying an exothermic character probably due to the structure of triethanolamine as cross-linking agent exhibits C-N, C-O bond resulting in various decomposition. For $\text{Mg(1)OH(6)TMA(6.3)FI_gc}$, it was observed that the decomposition was the highest at 170°C. Then, for $\text{Mg(1)OH(6)TMA(6.3)FI_gcr}$, there is a significant peak at 270°C indicating the alcohol dissociation. Finally, $\text{Mg(1)OH(6)TMA(6.3)FI_trEtOH}$ showed many peaks, which are referred to different compositions..

4.2.2 The catalytic activities of ethylene polymerization

4.2.2.1 Effect of cross-linking agents

The MgCl₂-supported FI catalysts were immobilized by cross-linking agents (CAs) as spacer groups including glycol, glycerol and triethanolamine. The yield of polyethylene and activity are shown in **Table 4.10**.

Table 4.10 Catalytic activities of various catalysts having different cross-linking agents

Catalysts	CAs:TMA ratio	Yield (g)	Activity (kg PE/mmol cat .h)
Mg(1)OH(6)TMA(6.9)FI_gc		7.07	2.65
Mg(1)OH(6)TMA(6.9)FI_gcr	1 : 3	7.54	3.59
Mg(1)OH(6)TMA(6.9)FI_trEtOH		3.03	1.34
Mg(1)OH(6)TMA(6.3)FI_gc		10.91	4.60
Mg(1)OH(6)TMA(6.3)FI_gcr	0.2 : 0	12.17	5.06
Mg(1)OH(6)TMA(6.3)FI_trEtOH		6.37	2.65
Mg(1)OH(6)TMA(6.3)FI	-	16.67	7.03

^a condition of ethylene polymerization using 0.5 g MgCl₂-supported FI catalyst in 10 ml, co-catalyst= TMA, reaction time= 30 mins, temperature= 55°C, stir= 450 rpm, P_{ethylene}= 1 barg

As presented in **Table 4.10**, the addition of CAs:TMA molar ratios have two values including 1:3 and 0.2:0 (no adding of TMA). The comparison between Mg(1)OH(6)TMA(6.9)FI_gcr as adding of TMA and Mg(1)OH(6)TMA(6.3)FI_gcr as without adding of TMA can be found that Mg(1)OH(6)TMA(6.3)FI_gcr exhibited higher activity than Mg(1)OH(6)TMA(6.9)FI_gcr obviously. It can conclude that the CAs:TMA molar ratios of Mg(1)OH(6)TMA(6.3)FI_gcr as without adding of TMA gives better activity than adding TMA. Then, it considers on the roles of cross-linking agent types. It can be found that Mg(1)OH(6)TMA(6.3)FI_gcr exhibited the highest PE yield up to 12.17 g with the highest activity of 5.06 kg PE/mmol cat. h. when compared to Mg(1)OH(6)TMA(6.3)FI_gc and Mg(1)OH(6)TMA(6.3)FI_trEtOH catalysts. The structure of glycol and triethanolamine may be more bulky and hindered the reaction. In addition, the Ti/Mg ratio measured by ICP of Mg(1)OH(6)TMA(6.3)FI_gcr, as shown in **Table 4.8** was 0.44, which is also the highest. Normally, high Ti/Mg ratio of catalyst can result in high activity due to Ti species are active sites. However, from **Table 4.5**, Mg(1)OH(6)TMA(6.3)FI_gcr exhibited the highest activity, although it had the lowest Ti/Mg ratio value. However, this is perhaps due to most of Ti species were present in the highly-dispersed form. On the other words, the highly-dispersed form is more isolated and being more active [41-43]. Finally, the comparison between Mg(1)OH(6)TMA(6.3)FI and Mg(1)OH(6)TMA(6.3)FI_gcr was concluded that Mg(1)OH(6)TMA(6.3)FI (without adding cross-linking agent) had the highest PE yield and activity.

4.2.3 The characterization of polyethylene

4.2.3.1 Scanning Electron Microscopy (SEM)

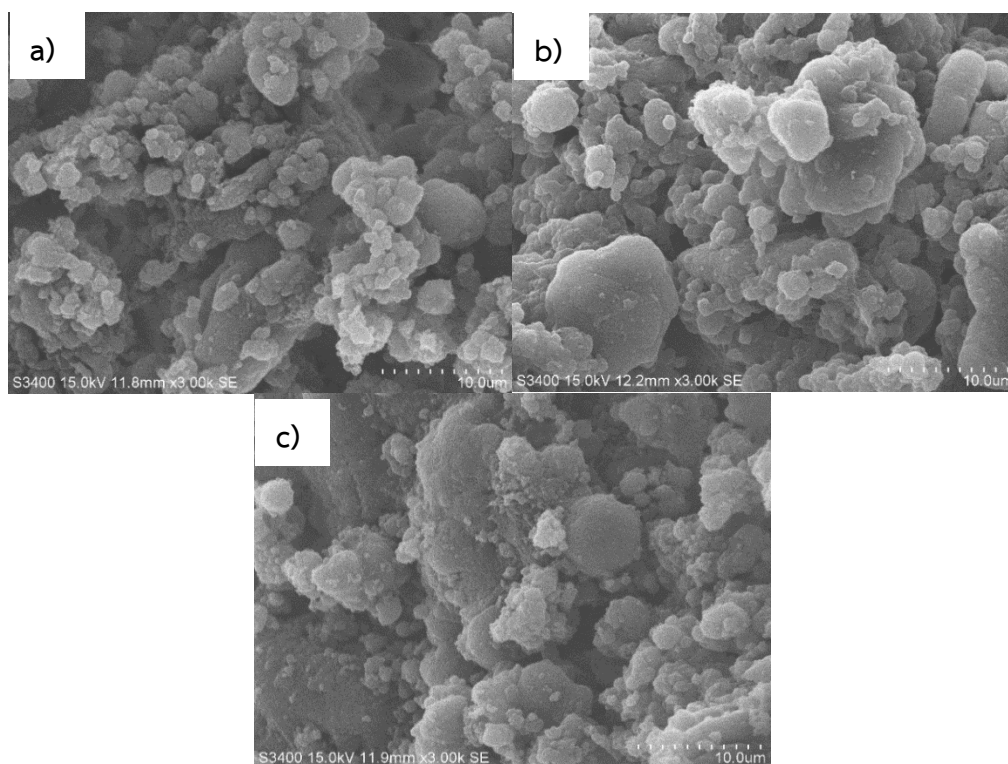


Figure 4.13 SEM micrographs of the polyethylene at 3 kx magnification

a) Mg(1)OH(6)TMA(6.3)FI_gc b) Mg(1)OH(6)TMA(6.3)FI_gcr
and c) Mg(1)OH(6)TMA(6.3)FI_trEtOH

As displayed in **Figure 4.13**, it explained about polyethylene from polymerization of using the modified MgCl_2 -supported FI catalyst. From above, all polymers obtained have also both large spheroidal lump and small spherical shape. It was found that not only in the addition of cross-linking agents, but also without cross-linking agent addition. On the other words, the polymer obtained was lump and also similar. It can conclude that the addition of crosslinking agents did not affect the polyethylene morphology. In addition, polyethylene obtained from Mg(1)OH(6)TMA(6.3)FI_gcr exhibited the similar shape as replicated from the morphology of Mg(1)OH(6)TMA(6.3)FI_gcr as seen in **Figure 4.8** revealing high porosity and a well-done distribution of active sites [14].

4.2.3.2 Gel Permeable Chromatography (GPC) and Differential Scanning Calorimeter (DSC)

Molecular weight of polymer and molecular weight distribution (MWD) were analyzed using GPC as displayed in **Table 4.11**. Furthermore, **Table 4.11** shows melting temperature of polymer, which can be proven from the DSC measurement.

Table 4.11 Influence of cross-linking agent types on polyethylene properties

Catalysts	Mn ($\times 10^5$) ^a	Mw ($\times 10^5$) ^a	MWD ^a	T _m (°C) ^b
Mg(1)OH(6)TMA(6.3)FI	5.86	13.21	2.25	126.3
Mg(1)OH(6)TMA(6.3)FI_gc	5.91	14.22	2.41	127.1
Mg(1)OH(6)TMA(6.3)FI_gcr	8.03	15.38	1.92	126.8
Mg(1)OH(6)TMA(6.3)FI_trEtOH	5.07	13.22	2.65	127.8

^a Determined by GPC

^b Determined by DSC

From **Table 4.11**, it considers in polymer molecular weight distribution between adding cross-linking agents and polymer obtained without cross-linking agents. The Mg(1)OH(6)TMA(6.3)FI had lower molecular weight (MW) than polyethylene with addition of cross-linking agents. However, MWD of Mg(1)OH(6)TMA(6.3)FI was narrower than that with addition of cross-linking agents.. For polyethylene of addition of different cross-linking agents. The Mg(1)OH(6)TMA(6.3)FI_gcr had the narrowest MWD (only 1.92), which was nearly homogeneous system and also produced UHMWPE, HMWPE [35]. For the result of this part, when cross-linking agents were introduced, the molecular weight distribution of polymer apparently decreased compared with Mg(1)OH(6)TMA(6.3)FI. In case of addition of cross-linking agents, it was found that molecular weight distribution was improved. As a consequence, the added spacer groups blocked catalyst active center, which can control molecular weight of polymer. However, the added spacer groups did not affect the melting temperature. According to the results in **Table 4.6 and 4.11**, it should be mentioned that the addition of different TMA mole ratios and cross-linking agents cannot alter, the melting temperature (T_m) of polymer, which was still similar at 126-127°C.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This research purposes to investigate the effect of TMA molar ratios and the different types of cross-linking agents used in the MgCl_2 -supported FI catalysts, which were effectively active catalysts for ethylene polymerization to produce UHMWPE.

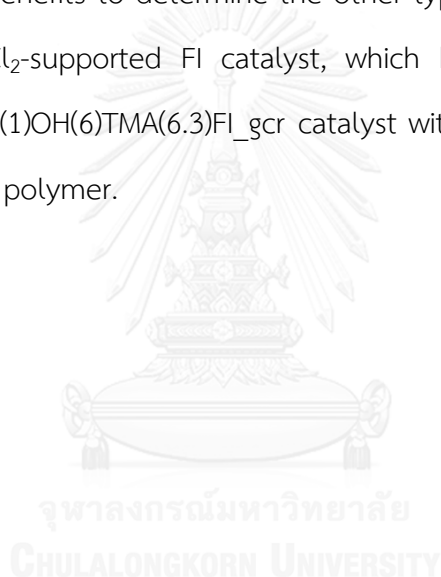
In the first part of this work, it studied the different TMA molar ratios having molar ratios of 1:6 (MgCl_2 :EtOH) with 3 different amounts of TMA including 1:6:6, 1:6:6.3 and 1:6:6.6. The MgCl_2 -supported FI catalysts are nearly similar in all of analysis. In the part of polymer obtained, $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$ gave the highest catalytic activity among the FI catalyst (homogeneous system), $\text{Mg}(1)\text{OH}(6)\text{TMA}(6)\text{FI}$, and $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.6)\text{FI}$. In addition, $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$ catalyst gave also the narrowest molecular weight distribution (MWD) among others TMA mole ratios. However, it exhibited broader MWD than FI catalyst as 1.67. The polymerization temperature at 55°C was the optimal polymerization temperature, leading to the highest catalytic activity. Hence, $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$ had the suitable TMA mole ratio for ethylene polymerization. All supported catalysts were found to have no fouling in the reactor and the high catalytic activity can be obtained. Moreover, the morphology of supported catalyst and polymer obtained was almost spheroidal shapes. From above, it confirmed by ^1H NMR that TMA was transformed to MAO by -OH group from the MgCl_2 :EtOH adduct.

According to MgCl_2 -supported FI catalysts modified with different cross-linking agents including glycol, glycerol, and triethanolamine to improve catalytic activity and MWD, it can be observed that adding of cross-linking agents did not increase the catalytic activity when compare $\text{Mg}(1)\text{OH}(6)\text{TMA}(6.3)\text{FI}$. For MWD, it was found that

adding glycerol exhibited narrower MWD than that without adding cross-linking agents. So, the addition of cross-linking agents can control molecular weight distribution of polymer obtained.

5.2 Recommendations

- The different synthesis methods should be obtained with the different co-catalysts.
- It is of great benefits to determine the other types of cross-linking agents for modified MgCl_2 -supported FI catalyst, which has the higher activity than glycerol in $\text{Mg(1)OH(6)TMA(6.3)FI_gcr}$ catalyst with narrower molecular weight distribution of polymer.



APPENDIX A
SCANNING ELECTRON MICROSCOPY (SEM)



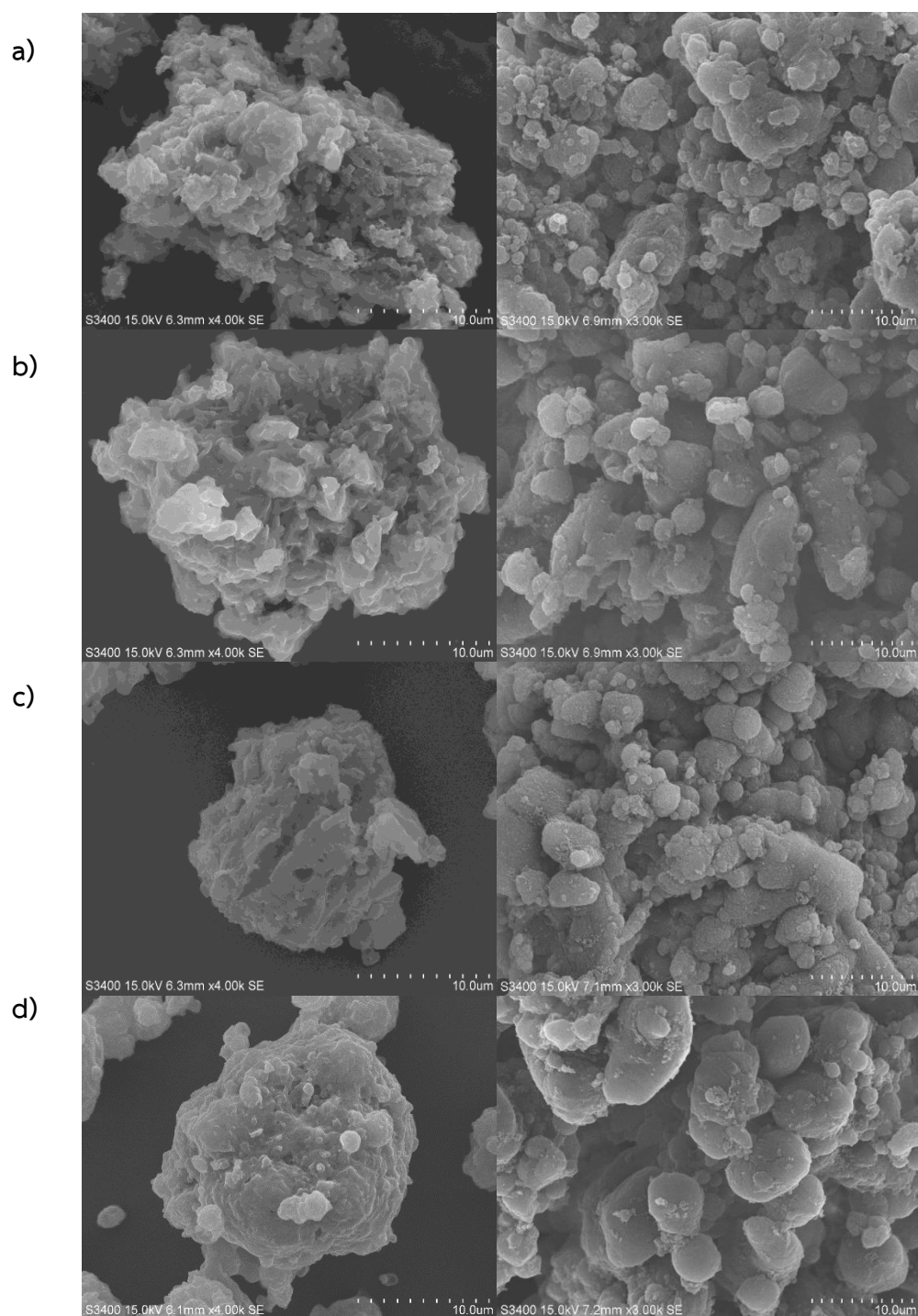


Figure A-1 SEM micrographs of MgCl₂-supported FI catalyst (left) and polymer obtained (right) at 4 kx magnification a) Mg(1)OH(4)TMA(4.3)FI b) Mg(1)OH(6)TMA(6.3)FI c) Mg(1)OH(8)TMA(8.3)FI and d) Mg(1)OH(10)TMA(10.3)FI



APPENDIX B

INDUCTIVELY COUPLED PLASMA AND ENERGY DISPERSIVE X-RAY

SPECTROSCOPY (EDX)

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Table B-1 the element of MgCl₂ supported FI catalyst by ICP

Catalysts	%Ti	%Al	%Mg	Ti/Mg (mol/mol)
Mg(1)OH(4)TMA(4.3)FI	53.86	4.01	68.69	0.40
Mg(1)OH(8)TMA(8.3)FI	84.12	6.20	92.18	0.46
Mg(1)OH(10)TMA(10.3)FI	77.17	6.16	96.10	0.41

Table B-2 Ti, Al and Mg percentages disperse on bulk surface supported by EDX

Catalysts	%Ti	%Al	%Mg	Ti/Mg (mol/mol)
Mg(1)OH(4)TMA(4.3)FI	3.18	50.24	46.59	0.04
Mg(1)OH(8)TMA(8.3)FI	3.31	51.53	45.16	0.04
Mg(1)OH(10)TMA(10.3)FI	10.27	89.73	96.099	0.05

The logo of Chulalongkorn University, featuring a central emblem with a sunburst and a crown, surrounded by a circular border.

APPENDIX C

N₂ PHYSISORPTION OF MgCl₂ SUPPORTED FI CATALYST

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Table C-1 N₂-physisorption of MgCl₂ supported FI catalyst

catalysts	surface area^a (m²/g)	pore volume^a (cm³/g)	pore size^a (Å)
Mg(1)OH(4)TMA(4.3)FI	138.9	0.2104	36.98
Mg(1)OH(8)TMA(8.3)FI	208.2	0.164	36.99
Mg(1)OH(10)TMA(10.3)FI	228.9	0.1809	38.26

^a analyzed by Brunauer Emmett Teller technique (BET)





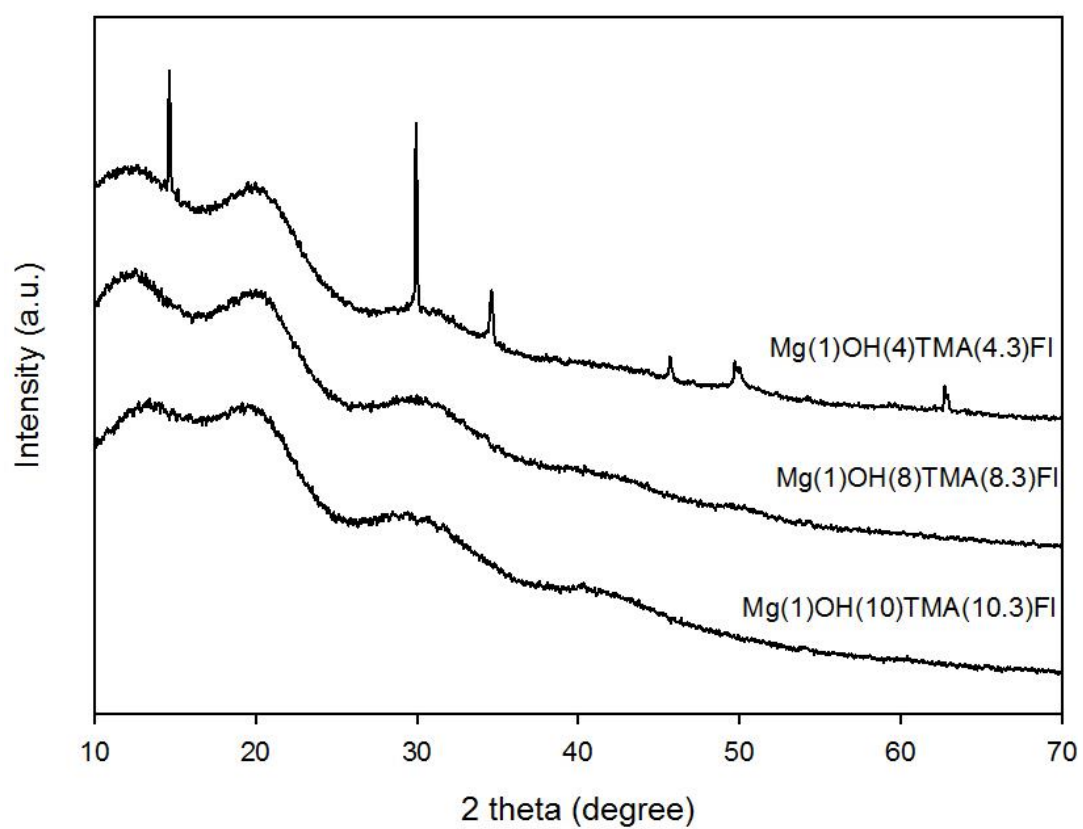


Figure D-1 XRD patterns of MgCl₂ supported FI catalysts



APPENDIX E

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

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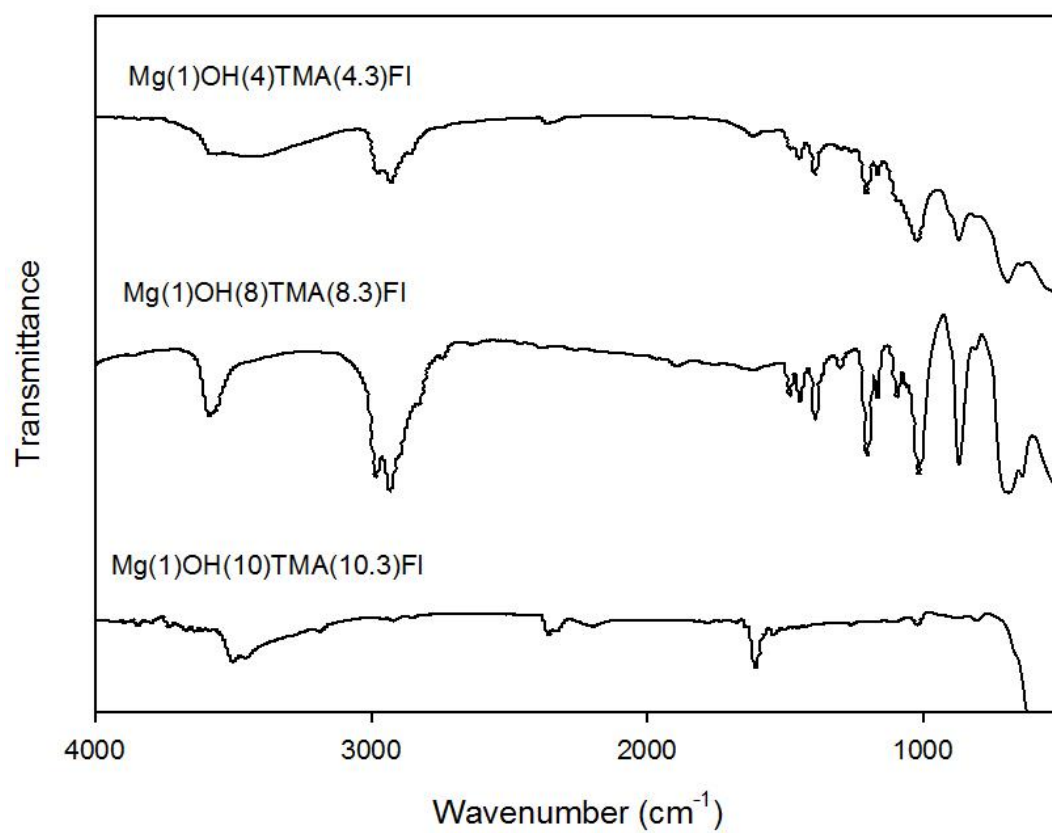


Figure E-1 FTIR spectra of MgCl₂ supported FI catalysts

APPENDIX F
THERMAL GRAVIMETRIC ANALYSIS (TGA)



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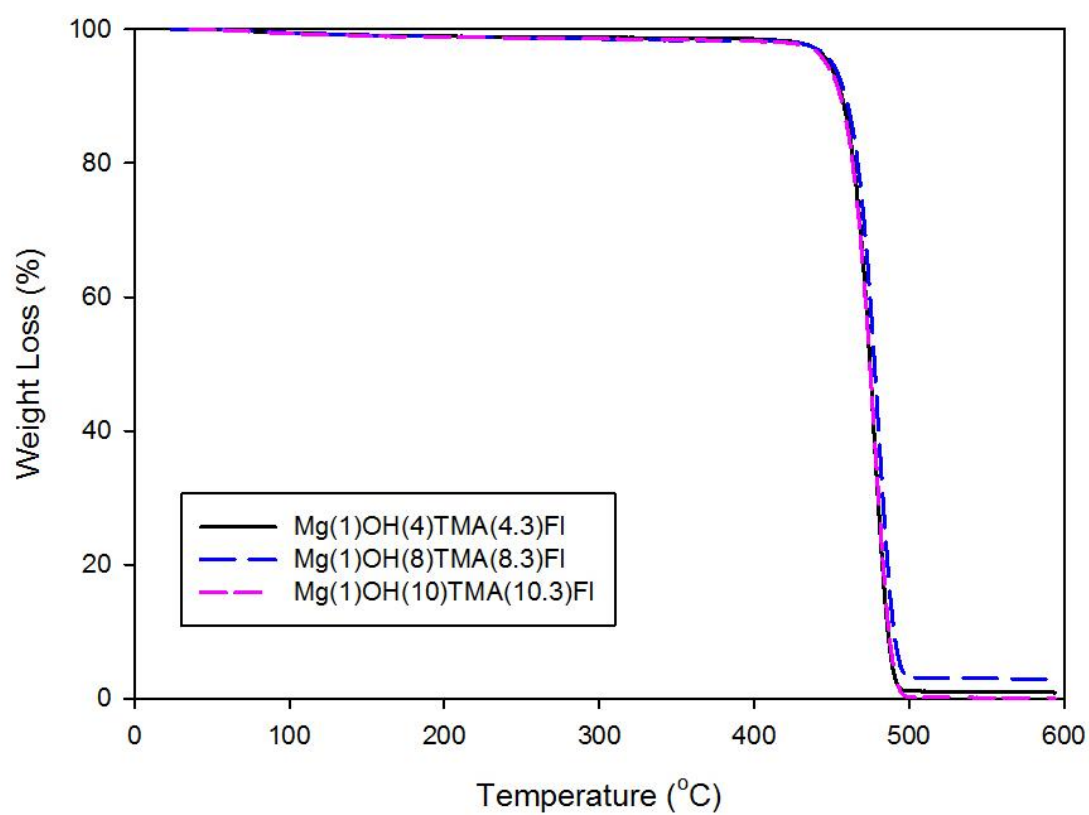
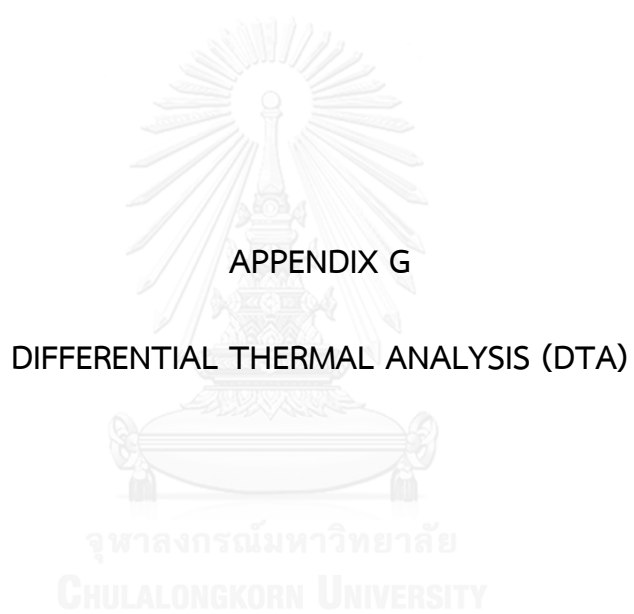


Figure F-1 TGA profiles of MgCl₂ supported FI catalysts



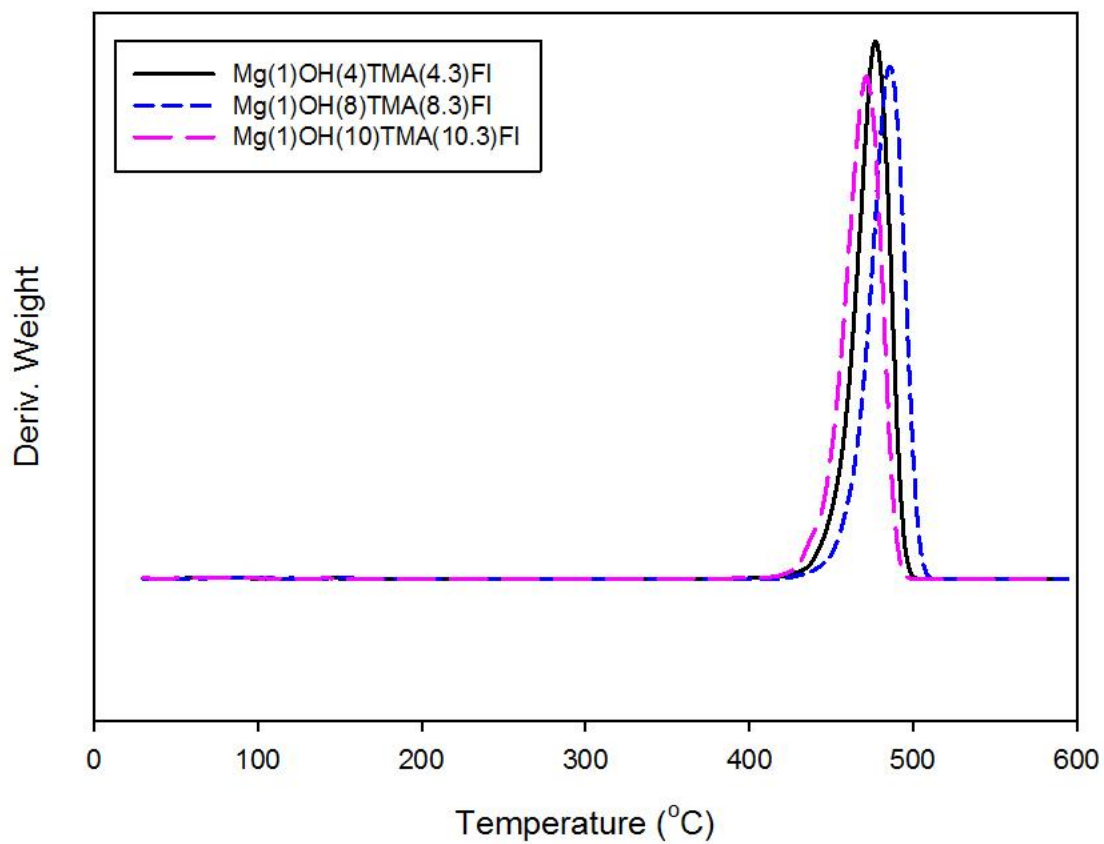


Figure G-1 DTA profiles of MgCl₂ supported FI catalysts



APPENDIX H

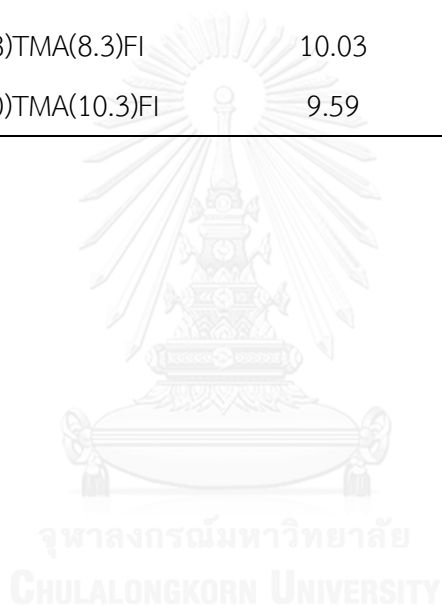
CATALYTIC ACTIVITIES OF MgCl_2 SUPPORTED FI CATALYST

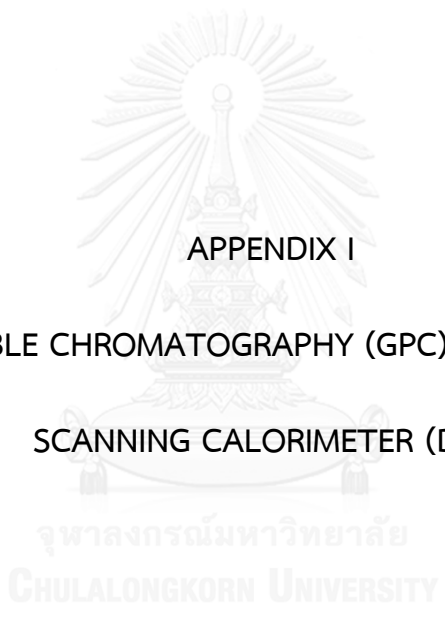
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Effect of MgCl_2 adduct ratios

Table H-1 Effect of ethanol mole ratios on the ethylene polymerization

catalysts	PE yield (g)	activity (kg PE/mmol cat .h)
FI catalyst (homogeneous)	3.40	1.51
Mg(1)OH(4)TMA(4.3)FI	11.89	2.97
Mg(1)OH(6)TMA(6.3)FI	16.67	7.03
Mg(1)OH(8)TMA(8.3)FI	10.03	3.91
Mg(1)OH(10)TMA(10.3)FI	9.59	4.17





APPENDIX I

GEL PERMEABLE CHROMATOGRAPHY (GPC) AND DIFFERENTIAL
SCANNING CALORIMETER (DSC)

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Table I-1 Influence of various TMA ratios and ethanol ratios on polyethylene

catalysts	Mn x10 ⁵	Mw x10 ⁵	MWD	T _m (°C)
FI catalyst (homogeneous)	8.40	14.06	1.67	127.6
Mg(1)OH(4)TMA(4.3)FI	3.60	11.93	3.32	125.5
Mg(1)OH(8)TMA(8.3)FI	6.40	14.28	2.28	125.6
Mg(1)OH(10)TMA(10.3)FI	6.06	13.69	2.27	125.4





J. List of publication

Thanyaporn Pongchan, Supaporn Khubunsongserm, and Bunjerd Jongsomjit “The effect of addition TMA on $MgCl_2/EtOH$ for ethylene polymerization” (The 26th National Thai Institute of Chemical Engineering and Applied Science Conference (TIChE2016) and the 6th International Thai Institute of Chemical Engineering and Applied Science Conference (ITIChE2016), Bangkok, Thailand)



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