ผลของไตรเมทิลอะลูมินัมที่เหลือในเมทิลอะลูมินอกเซนต่อคุณลักษณะและสมบัติการเร่งปฏิกิริยา

ของตัวเร่งปฏิกิริยาเซอร์โคโนซีน/เมทิลอะลูมินอกเซนสำหรับเอทิลีนพอลิเมอไรเซชัน

นายชยุต ฉินธนะปทุมพร

EFFECT OF RESIDUAL TRIMETHYLALUMINUM IN
METHYLALUMINOXANE ON CHARACTERISTICS AND CATALYTIC
PROPERTIES OF SiO$_2$-SUPPORTED ZIRCONOCENE/MAO CATALYST 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 2012

Thesis Title	EFFECT OF RESIDUAL TRIMETHYLALUMINUM IN METHYLALUMINOXANE ON CHARACTERISTICS AND CATALYTIC PROPERTIES OF SiO2-SUPPORTED ZIRCONOCENE/MAO CATALYST FOR ETHYLENE POLYMERIZATION
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Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

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ชยุต ฉินธนะปทุมพร : ผลของไตรเมทิลอะลูมินัมที่เหลือในเมทิลอะลูมินอกเซนต่อคุณลักษณะและสมบัติการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาเซอร์โคโนซีน/เมทิลอะลูมินอกเซนสำหรับเอทิลีนพอลิเมอไรเซชัน. (EFFECT OF RESIDUAL TRIMETHYLALUMINUM IN METHYLALUMINOXANE ON CHARACTERISTICS AND CATALYTIC PROPERTIES OF SiO$_2$-SUPPORTED ZIRCONOCENE/MAO CATALYST FOR ETHYLENE POLYMERIZATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ศ.ดร. ปิยะสาร ประเสริฐธรรม, 91 หน้า.

ในวิทยานิพนธ์ฉบับนี้ได้ทำการศึกษาเกี่ยวกับไตรเมทิลอะลูมินัมที่เหลือในเมทิลอะลูมินอกเซนโดยจะศึกษาถึงกระทบต่อความว่องไวของตัวเร่งปฏิกิริยาในกระบวนการเอทิลีนพอลิเมอไรเซชัน ซึ่งขั้นตอนแรกจะทำการศึกษาถึงอุณหภูมิในการแคลไซน์ซิลิกาและอัตราส่วนโดยโมลระหว่างซิลิกาและเมทิลอะลูมินอกเซน โดยพบว่าอุณหภูมิที่ 600 องศาเซลเซียสและอัตราส่วนโดยโมลระหว่างซิลิกาและเมทิลอะลูมินอกเซนที่ 1.5 มีความเหมาะสมมากที่สุด หลังจากนั้นจะนำเมทิลอะลูมินอกเซนที่นำการกำจัดไตรเมทิลอะลูมินัม(dried-MAO or dMAO) มาผสมกับปริมาณต่างๆที่ต้องการของไตรเมทิลอะลูมินัม ซึ่งส่วนผสมของ dMAO กับไตรเมทิลอะลูมินัมจะถูกยึดเกาะลงบนซิลิกาแล้วตามด้วยตัวเร่งปฏิกิริยาเมทัลโลซีน จากการทดลองพบว่าdMAO กับไตรเมทิลอะลูมินัมที่ปริมาณ 28.6 เปอร์เซ็นต์โดยน้ำหนักจะมีความว่องไวของตัวเร่งปฏิกิริยาที่มากที่สุด เนื่องจากปริมาณของไตรเมทิลอะลูมินัมที่น้อยกว่า 28.6 เปอร์เซ็นต์โดยน้ำหนัก จะพบว่ามีหมู่ไฮดรอกซิลของdMAO กับไตรเมทิลอะลูมินัมบนซิลิกาที่หลงเหลืออยู่ ซึ่งเมื่อทำปฏิกิริยากับตัวเร่งปฏิกิริยาเมทัลโลซีนจะเกิดสารปนเปื้อนขึ้นซึ่งส่งผลต่อความว่องไวของปฏิกิริยา ในส่วนของไตรเมทิลอะลูมินัมที่มากกว่า 28.6 เปอร์เซ็นต์โดยน้ำหนัก จะพบว่าเกิดสปีชี่ส์ที่มีความว่องไวต่ำซึ่งส่งผลให้ระบบมีความว่องไวของปฏิกิริยาที่น้อยลง

ภาควิชา   วิศวกรรมเคมี   ลายมือชื่อนิสิต _____

สาขาวิชา   วิศวกรรมเคมี   ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก _____

ปีการศึกษา   2555

5370631121 : MAJOR CHEMICAL ENGINEERING

KEYWORDS : METALLOCENE CATALYST / RESIDUAL TMA / SILICA / HETEROGENEOUS SYSTEM

CHAYUT CHINTANAPATUMPORN : EFFECT OF RESIDUAL TRIMETHYLALUMINUM IN METHYLALUMINOXANE ON CHARACTERISTICS AND CATALYTIC PROPERTIES OF SiO_2-SUPPORTED ZIRCONOCENE/MAO CATALYST FOR ETHYLENE POLYMERIZATION. ADVISOR : PROF. PIYASAN PRASERTHDAM, Dr.Ing., 91 pp.

In this study, the effect of residual trimethylaluminum in methylaluminoxane was studied through catalytic activity of ethylene polymerization. The conditions of support calcination temperatures and SiO_2:MAO molar ratios were first investigated, which the heating temperature at   600 ℃ and SiO_2:MAO ratio of 1.5 provided the suitable condition. Afterwards, the MAO having TMA (dried-MAO or dMAO) removed was prepared and reacted with various amounts of TMA. Then, the mixture of dMAO+TMA was impregnated on to the commercial silica support followed by metallocene catalyst. The silica-supported zirconocene/dMAO+TMA was prepared. The activity of ethylene polymerization of residual TMA at 28.6 wt% offered the highest catalytic activity. The reason is that at the amount of TMA less than 28.6 wt% of silica-supported dMAO+TMA, isolated silanol group was observed and when it reacted with metal complex, the catalyst poison was formed. In case of TMA higher than 28.6 wt%, the cocatalyst resulted in the inactive species, which affected on the reduction of catalytic activity.

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

Field of Study : Chemical Engineering   Advisor's Signature ....

Academic Year : 2012 ....

ACKNOWLEDGEMENTS

The author would like to express my deepest appreciation to my advisor, teachers, friends, and my family for their support and guidance for all over the time through my thesis. I would like to gratitude, first and foremost, my thesis advisor, Professor Dr. Piyasan Praserthdam, for his valuable suggestions, guidance, and discussions in academic perspective throughout my dissertation. His advices are persistently helpful.

Moreover, I am sincerely grateful Associate Professor Dr. Bunjerd jongsomjit, Associate Professor Dr. Joongjai Panpranot, Associate Professor Dr. Supakanok Thongyai, and Dr. Saovalak Sripothongnak for their appreciated suggestions and guidance.

I would like to thank to the Thai Polyethylene Co., Ltd. for the support of financial, chemicals, instruments and opportunity during this research.

In addition, thanks to friends in the Center of Excellence on Catalysis and Catalytic Reaction Engineering especially of Ziegeler-Natta and Metallocene group which always share happy and encouraging moment with me.

Finally, I would like to owe my warm gratitude to my family that always supporting me throughout my life.

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CHAPTER I

INTRODUCTION

Polyolefins, polyethylene (PE) and polypropylene (PP), which are produced from the monomer of α-olefins (alkene), are the most extensively used of synthetic polymers or thermoplastic polymers. Polyolefins themselves own a diversity of properties including strength, lightness, processability, high chemical resistance, stability, durability, well defined molecular structures and properties and furthermore to reuse and recycle. The worldwide production from polyolefins has been produced larger than 145 million tons in 2010, which can calculate to be 50% of all polymers. Their applications are utilized generally in daily life such as packing materials, films, piping, containers and electronic parts [1-3].

Polyolefins can be produced via the Ziegler-Natta catalyst or metallocene catalyst, which both catalysts provide the dissimilar properties of polymer. Ziegler-Natta catalyst was firstly used in the production of polyolefins in 1953 by the combination of $TiCl_4$ and $Al(C_2H_5)_3$. This system contains a wide range of active species and generated the polymer with relatively broad molecular weight distribution that in contrast to metallocene catalytic system [4].

Metallocene catalysts are single site catalysts, which have ability of high catalytic activity, excellent stereochemical structure and the possibility of tailoring polymer properties such as molecular weight and molecular weight distribution (polydispersity) [5,6]. These catalysts also produced uniform polymer with narrow molecular weight distribution [7].

The homogenized metallocene catalysts provide the high catalytic activity, but also have many disadvantages in industrial applications due to the lacks of

morphology control, require excess amount of methylaluminoxane and also reactor fouling [6,8]. The immobilization of metallocene catalysts on supports, such as silica, magnesium chloride, and aluminum oxide [9-11], is an alternative approach to employ in the industrial plants. The main objective for using support is to preserve the advantages of homogeneous catalytic system [12]. Moreover, the catalyst should not be leached from the support when polymerization and reduced the amount of cocatalyst. The nature of the support also plays an important role in catalytic activity and final properties of the polymer such as particle size distribution and bulk density [9,13-14].

The commercial cocatalyst, for metallocene catalytic system, can be synthesized in several methods, but the influent method is the partial hydrolysis of trimethylaluminum (TMA) and a certain amount of residual TMA is always remain in methylaluminoxane (MAO) solution.

In this study, the first part was focused on the effect of calcination temperatures of silica support and SiO_2:MAO ratios. The silica support was calcined at 3 different temperatures, and then it was reacted with MAO. After that, the metallocene catalyst was injected in the reactor contains SiO_2-supported MAO and solvent for ethylene polymerization. The commercial silica support was characterized to investigate the main physical properties (BET surface area, average pore size diameter, and pore volume) by using nitrogen physisorption and the type of species on the support by fourier transform-infrared spectroscopy (FT-IR). Then, the SiO_2-supported MAO was characterized using inductively couple plasma-optical emission spectrometer (ICP-OES) to determine the aluminum content. Surface species were characterized by Fourier transform-infrared spectroscopy (FT-IR). The catalytic behavior of the supported systems was evaluated in terms of ethylene slurry homopolymerization to study the effect of calcination temperatures.

The second part was focused on the effect of residual TMA through the aluminum loading, catalytic activity and also polymer properties. Firstly, MAO solution was removed "free TMA" by evacuated and washed with solvent at room

temperature. Afterward the dried-MAO (dMAO) was added with several amounts of TMA. Then, silica support was loaded with dMAO+TMA mixture and metallocene catalyst respectively. The SiO_2-supported dMAO+TMA was characterized using inductively couple plasma-optical emission spectrometer (ICP-OES) to determine the aluminum content. Surface species were characterized by fourier transform-infrared spectroscopy (FT-IR). The homopolymerization of ethylene was studied in order to study the effect of residual TMA on catalytic activity. Moreover, the polyethylene was characterized by differential scanning calorimetry (DSC) and gel permeation chromatography (GPC) for polymer properties.

1.1 Objectives

The studies of the effect of calcination temperatures on silica support and SiO_2:MAO ratios in the *ex situ* impregnation method through the Al content are the main objectives in this research. Moreover, the quantity of residual trimethylaluminum (TMA) contained in methylaluminoxane solution for *ex situ* metallocene/methylaluminoxane heterogeneous system was studied over the catalytic activity in ethylene homopolymerization.

1.2 Research scopes

The scopes of this research are to study the effect of residual TMA in the heterogeneous metallocene system via the catalytic activity of ethylene polymerization and polymer properties. The scopes are summarized in the detail as follows:

- Thermal treatment of commercial silica support at 3 different temperatures i.e. 400°C, 600°C and 800°C.
- Characterize of calcined silica by nitrogen physisorption, SEM, and FT-IR.
- Prepare the silica-supported MAO with various SiO_2:MAO ratios and characterize by ICP-OES, FT-IR, SEM, and SEM-EDX.

- Study and choose the suitable conditions of calcination temperatures and SiO_2:MAO ratios.

- Prepare dried MAO which not contain free TMA and characterize by ^{1}H NMR

- Vary TMA amount to add in dMAO and react with the carrier for SiO_2-supported dMAO+TMA

- Characterize the SiO_2-supported dMAO+TMA by ICP-OES, FT-IR, SEM, and SEM-EDX.

- Prepare and characterize SiO_2-supported zirconocene/dMAO+TMA

- Study the effect of residual TMA on catalytic activity and polymer properties of polyethylene by SEM, DSC, and GPC

1.3 Research methodology

The methodology of this research is shown in Figure 1.1.
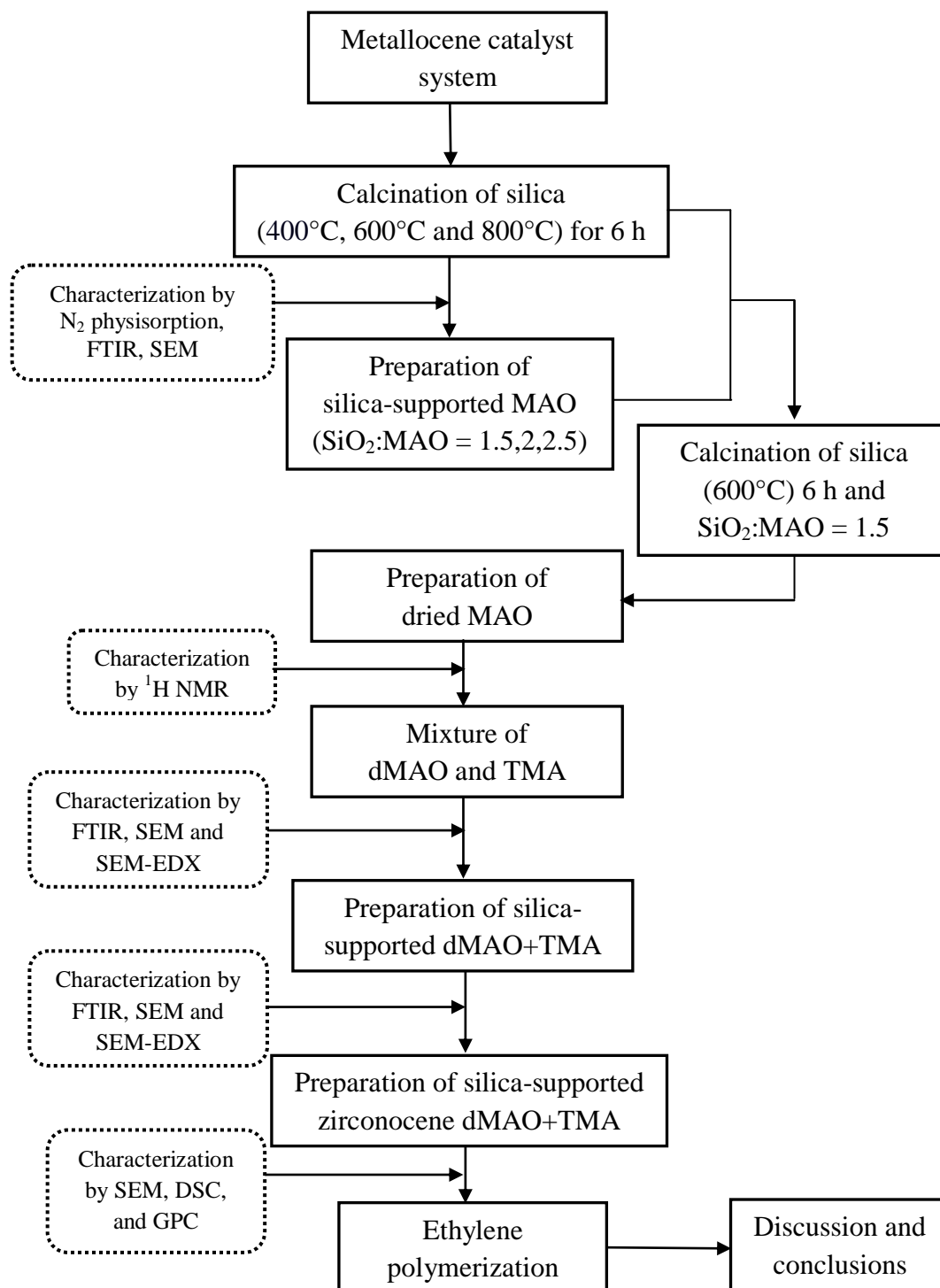
Figure 1.1 Flow diagram of research methodology

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Polyethylene classification

Polyethylene is a synthetic polymer consisting of long chains of ethylene monomer. In term of industrial, polyethylene is the most widely used and produced polymer in the world due to its ability of good physical and mechanical properties, inexpensive to produce, high chemical resistance and etc. In the ethylene polymerization, it can be produced in several methods as radical polymerization, anionic addition polymerization, and cationic addition polymerization, which each of these approaches resulting in different types of polymer. Based on its density and branching, polyethylene can be classified in 4 categories (Figure 2.1) [15].

2.1.1 High density polyethylene (HDPE)

HDPE has a density within the range of $0.941 - 0.965$ g/cm^3. This kind of PE has a low degree of branching which provides the HDPE to have ability of strong and tough polymer and also least flexible when compare with other types of polyethylene. The application of HDPE is widely used as plastic bottle, bottle cap, food storage container, pipeline, and pipe system.

2.1.2 Low density polyethylene (LDPE)

LDPE is generally has a density in the range of $0.910 - 0.940$ g/cm^3. LDPE is a thermoplastic with a low crystalline structure and high degree of short and long chain branching. It is mostly used for plastic bag, various container, tubing, and plastic wrap. The production of LDPE is formed by radical polymerization with a high pressure process.

2.1.3 Linear low density polyethylene (LLDPE)

LLDPE has a density of 915–0.925 g/cm^3. This kind of polymer has a high tensile strength due to the significantly numbers of short branches in polymer chain. The production of LLDPE is a copolymerization of ethylene and α-olefins as 1-butene, and 1- hexene either in production of solution process or gas-phase process. The application of LLDPE is widely used as plastic bag, plastic wrap, pipe, container, and flexible tubing.

2.1.4 Very low density polyethylene (VLDPE)

VLDPE has a density within the range of 0.880–0.915 g/cm^3. This kind of polymer is a substantially linear polymer with high levels of short-chain branches. It can be produced by metallocene catalyst which ethylene incorporates with short chain α-olefins. The application of LLDPE is widely used as frozen bag, tubing, and stretch wrap.

(A)

(B)

(C)

(D)
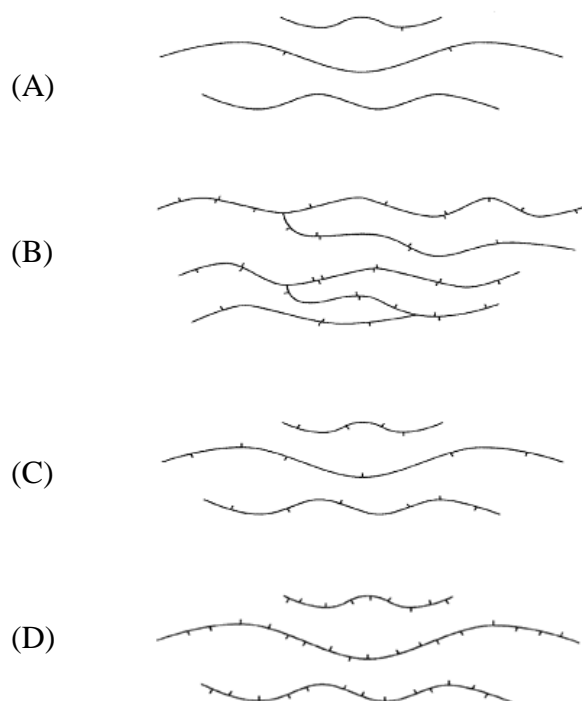
Figure 2.1 Schematic representations of the different classes of polyethylene [15].
(A) HDPE (B) LDPE (C) LLDP (D) VLDPE

2.2 Transition metal catalysts for olefin polymerization

More than 50 years, the Ziegler-Natta catalyst was discovered for production of polyolefins, polyethylene and polypropylene, under low pressure condition. This catalyst composes of halides transition metal ($TiCl_4$, $TiCl_3$, and $ZrCl_4$) in combination with alkylaluminum compounds. Ziegler-Natta catalyst produces polymer with high catalytic activity and excellent morphology which can be high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and isotactic polypropylene. The $MgCl_2$-supported catalyst is the most common type of Ziegler-Natta catalyst because $MgCl_2$ is a support material which promoted the complex with titanium active sites that give a very high active catalyst and also narrow molecular weight and chemical composition distributions, compared to $TiCl_3$ based catalyst [16-18].

Phillips catalysts are catalyst based chromium oxide and inorganic carriers as silica which widely used for production of high density polyethylene (HDPE). In this system, cocatalyst is not required but the reaction should be at high temperature. Both Ziegler-Natta and Phillips catalysts have multiple active sites which produce narrow molecular weight distribution (MWD) and chemical composition distribution (CCD) [17-19].

Metallocene catalysts are single-site catalysts which produced broad molecular weight distribution (MWD) and lower polydispersities and also produced polyolefins containing more uniform distribution of comonomers [20, 21].

2.3 Metallocene catalysts

Metallocene catalysts are composed of group 4B transition metal (Ti, Zr, Hf) substituted with cyclopentadienyl ligands (Cp) and halogen ligands. The structure of metallocene sometimes called "sandwich complexes" which shown in Figure 2.2 [22]. The metal center (Zr) is bonded with two cyclopentadienide anions and the cyclopentadienyl type ligands can bear various alkyl or silyl substituents.

(A)   (B)
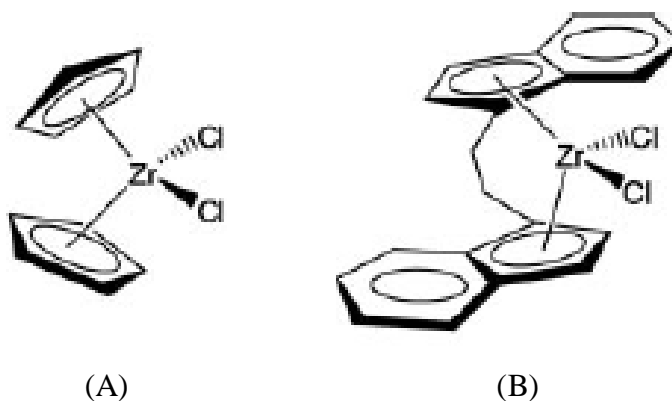
Figure 2.2 Structure of metallocene catalysts for olefin polymerization [22]:

(A) Cp_2ZrCl_2 (B) *rac*-Et(Ind)$_2$ZrCl$_2$

The steric interaction of the cyclopentadienyl ligand surrounding the active center plays a key role in the stereoselectivity of the polymerizations with these homogeneous catalysts. It is means that when the ligand structure is modified, the polymer structure is changed due to the electronic and steric environment around the metal center. This is why metallocene are sometimes called "tailor made catalysts" [17,19,23].

Metallocene catalysts are become an important class of polymerization catalyst in academic and industrial due to the main factors of:

- High productivity of the catalyst 10-100 times higher than conventional Ziegler-Natta catlyst
- Narrow molecular weight distribution (MWD) as a single-site catalyst
- Better tailoring of the resin which can produce varying molecular weight and comonomer incorporation
- Ability to control the stereoregurarity (isotactic, syndiotactic, and atactic)

2.4 Cocatalyst

Metallocene catalysts by themselves are not in the active form. The cocatalyst has the major responsibility for activate the metallocene as a highly active catalytic system. Cocatalysts such as methylaluminoxane (MAO) or boron-based compounds are necessary for metallocene activation.

2.4.1 Alkylaluminoxane

Aluminoxane is described as a molecular species contain at least one oxo group (O^{2-}) bridged two aluminum atoms which the simplest of alkylaluminoxane is the two aluminum atoms bridged by a single oxygen atom with n additional ligands (X) as $X_nAl-O-AlX_n$ [24]. Alkylaluminoxanes are oligomer compounds that represented by the general formula $[(R)Al(O)]_n$ and $R[(R)Al(O)]_nAlR_2$. In the formula, R is alkyl group which can be methyl, ethyl, propyl, and etc.

Methylaluminoxane (MAO) compound is a commonly used for metallocene catalyst which provide highest catalytic activity when compared with others alkylaluminoxane. MAO is the mixture of chains and rings that consist of repeating unit ($-O-Al(CH_3)-$). The functions of MAO in metallocene catalyst are methylates the metallocene dihalide (Cp_2ZrCl_2) to give the species $Cp_2ZrMeCl$ and Cp_2ZrMe_2, and a scavenger for deactivating impurities in the monomer or solvent [23,25]. The formation of MAO structure is still a "black box" chemical but it can be idealized the MAO structure as shown in Figure 2.3 [26]. The activation of MAO was shown in Figure 2.4.
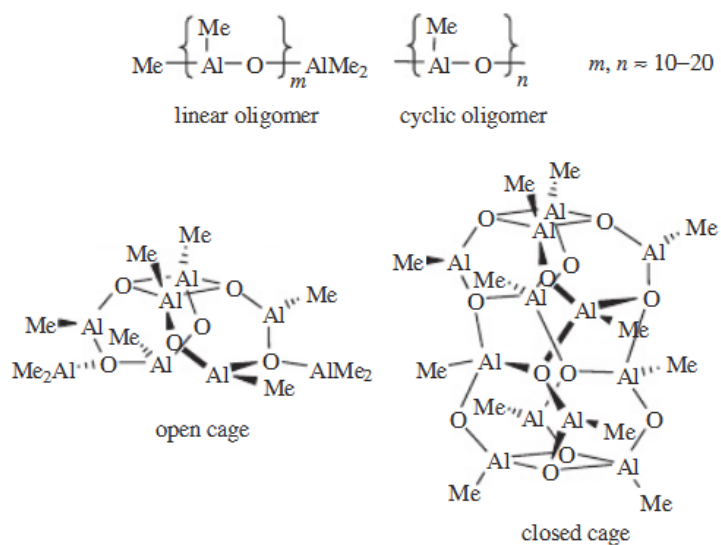
Figure 2.3 Idealized the MAO structure as linear and cyclic oligomers or open and closed cage-type clusters [26]
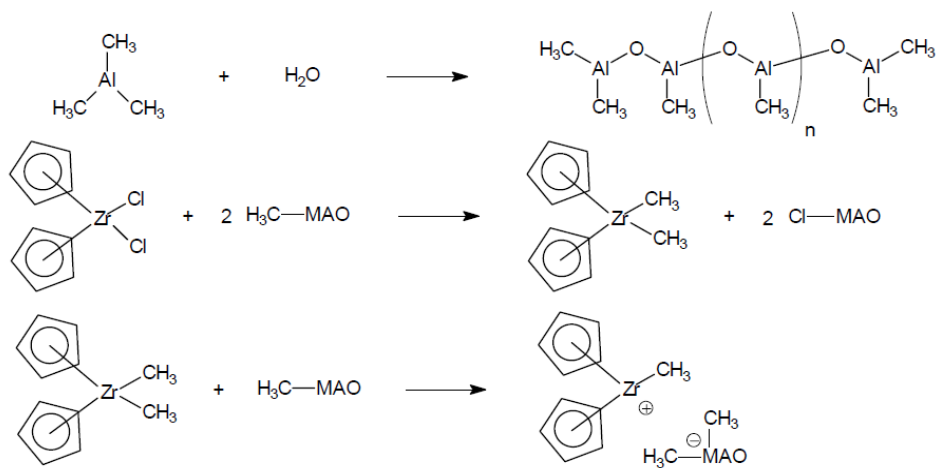
Figure 2.4 Activation of metallocene by methylealuminoxane [26]

2.4.1.1 Synthesis of MAO

MAO can be manufactured in several approaches which mainly divided in 2 groups as hydrolytic method and non-hydrolytic method.

1. Hydrolytic method

This procedure provided inorganic hydrated salts such as $Al_2(SO)_4$, $CuSO_4$, or $FeSO_4$ formed with TMA or others trialkylaluminums [24]. A good controlled of the reaction is done, but the presence of disadvantages occurred. The salts remain in product, and long reaction times are the major problems of this system. Moreover, the drawback of salt hydrates is the lower yield of product (loss 40% of aluminum to insoluble species).

Industrially, the use of directly contact trialkylaluminums with water from emulsified water vapour, or from water-saturated nitrogen vapour can offset the problem of remaining salts in product. MAO was obtained via partial hydrolysis of TMA, but the production should be carefully controlled to beware the risk of runaway reaction and the resulting product must contain some amount of residual TMA usually 5-20% [27]. The function of TMA is provided the alkylaluminoxane soluble in organic solvent, remove impurity form the catalytic system, and act as reactive source of alkyl radicals. However, TMA also inhibit the catalytic activity of the methylaluminoxane/zirconocene catalyst system by the complexation to the metallocene [28].

2. Non-hydrolytic method

A numbers of literatures provide the routes for synthesis of MAO without the use of water. This production comprises the reaction of TMA with trialkylboroxine, phenylboronic acid, etc. is one example of the non-aqueous route. Another route is the thermal treatment of TMA with carbonyl compounds, such as benzoic acid,

benzophenone, which this procedure does not require to handle of the reaction temperature contrarily to the hydrolytic method.

Akzo-Nobel [29] produces MAO by the reaction of TMA via non-hydrolytic route as shown in scheme 2-1. The system uses MAO with hydrolytic and non-hydrolytic method in silica-supported metallocene/MAO catalyst system. In propylene polymerization, the activity of MAO with hydrolytic method shows the higher in activity of 5 times than non-hydrolytic route. In ethylene polymerization, the activity of MAO with hydrolytic system shows the higher in activity of 6 times than non-hydrolytic method. Then, it can be simplify that even though the remaining TMA in MAO of hydrolytic route still provided the catalytic activity higher than non-hydrolytic method.

$$Me_3Al + 0.8Me_3COH \rightarrow Me_{2.2}Al(OCMe_3)_{0.8} + 0.8MeH$$
$$\downarrow$$
$$Me_{1.4}AlO_{0.8} + \text{hydrocarbons}$$
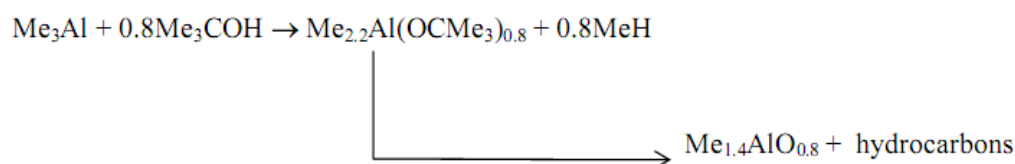
Scheme 2.1 A non-hydrolytic route to obtain methylaluminoxane [29]

2.4.1.2 Determination of residual TMA content in MAO solution

Residual TMA always contained in the production of MAO solution via partial hydrolysis. There are two forms of TMA exist in MAO solution: free TMA and associated TMA. The method to determine TMA in MAO is necessity because the TMA content significantly affects the catalytic activity. Then, it is an essential to determine the accurate amount of TMA. Several approaches presented to determine the quantity of TMA which describe below:

1. Titration with pyridine

Power et al. [30] and Smith et al. [31] studied in this method and realized that the pyridine titration is not an accurate method. The assumption of this titration is pyridine complexes only with TMA. However, the side reaction of pyridine with isolobal gallium sulfide cages and other aluminoxanes is observed. Then, the analysis yields a high amount of residual TMA which given this method is constraint for determination of TMA residue.

2. ^{31}P NMR spectroscopy

Barron A.R. [32] investigated the new method to determine TMA content in MAO by using ^{31}P NMR spectroscopy. The trialkylaluminum with triphenylphosphine (PPh$_3$) formed a reversible reaction and yield of lewis acid-base complex (scheme 2-2).

$$AlR_3 + PPh_3 \rightleftharpoons R_3Al \cdot PPh_3$$
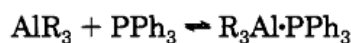
Scheme 2.2 Reaction of trialkylaluminum and PPh$_3$ [32]

Addition an excess of PPh$_3$ (scheme 2-3) was used to exhibit a chemical shift which depend on Al:PPh$_3$ ratio. The equation of standard solution between Al:PPh$_3$ ratio and ^{31}P chemical shift of AlMe$_3$, AlEt$_3$, and Al(^{i}Bu)$_3$ was proposed. Then, the mass of aluminum in the AlR$_3$ form can be calculated from the obtained ^{31}P chemical shift of product. It was found that this method provide an accurate data and easy to reproduce than pyridine titration method.

$$R_3Al \cdot PPh_3 + P^*Ph_3 \rightleftharpoons R_3Al \cdot P^*Ph_3 + PPh_3$$
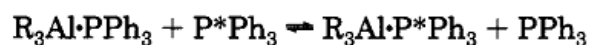
Scheme 2.3 Equilibrium between coordinated and free phosphine [32]

3. ^{1}H NMR spectroscopy

Resconi et al. [33] studied the role of MAO in olefin polymerization by protron spectrum. The ^{1}H NMR spectroscopy of MAO sample in toluene-d_8 showed two main resonances (broad peak at -0.21 ppm and slightly broad at -0.36 ppm). Even though, the peaks of MAO and TMA are partially overlapped, but the molar ratio can be evaluated which is 3.5% of free TMA.

Imhoff et al. [34] characterized residual TMA by ^{1}H NMR. In this study, the new approach for eliminate the overlap spectral of TMA/MAO and provide the narrow methyl group resonance of TMA. The addition of excess tetrahydrofuran (THF-d_8) to TMA shifts the equilibrium to the right which observed the TMA resonance at 0.5 ppm.

Tritto et al. [29] studied and found that the removal or addition of residual TMA affected to molar mass of cocatalyst. In common, the addition of residual TMA lead to the decrease of MAO molar mass. As a 30 mol% or approximate 52 wt% of TMA, the molar mass of MAO was reduced from 1480 g/mol to 480 g/mol. The other literature [35] suggested that the molar mass of MAO should be in the range of 800 - 1500 g/mol to provide the high catalytic activity of ethylene polymerization.

Wu Q. [36] investigated the effect of TMA content in MAO through metallocene catalyst. Retained TMA played an important role in ethylene polymerization and acted as the reducing agent in the heterogeneous metallocene catalyst system. The higher concentration of free TMA provided the reduction of oxidation state from Zr^{4+} active species to Zr^{3+} inactive species for ethylene homopolymerization. Then, the formation of Zr^{3+} was inhibited the catalytic activity.

2.4.2 Boron-based compound

After the boron-based cocatalyst was discovered in the late 1980s, some of the researcher conducted the research in this field due to the major disadvantage of very sensitive to impurities during the polymerization process when compared with the MAO-activated catalyst system. However, the boron-based compound with metallocene catalysts exhibited the same activity as MAO-activated catalysts. The mechanism for activation of metallocene by boron-based cocatalyst was shown in Figure 2.5 [39].
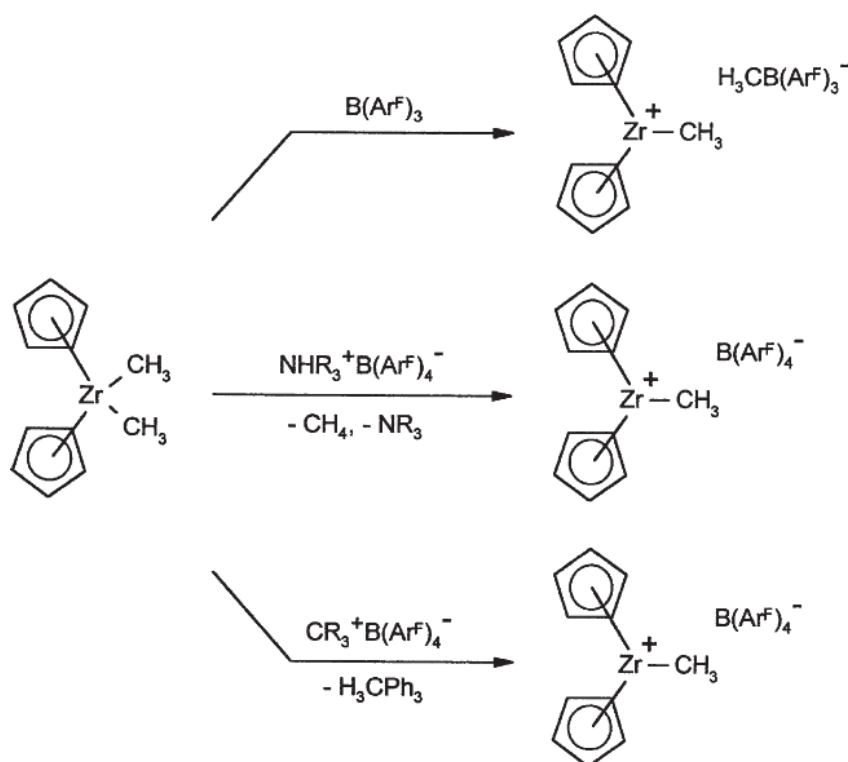
Figure 2.5 Activation of metallocene by boron-based cocatalyst [39]

Yang et. al. [37-39] conducted the boron-based compound with the cationic zirconocene olefin Polymerization Catalysts. The organoboranes, such as $B(C_6F_5)_3$, or organoborates, such as $[PhNMe_2H]^+[BC_6F_5)_4]^-$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$, combined with dialkyl metallocenes produced the highly active catalyst for polymerization

which means that the boron compounds can isolate several cationic alkylzirconozene complxes.

Bochmann et. al. [40] synthesized a wide variety of different borate cocatalysts with reduced nucleophility based on $[CN\{B(C_6F_5)_3\}_2]$, $[M\{CNB(C_6F_5)_3\}_4]^{-2}$, and $[H_2N\{B(C_6F_5)_3\}_2]$anions. These very weakly interacting cocatalysts are reported to give high polymerization activity with metallocene dialkyls.

2.5 Support

Homogeneous metallocene/MAO catalyst system presented disadvantages through the industry in slurry and gas-phase processes. The excess use of cocatalyst, MAO, required in this system that makes it somewhat very expensive. Moreover, homogeneous system also caused the reactor fouling and polymer with low bulk density. A solution to solve those problems is the immobilization method of metallocene/MAO catalyst on the supporting materials. Heterogeneous catalyst system has been used to preserve the high catalytic activity of homogeneous catalyst system and to provide good morphology of polymer which the nature of the support plays an important role in catalytic activity and final properties of the polymer such as particle size distribution and bulk density.

The characteristic of good support used in heterogeneous system should have high specific area to maximize the number of available active sites per unit volume. The supporting material should be very stable but it must be able to form catalyst fragmentation when the beginning of polymerization.

Many types of inorganic and organic support were used in heterogeneous single-site catalyst such as magnesium chloride, silica, zeolites, clays, and polymers. Silica has properties which preferred to use as a support in supporting system through the controllable of polymer morphology, wide range of surface area, pore volume, and porosity. In addition, it also has good mechanical properties which direct to good

morphological of polyolefins [41]. Silica contains silanol groups at the surface which prefer to germinal, vicinal, and isolated hydroxyl groups (Figure 2.6).

Silica support is a hydrophilic material which usually contains 2 - 5 weight% of adsorbed water from the moisture in the air. The physically adsorbed water content and types of hydroxyl groups can be controlled by dehydration or calcination process.

Fink G. et al [42] studied the physical and chemical of supporting material for propene polymerization. Heating the silica at 100 - 200 ℃ can desorbed the adsorbed water but the vicinal (Figure 2.6B) and geminal (Figure 2.6C) hydroxyl groups still remained at temperature below of 200 ℃. Raising the temperature to 200 - 800 ℃, the hydroxyl groups decreased continuously. Especially at temperature of 600 - 800 ℃, the silica was almost totally dehydroxylted of silanol groups which the surface of silica is a hydrophobic as illustrated in Figure 2.7.

(A)	(B)	(C)	(D)
Isolated	Vicinal	Geminal	Siloxane
3746 cm^{-1}	3600-3200 cm^{-1}	3600 cm^{-1}	1350-910 and 800 cm^{-1}
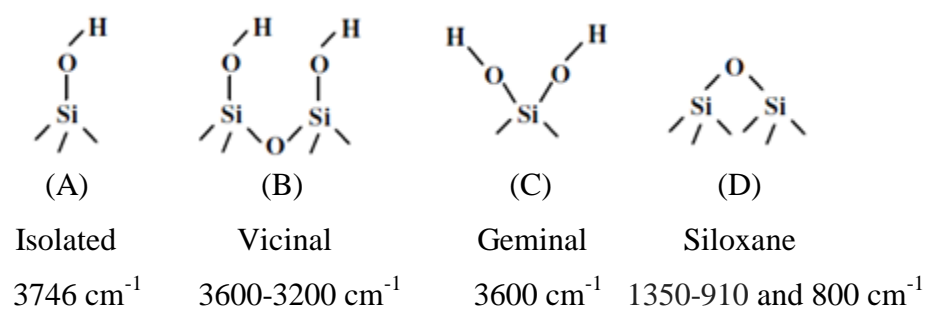
Figure 2.6 Possible hydroxyl groups presented on silica surface [41]
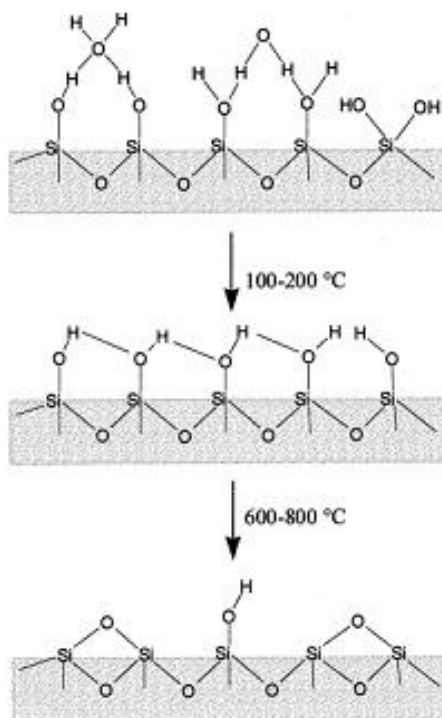
Figure 2.7 Demonstration of the calcination process of silica surface [41]

Chien J.C.W. [43,44] studied the heat treatment of the silica support at different temperatures to consider the effect of temperature with the species and amount of hydroxyl group. Silica has 4 mmol OH/g when heat treatment at 200 $^{\circ}$C provided partially dehydroxylated silica with 2.3 mmol OH/ g which is germinal and vicinal hydroxyl pairs. Above 600 $^{\circ}$C, silica support contains only 0.7 mmol OH/ g which refer to germinal and isolated groups.

Grieken R.V. et al. [45] investigated the influene of support properties of SiO_2, SiO_2-Al_2O_3, and $AlPO_4$ for ethylene polymerization. FT-IR spectroscopy of silica support provided a sharp band of isolated silanol group at 3736 cm^{-1} and a shoulder of germinal and vicinal OH group around 3665 cm^{-1}. After the immobilization of MAO, the disappear of silanol groups was observed and the band at 3615 cm^{-1} was presented due to the methyl group of MAO or the reaction TMA with terminal OH group that provided the -Al-CH$_3$. The results showed that the MAO/(nBuCp)$_2$ZrCl$_2$ catalytic system supported on silica–alumina and alumino-phosphated provided the decreasing

of catalytic activity when the increase of calcination temperature. For the silica support, the remaining of activity was observed.

Britcher L. et al. [46] prepared silica-supported metallocene catalyst. The silica support was characterized by diffuse reflectance infrared spectroscopy (DRIFT). The DRIFT spectra of calcined silica at 3747 cm^{-1} is due to the isolated silanol group. The peaks at 3670 – 3650 cm^{-1} assigned to hydrogen-bonded OH group and at 1870 and 1998 cm^{-1} is the siloxane (Si-O-Si).

2.6 Heterogeneous catalyst system

Various researchers have been studied the method for immobilization of single-site catalyst/MAO on silica support to retain the advantage of homogeneous system in activity and control of polymer morphology. These methods are described below:

1. Method A: SiO$_2$/metallocene/activator

The metallocene is directly deposited on pretreated silica support. After that, it was reacted with an activator like MAO as shown in Scheme 2.4. This method is very simple but provides the low activity due to the inactive sites of treated silica surface and producing of catalyst poisons [47,48].
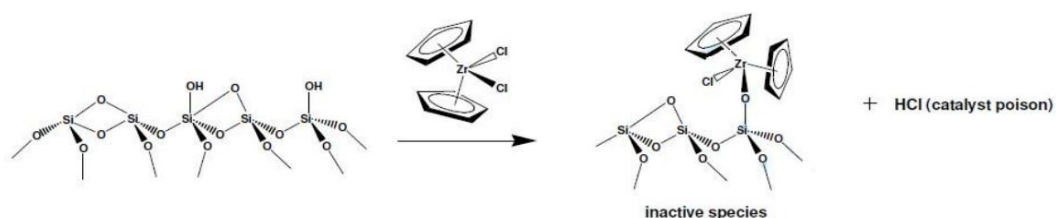
Scheme 2.4 Supportimg method A: SiO$_2$/metallocene/activator [48]

2. Method B: SiO$_2$/activator/metallocene

Silica support is reacted with activator as aluminoxane, and then the silica-supported activator was washed with a toluene and dried to remove any unanchored

activator. Later, it was reacted with the metallocene complex. Alkylaluminum as TMA can be used instead of aluminoxane [49]. However, TMA needs to be contacted with adsorbed water on the silica surface (no need of calcination) to form *in-situ* aluminoxane [50].

3. Method C: SiO_2/(metallocene+activator)

The pre-contact of metal complex and activator was mixed together in a solution, and then it was contacted with dehydrated silica for an amount of time. Then, the finish catalyst has to wash with solvent and remove any unanchored metal complex in the system.

Zheng X. et al. [51] conducted a research in silica-supported metallocene/MAO catalyst's fragmentation behavior. In this study, the impregnation method was investigated the distribution of cocatalyst which characterized by Energy Dispersive X-ray Spectroscopy (EDX) analysis. The silica support was calcined at 250 ^{o}C. Then, the immobilization of MAO at ambient temperature provided the support/MAO with a core shell of Al content which a high concentration of aluminum near the silica surface. However, the silica-supported MAO impregnation at elevated temperature offered homogeneously distribution of MAO which means the improved penetration of cocatalyst inside the support particles without the formation of concentration gradient. Moreover, this research observed the effect of calcination temperatures (250 ^{o}C and 600 ^{o}C) through dispersion of aluminum with the impregnation at elevated temperature. The silica calcined at 600 ^{o}C contributed a homogeneously distribution of MAO, but a core shell distribution was observed from calcination temperature of silica at 250 ^{o}C.

Chaichana E. et al. [52] studied the heterogeneous metallocene catalyst system for *in situ* and *ex situ* impregnation (Al/Ti molar ratio of 400) of ethylene/1-hexene copolymerization. The supported system offered the lower activity than homogeneous system which probably derives from the strong interaction between cocatalyst (MMAO) and silica support. For the heterogeneous system, the *in situ* immobilized catalytic system exhibited higher catalytic activities compared with the *ex situ*

immobilized system. The reason is that the more active catalytic species was present in the *in situ* heterogeneous catalytic system than the *ex situ* system.

2.7 Ethylene homopolymerization

The polymer properties such as molecular weight and molecular weight distribution (MWD) can be controlled by the metallocene ligand and concentration, and also the reaction temperature in the ethylene homopolymerization system. Ethylene polymerization are usually performed to study the basic effects of catalyst concentration, cocatalyst characteristics, alkylaluminum types, Al/Zr ratio, and reaction temperature through the catalytic activity and polymer properties because the copolymerization has the effect of stereoregularity which strongly affects the catalytic activity.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The chemicals used in this study were specified as below:

1. Polymerization grade ethylene gas (99.96%) was purchased from Linde (Thailand) PLC.
2. Ultra high purity argon gas (99.999%) was purchased from Linde (Thailand) PLC.
3. *n*-hexane (95%) was purchased from Merck Co., Ltd., Thailand, and purified by distillation with sodium lump/benzophenone under argon atmosphere.
4. Toluene was purchased from Merck Co., Ltd., Thailand, and purified by distillation with sodium lump/benzophenone under inert atmosphere.
5. *n*-heptane (95%) was purchased from RCI labscan Co., Ltd., and purified by distillation with sodium lump/benzophenone under argon atmosphere.
6. *rac*-ethylenebis (indenyl) zirconium dichloride (*rac*-Et[Ind]$_2$ZrCl$_2$) was purchased from Strem Chems.
7. Commercial silica, donated from Thai Polyethylene Co., Ltd., Thailand, was calcined at elevated temperature before use.
8. Methylaluminoxane (30 wt% in toluene) was donated from Thai Polyethylene Co., Ltd., Thailand.
9. Trimethylaluminum was donated from Thai Polyethylene Co., Ltd., Thailand.
10. Hydrochloric acid (Fuming, 36.7%) was purchased from QREC chemical Co., Ltd., and used as received.
11. Methanol (Commercial grade) was purchased from SR lab and used as received.

12. Sodium (Lump in kerosene, 99.0%) was purchased from Aldrich Chemical Company, Inc.

13. Benzophenone (Purum 99.0%) was purchased from Fluka Chemie A.G. Switzerland.

3.2 Preparation of SiO$_2$-supported methylaluminoxane

Commercial silica support was calcined at 3 different calcination temperatures (400°C, 600°C and 800°C). The support was heated at desired temperature for 6 h under inert atmosphere in order to remove moisture.

The impregnation of silica-supported MAO was performed at 65 °C in a glass reactor. The desired amount of commercial MAO (SiO$_2$:MAO molar ratio of 1.5, 2, and 2.5) was dropped into the reactor contains calcined silica and 35 ml of dried toluene. Then, the mixture was heated to the desired temperature and washed with dried toluene and hexane. The white powder of silica-supported MAO was obtained by removed solvent and dried under vacuum. Then, the white solid of SiO$_2$-supported MAO was obtained and stored in glove box under argon atmosphere.

3.3 Preparation of SiO$_2$-supported dried-methylaluminoxane/trimethylaluminum

3.3.1 Preparation of dried-methylaluminoxane

dried-methylaluminoxane (dMAO) was prepared by the purification of methylaluminoxane to remove trimethylaluminum residue. At first, the 100 ml of MAO solution in toluene was transferred to schlenk tube and dried under vacuum for 6 h at room temperature. After that, the solid residue was washed with toluene (100 ml) for 3 times and heptane (100 ml) for 4 times to remove impurities and remaining trimethylaluminum (Me$_3$Al or TMA). Then, the white powder of dMAO was obtained and kept in glove box.

3.3.2 Preparation of dMAO+TMA mixtures

After the impregnation of support/dMAO+TMA, the mixture of dMAO and free residual TMA was prepared under inert atmosphere. dMAO was dissolved in toluene and placed into the schlenk tube. After that, the TMA was dropped in the solution at 0 °C and stirred for 1 h.

3.3.3 Preparation of SiO$_2$-supported dMAO+TMA

Commercial silica support was calcined at 600 °C for 6 h under inert atmosphere in order to remove moisture.

The impregnation of silica-supported dMAO+TMA was performed at 60 ºC in a schlenk tube. The desired amount of commercial dMAO+TMA (SiO$_2$:MAO molar ratio of 1.5) was dropped into the reactor contains calcined silica and 15 ml of dried toluene. Then, the mixture was evacuated at room temperature to obtain white powder of silica-supported dMAO+TMA.

3.4 Preparation of SiO$_2$-supported zirconocene/dMAO+TMA

The impregnation of silica-supported zirconocene/dMAO+TMA was performed at 60 ºC. The desired amount of *rac*-ethylenebis (indenyl) zirconium dichloride (Al/Zr molar ratio of 200), dissolved in toluene, was dropped into the glass reactor contains silica-supported dMAO+TMA. Then, the mixture was evacuated at room temperature to obtain peach powder of silica-supported zirconocene/dMAO+TMA.

3.5 Polymerization reactions

The ethylene polymerization was carried out in a 100 ml stainless steel autoclave reactor equipped with a magnetic stirrer. 10 mg of SiO_2-supported zirconocene/dMAO (Al:Zr molar ratio of 200) was introduced into the reactor containing hexane under 6 bar of ethylene and temperature at 70 ℃. The polymerization reactions were stopped by addition of methanol. The polyethylene obtained was separated by filtration and dried at room temperature for overnight. Experimentally, the polymerization was performed at least three times for each run and only the average yield and activity are reported.

3.6 Instruments for characterization

3.6.1 N_2 Physisorption

Surface area, average pore diameter and pore size of silica was determined by Brunauer Emmett Teller (BET) analysis via nitrogen adsorption/desorption by AUTOSORB 1-MP, Quantachrome Instruments.

3.6.2 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 samples were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

3.6.3 Inductively Coupled Plasma (ICP)

Inductively coupled plasma optical emission spectroscopy equipment (ICP-OES optima 2100 DV from PerkinElmer) was used to identify Al, Zr content in heterogeneous metallocene catalyst system. The support/catalyst was digested with hydrofluoric acid (HF) and the mixtures were stirred for 30 minutes. After catalyst was completely dissolved, the solution sample was diluted with DI water.

3.6.4 Fourier transforms infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FT-IR) was used to evaluate the species presented of silica and silica-supported MAO. The measurements were in the range of 4000-1300 cm^{-1}. Absorbance FT-IR spectra were recorded by a Bomem MB-102 spectrometer with 32 scans at resolution of 4 cm^{-1}.

3.6.5 ^{1}H Nuclear Magnetic Resonance (^{1}H NMR)

The ^{1}H-NMR spectra was recorded at room temperature using JEOL JNM-A500 operating at 125 MHz. The cocatalyst was prepared by using d_8-THF as a solvent.

3.6.6 Thermogravimetric Analysis (TGA)

TGA was performed using TA Instruments SDT Q 600 analyzer. The samples of 10-20 mg and a temperature ramping from 40 to 800°C at 10°C/min were used in the operation. The carrier gas was N_2 UHP.

3.6.7 Differential Scanning Calorimetry (DSC)

The melting temperature (T_m) and percentage of crystallinity (%X_c) of polyethylene were determined using differential scanning calorimetry (Perkin-Elmer DSC7). The samples were heated at the temperature of 50 - 150 °C with the heating rate of 20 ^{o}C/min. The T_m of polymer was recorded in the second heating cycle in order to remove the thermal history. The overall crystallinity was calculated from the heat of fusion values using the formula

$$X_C = (H_m/H_p)*100$$

where H_m is the enthalpy of the samples

H_p is the enthalpy of a totally crystalline PE (assumed to be 293 J/g).

3.5.6 Gel Permeation Chromatography (GPC)

A high temperature GPC (Waters 150-C) equipped with a viscometric detector was used to determine the molecular weight (MW) of the poethylene. The solvent for GPC was 1,2,4- trichlorobenzene at temperature of 140 °C.

CHAPTER V

RESULTS AND DISCUSSION

4.1 Effect of calcination temperatures and SiO_2:MAO ratios through silica-supported MAO

The heterogeneous metallocene catalyst system of silica-supported MAO was investigated. In this part, the commercial silica support was heated at three different temperatures under argon atmosphere and characterized its physical properties and functional hydroxyl-group. After that, calcined silica was modified with cocatalyst; MAO, at the molar ratio of SiO_2:MAO ratios equals to 1.5, 2.0, and 2.5. Then, the silica-supported MAO was determined the amount of $[Al]_{MAO}$ attached to the silica support.

4.1.1 Characterization of silica support

Brunauer Emmett Teller (BET) surface measurements were performed after thermal treatment of the commercial material used as support. In BET analysis, the main physical properties as BET surface area (m^2/g), average pore size diameter (Å), and pore volume (cm^3/g) were determined via the adsorption/desorption behavior of gaseous nitrogen on a particular sample. These physical properties control the activator distribution on the support, which is very important for catalyst performance and product properties.

The silica support in this study was calcined at 400 °C, 600 °C, and 800 °C for 6 h under inert atmosphere. Then, the white powder of support was kept in the glove box to avoid the moisture in the air. The calcined and uncalcined silica was characterized using nitrogen physisorption for the data of surface area, pore volume, and average pore size diameter that are summarized in the Table 4.1.

Table 4.1 Physical properties of uncalcined and calcined support

|	Calcination temperature (ºC)	A_{BET} (m^2/g)	V_p (cm^3/g)	D_p (Å)
Silica	-	289	1.34	59.3
	400	300	1.36	59.2
	600	306	1.32	59.7
	800	250	1.17	59.6

The results showed that BET surface areas of silica calcined at 800 ºC was different in surface area and pore volume. It can be noticed that when the calcination temperatures increased, the surface area of silica support was apparently decreased from 306 m^2/g to 250 m^2/g at thermal treatment of 600 ºC to 800 ºC.

The other parameter as BET pore volume was appeared in the trend as BET surface area, which the pore volume was decreased from the calcination temperature from 600 ºC to 800 ºC. The pore structure was collapsed with increasing calcination temperature. It can be seen that when the temperature rose from 600 ºC to 800 ºC, the pore diameter remains unchanged

FT-IR technique can be used to study the thermal treatment effect and the type of species on the support. The FT-IR spectra of uncalcined and calcined silica are given in Figure 4.1. For uncalcined silica, the broad peak at 3700 - 2500 cm^{-1} is due to the H-O-H vibrations, which means that the uncalcined silica contained adsorbed water. The spectra of silica calcined between 400 ºC - 800 ºC show a sharp band at 3746 cm^{-1} assigned to isolated silanol groups (Figure 2.6A), but for the silica calcined at 400 ºC, it has a shoulder near the sharp band due to the contribution of vicinal OH groups (Figure 2.6B) and geminal hydroxyl groups (Figure 2.6C) [42,45,46]. Figure 4.2 shows FT-IR spectra of uncalcined silica and calcined silica at 400 ºC, 600 ºC, and 800 ºC which the vibrations are caused by siloxane bridges (Si-O-Si) at 800 cm^{-1} for the symmetric stretching vibration and at 1350 - 910 cm^{-1} for the asymmetric stretching vibration [42].
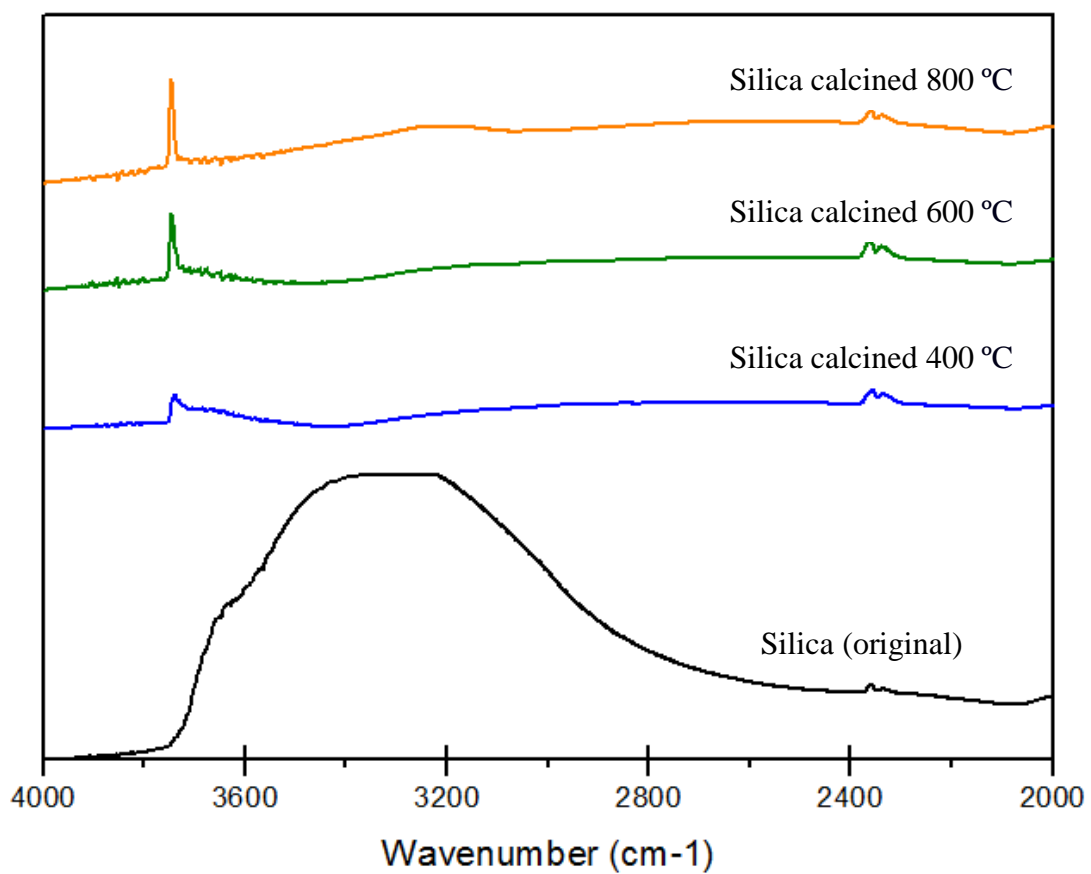
Figure 4.1 FT-IR spectra (4000-1500 cm^{-1}) of calcined silica at 400 °C, 600 °C, and 800 °C compared to uncalcined silica
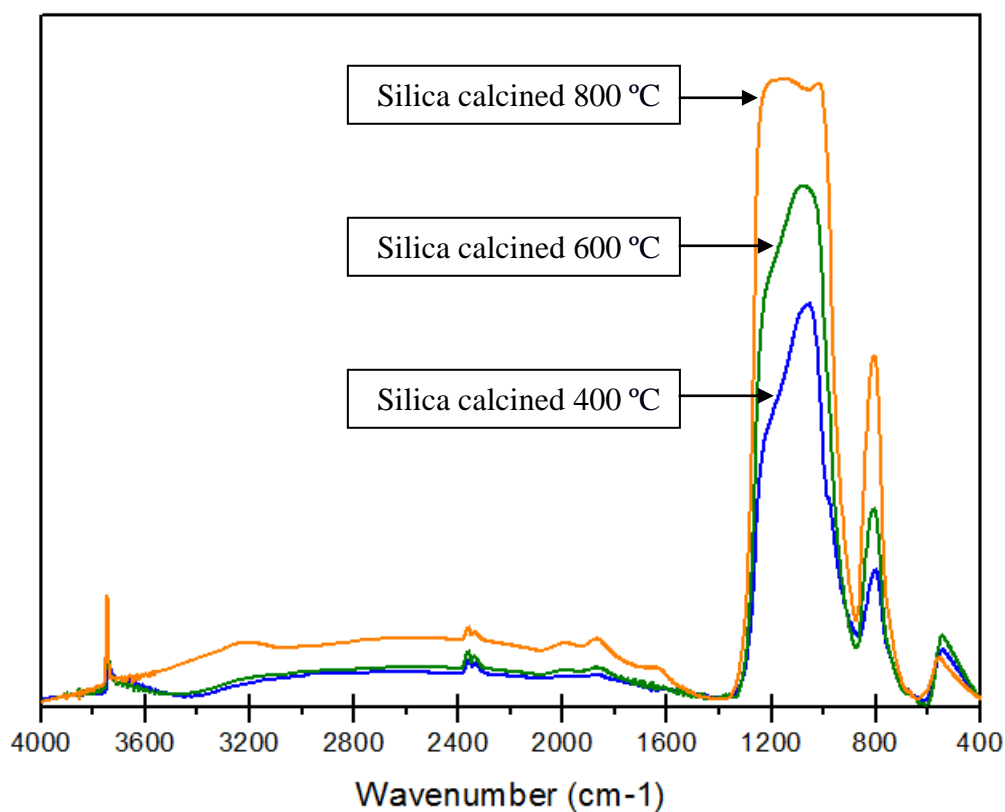
Figure 4.2 FT-IR spectra (4000-400 cm^{-1}) of support calcined

The morphology of uncalcined and calcined silica support was provided by scanning electron microscopy (SEM) as Figure 4.3 and 4.4. The particle size of uncalcined commercial silica was observed in the range of 10 - 30 μm. It can be noted that the particle morphology appeared to be spherical shape for uncalcined and calcined silica.
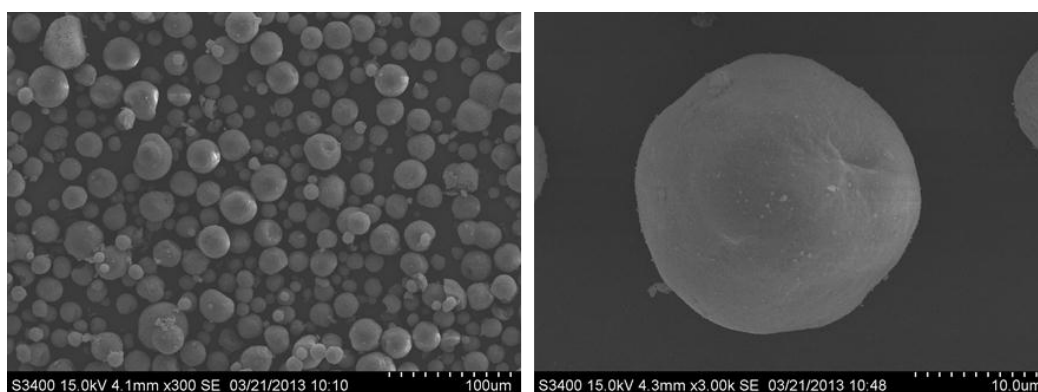
Figure 4.3 SEM micrographs of uncalcined silica
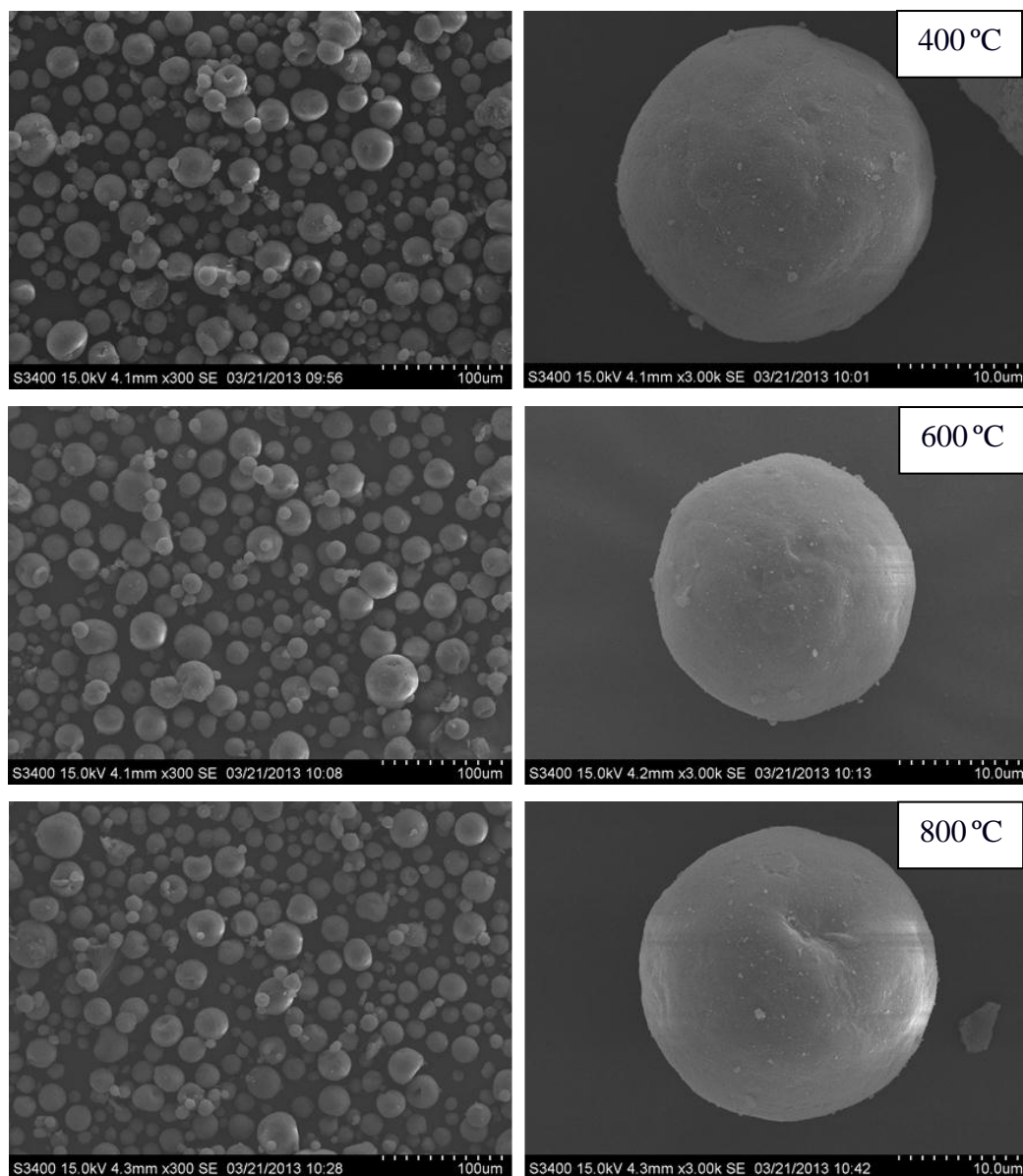
Figure 4.4 SEM micrographs of silica calcined at 400 ℃, 600 ℃, and 800 ℃

4.1.2 Characterization of SiO$_2$-supported MAO

After impregnation of MAO on the commercial silica support, the silica-supported MAO was characterized by ICP-OES and FT-IR spectroscopy to identify the amount of Al in the bulk and the species presented. Moreover, the SiO$_2$-supported MAO morphology was observed by SEM micrographs. The Al content from Table 4.2 shows the ratio between SiO$_2$:MAO at 1.5 providing a highest amount when

compared with the SiO$_2$:MAO molar ratio of 2 and 2.5 because of the high content of MAO solution used. When focused on the calcination temperatures, it can be seen that with the same molar ratio of SiO$_2$:MAO, the Al content with different temperatures provided the approximately similar result of Al content.

FT-IR spectra from Figure 4.5 shows the peak at 2960-2850 cm^{-1} are related to stretching vibrations of the methyl groups in MAO and the -Al-CH$_3$ fragments of surface alkylaluminum compounds formed in the reaction between TMA contained in MAO and silica isolated silanol groups [46].

Table 4.2 The content of [Al]$_{MAO}$ on MAO-modified silica at different calcination temperatures and SiO$_2$:MAO ratios

| Sample	Calcination temperature (°C)	OH content [a] (mmol OH/g support)	Al content (wt%)[b]		
			SiO$_2$: MAO = 1.5	SiO$_2$: MAO = 2.0	SiO$_2$: MAO = 2.5
Silica-supported MAO	400	5.50	13.92	12.30	10.56
	600	4.28	13.14	11.07	9.85
	800	5.85	14.26	12.71	11.32

[a] Determined by titration with *n*-BuLi
[b] Determined by ICP measurement (digested with hydrofluoric acid)
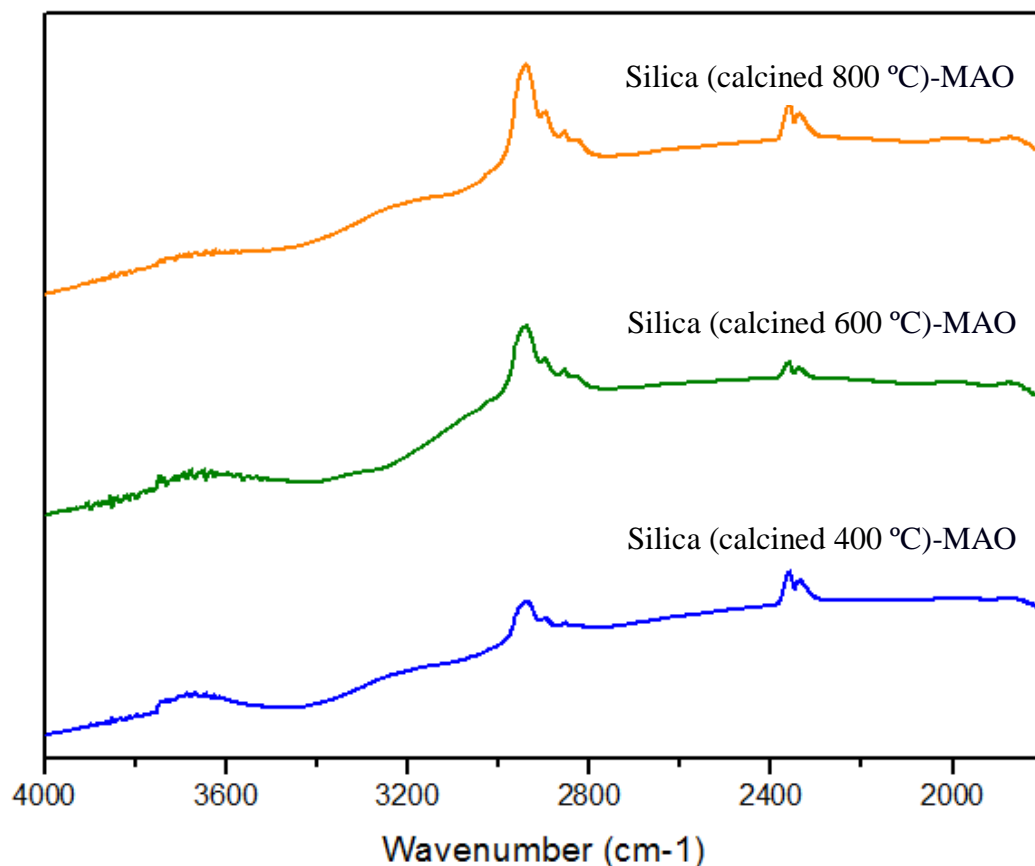
Figure 4.5 FT-IR spectra of silica-supported MAO ratio 1.5
at different calcination temperatures

The morphology of silica-supported MAO at molar ratio of SiO_2:MAO equal to 1.5 (calcination temperatures at 400 °C, 600 °C, and 800 °C) was observed by SEM as shown in Figure 4.6. When compared the silica and silica-supported MAO, it can be noticed that there is no different between support and support with activator. Moreover, the silica-supported MAO was further characterized by energy dispersive X-ray spectroscopy (EDX) and it was found that the homogeneity of the distribution of cocatalyst component was well distributed on silica surface as illustrated in Figure 4.7.
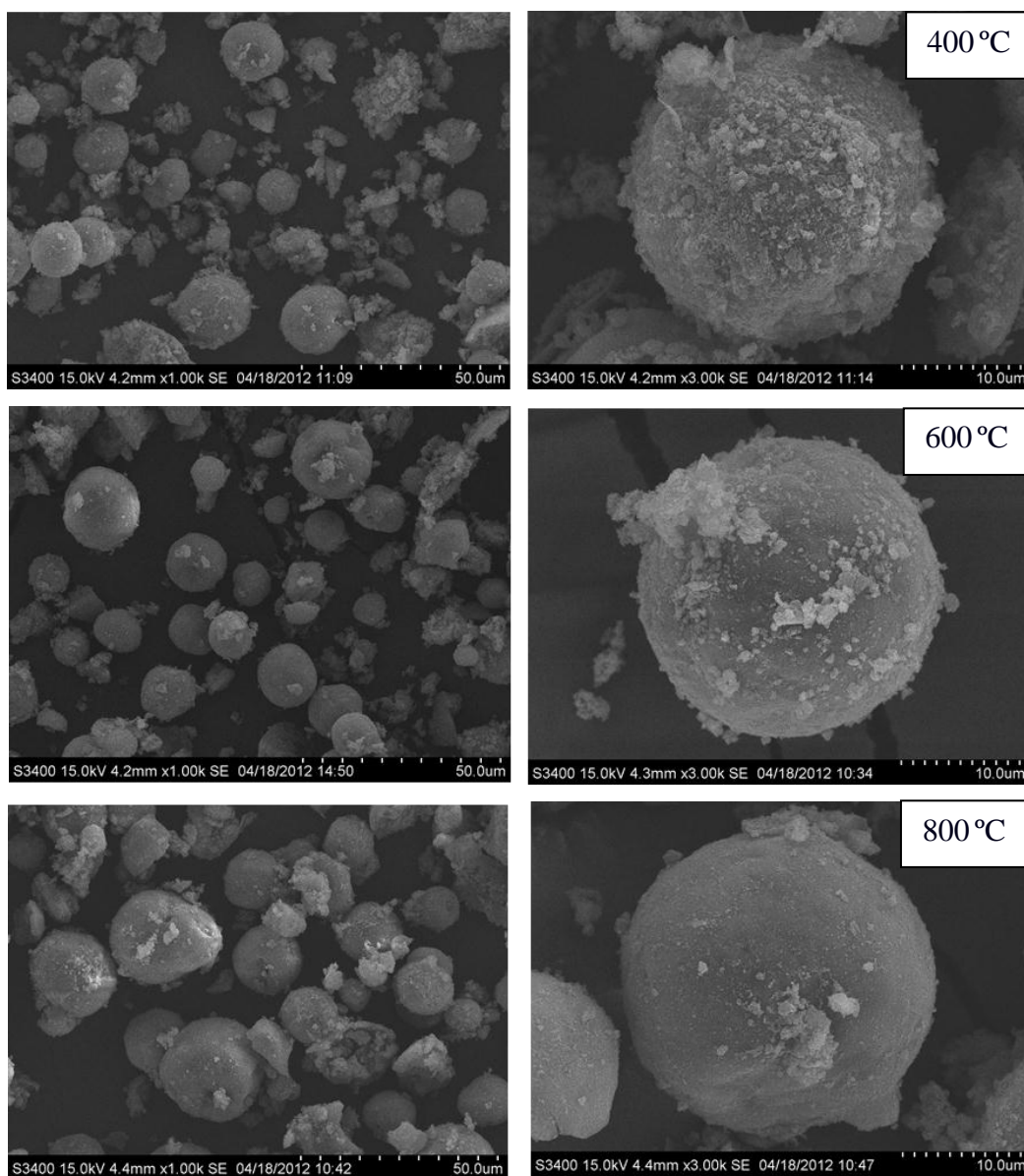
Figure 4.6 Scanning electron micrographs of silica-supported MAO ratio 1.5 at different calcination temperatures
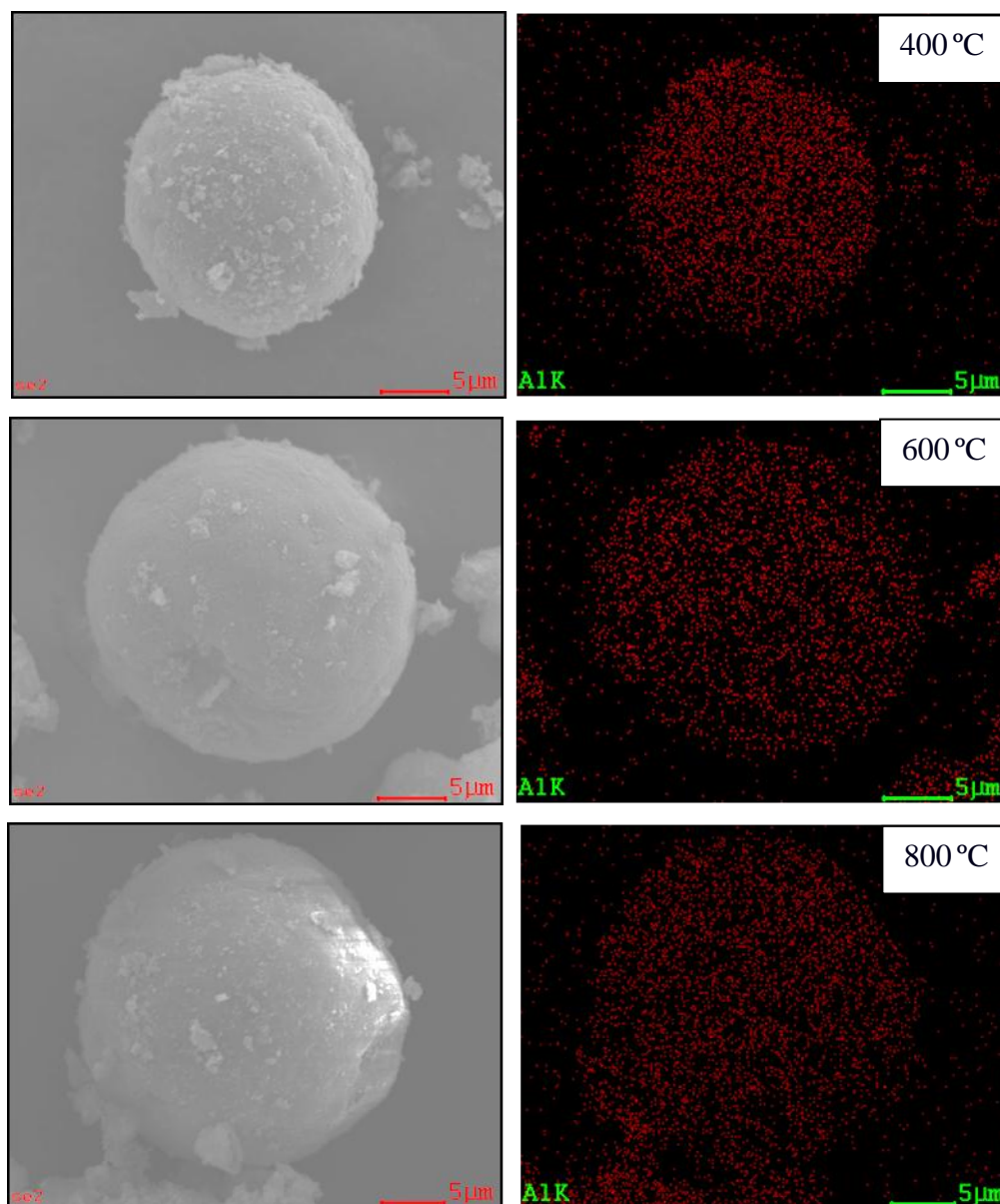
Figure 4.7 Al mappings of silica-supported MAO ratio 1.5 at
calcination temperatures of 400 ℃, 600 ℃, and 800 ℃

The EDX analysis of a cross section of silica-supported MAO particle at molar
ratio of SiO_2:MAO equal to 1.5 (calcination temperatures at 400 ℃, 600 ℃, and 800
℃) was considered to study the effect of heating temperatures through the Al
distribution of inside the support/MAO particle as presented in Figure 4.8. The EDX
Al mappings showed the homogeneously distributed of MAO on the support for all

silica-supported MAO, which means that the cocatalyst was completely penetrated into the porous silica support without the formation of concentration gradient.
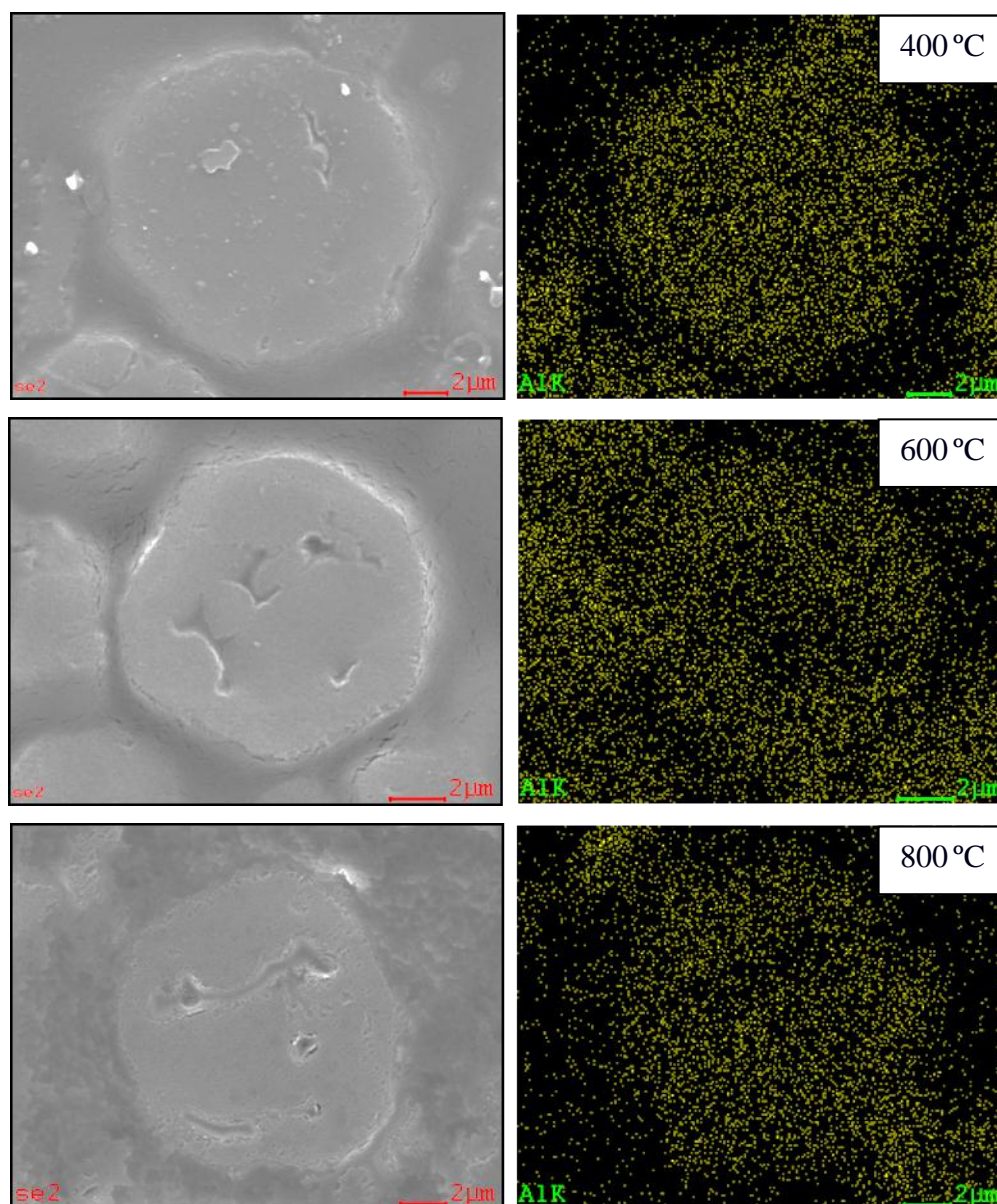

Figure 4.8 Al mappings of cross section silica-supported MAO ratio 1.5 at different calcination temperatures

4.2 Effect of residual TMA in MAO on silica-supported zirconocene/dMAO+TMA system

From part 4.1, the suitable condition to treat commercial silica support is at the calcination temperature at 600 ºC, which provided the excellent physical properties when compared with the others heating temperature. For SiO_2:MAO ratio, the ratio of 1.5 offered the highest amount of Al content. Then, the chosen condition to study in this part is under the thermal treatment of silica support at 600 ºC and SiO_2:dMAO ratio of 1.5.

4.2.1 Characterization of dMAO

The residual TMA was defined in two forms as free TMA and associated TMA. The free residual TMA can remove by evacuation under vacuum. The associated TMA cannot remove even the distillation of cumene [53]. The MAO cocatalyst in toluene solution was removed the free TMA for preparation of dMAO or TMA-depleted MAO [27,33-35]. The MAO solution was evacuated the solvent and washed with toluene and heptane. It was perceived that after washing the solid residue with 3 times of toluene and 4 times of heptane, the white solid was characterized by ^{1}H NMR spectroscopy method and showed the result of the ratio between MAO:TMA of 0.45:0.11 as shown in Figure 4.9. When compared with MAO solution (Figure 4.10), the dMAO provided the ratio of MAO:TMA of 0.45:0.02, which this method minimized the residual TMA at least 5 times.
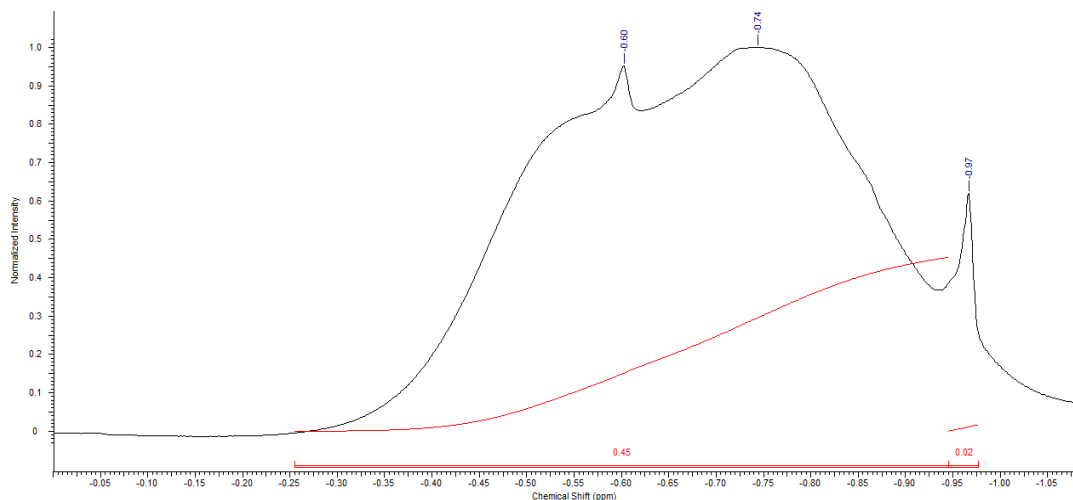
Figure 4.9 ^{1}H NMR spectra of dMAO
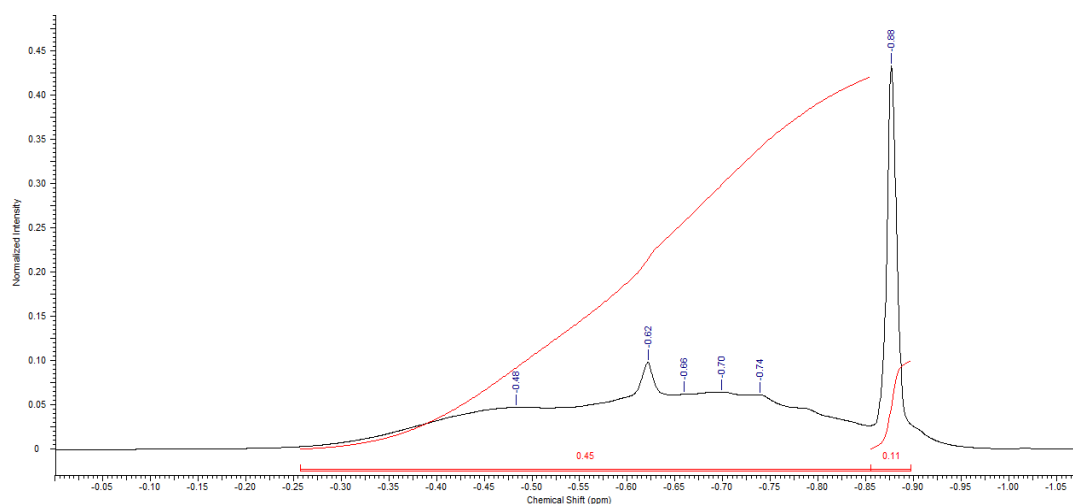
Figure 4.10 ^{1}H NMR spectra of MAO solution

4.2.2 Characterization of SiO$_2$-supported dMAO+TMA

After impregnation of activator on the commercial silica support, the silica-supported dMAO+TMA was characterized by ICP-OES to identify the amount of Al content, FT-IR spectroscopy to detect the species presented on silica surface and SEM-EDX to study the support/dMAO+TMA morphology and distribution of cocatalyst. The Al content from Table 4.3 shows the silica-supported dMAO+TMA with various amount of free residual TMA from 0 wt% to 41.2 wt% compared to dMAO solid. It was found that the Al content from ICP-OES result revealed the

highest amount of cocatalyst is the system of dMAO+TMA(28.6 wt%) and silica-supported only dMAO given the lowest amount of Al content.

Table 4.3 The Al content of silica-supported dMAO+TMA

Sample	wt% free residual TMA[a]	TMA : MAO (molar ratio)	Al content (wt%)[b]
	0 wt%	-	12.70
	9.1 wt%	0.04	13.31
	16.7 wt%	0.08	13.72
Silica-supported dMAO+TMA	23.1 wt%	0.12	14.15
	28.6 wt%	0.16	14.45
	33.3 wt%	0.20	14.87
	41.2 wt%	0.28	14.82

[a] The amount of dMAO is constant at 1.2876 gram or 0.02219 mol
[b] Determined by ICP measurement (digested with hydrofluoric acid)

Afterwards, silica-supported dMAO+TMA was determined by FT-IR spectroscopy. FT-IR spectra from Figure 4.11 shows the peak at 2960-2850 cm^{-1} as are related to stretching vibrations of the methyl groups in MAO and the -Al-CH$_3$ fragments of surface alkylaluminum compounds formed in the reaction between TMA contained in MAO and silica isolated silanol groups [45]. Moreover, the silica-supported dMAO+TMA of residual TMA from 0 wt% to 23.1 wt% exhibited a sharp band at 3746 cm^{-1}, which was assigned to isolated silanol groups [45]. It indicates that the support/dMAO+TMA with TMA lower than 23.1 wt% provided the free hydroxyl group, which can react with metallocene catalyst when the preparation of SiO$_2$-supported zirconocene/dMAO+TMA.
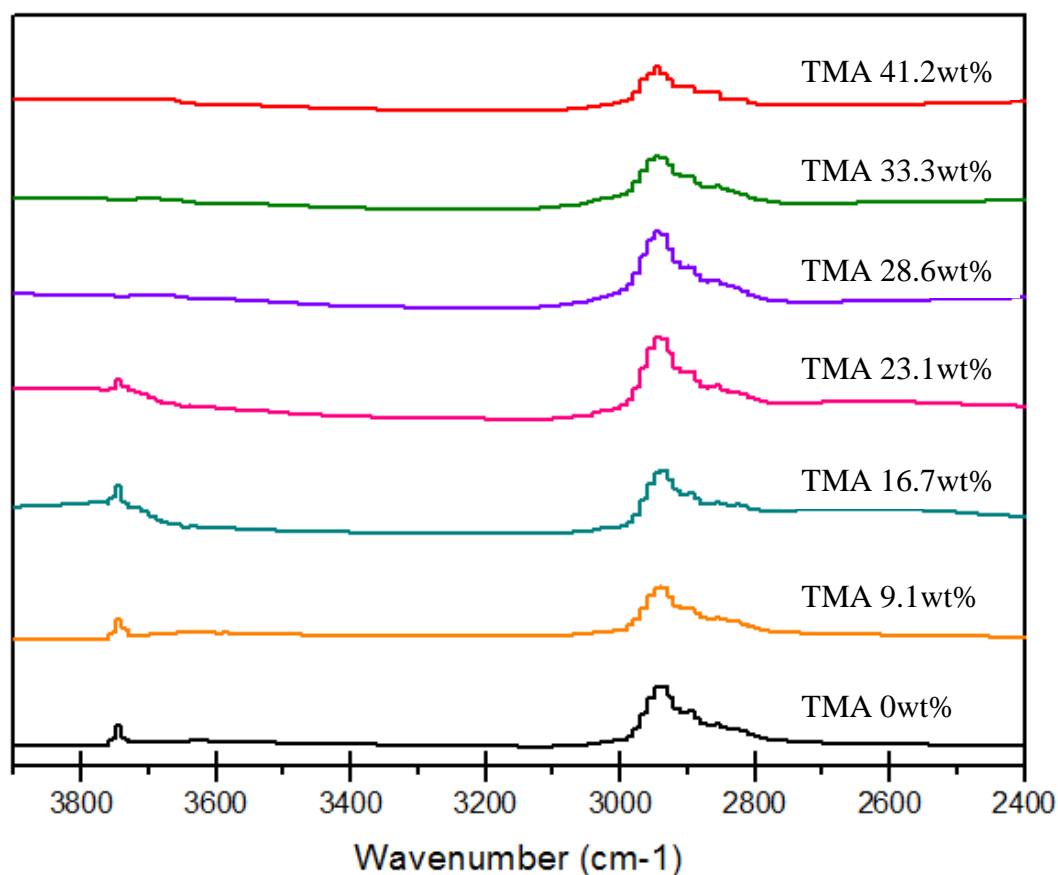
Figure 4.11 FT-IR spectra of silica-supported dMAO+TMA of residual TMA from 0 wt% to 41.2 wt%

The morphology of silica-supported dMAO+TMA at molar ratio of SiO$_2$:MAO equal to 1.5 (calcination temperatures at 400 ℃, 600 ℃, and 800 ℃) was observed by SEM micrograph in Figure 4.12. The support/dMAO+TMA with various amounts of residual TMA showed that there is no difference from the effect of TMA through the morphology of particles. Moreover, the silica-supported dMAO+TMA was further characterized by energy dispersive X-ray spectroscopy (EDX) and it was found that the homogeneity of the distribution of dMAO+TMA was well distributed on silica surface as seen in Figure 4.13.
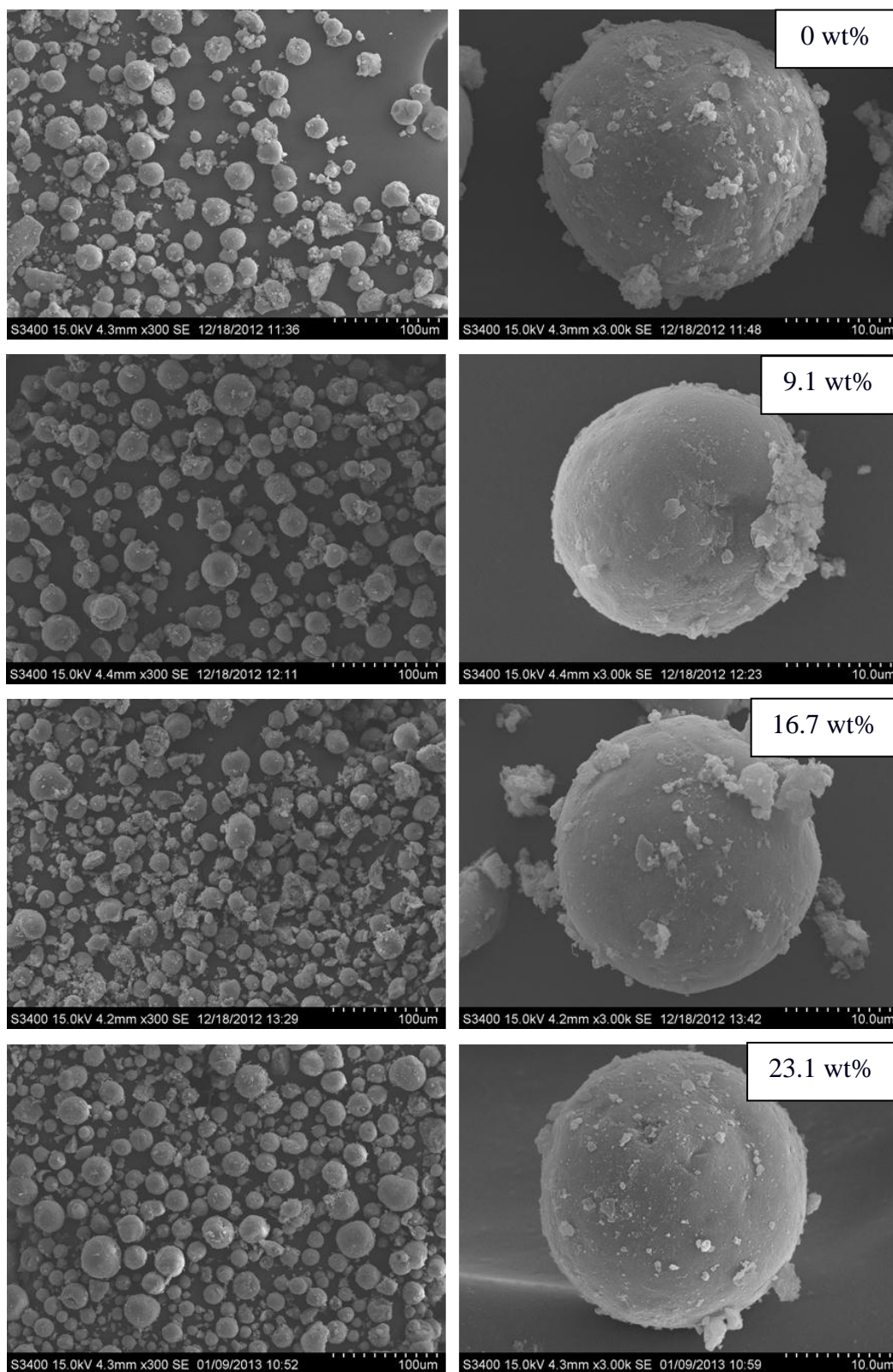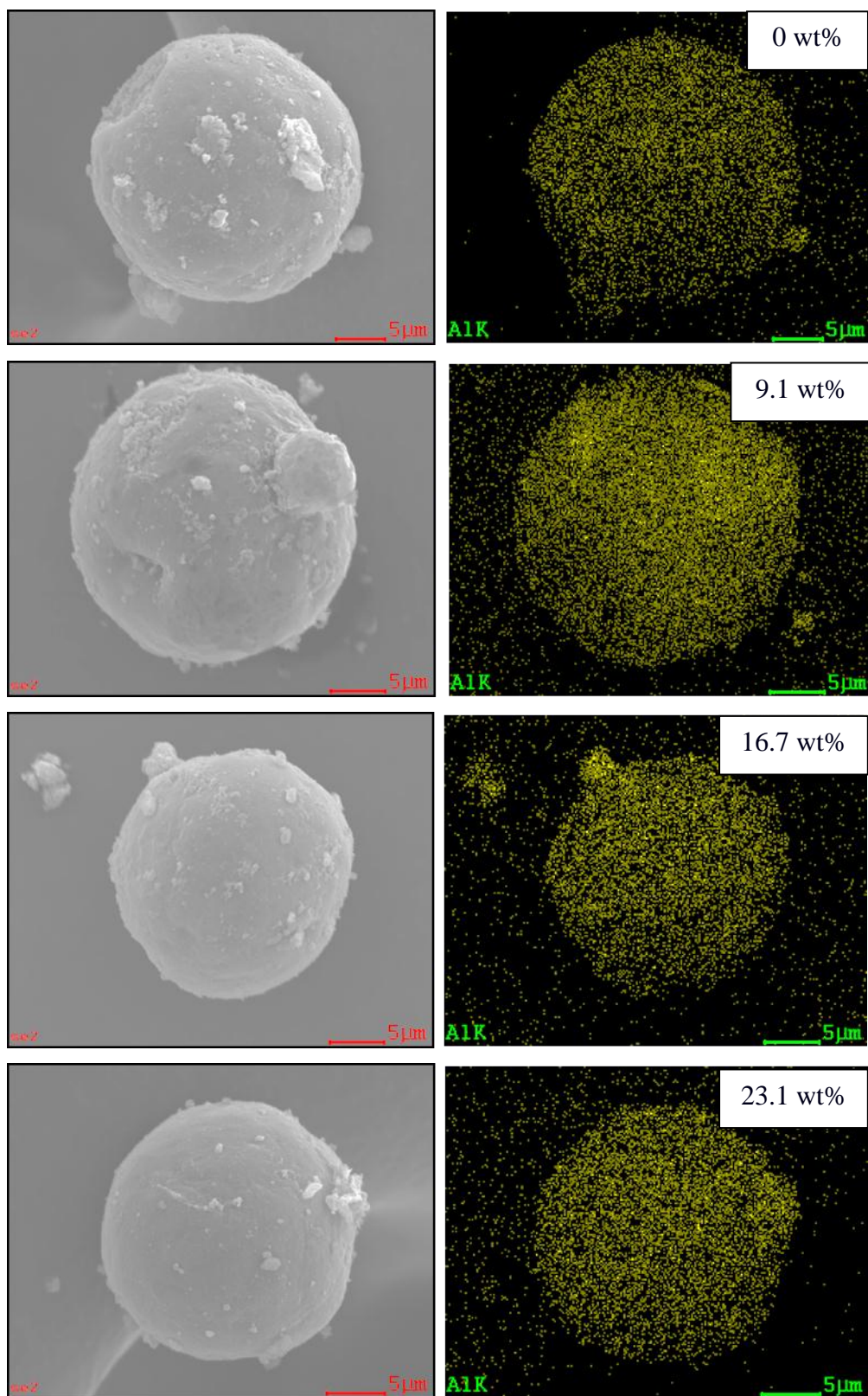
Figure 4.12 SEM micrographs of silica-supported dMAO+TMA at different residual TMA
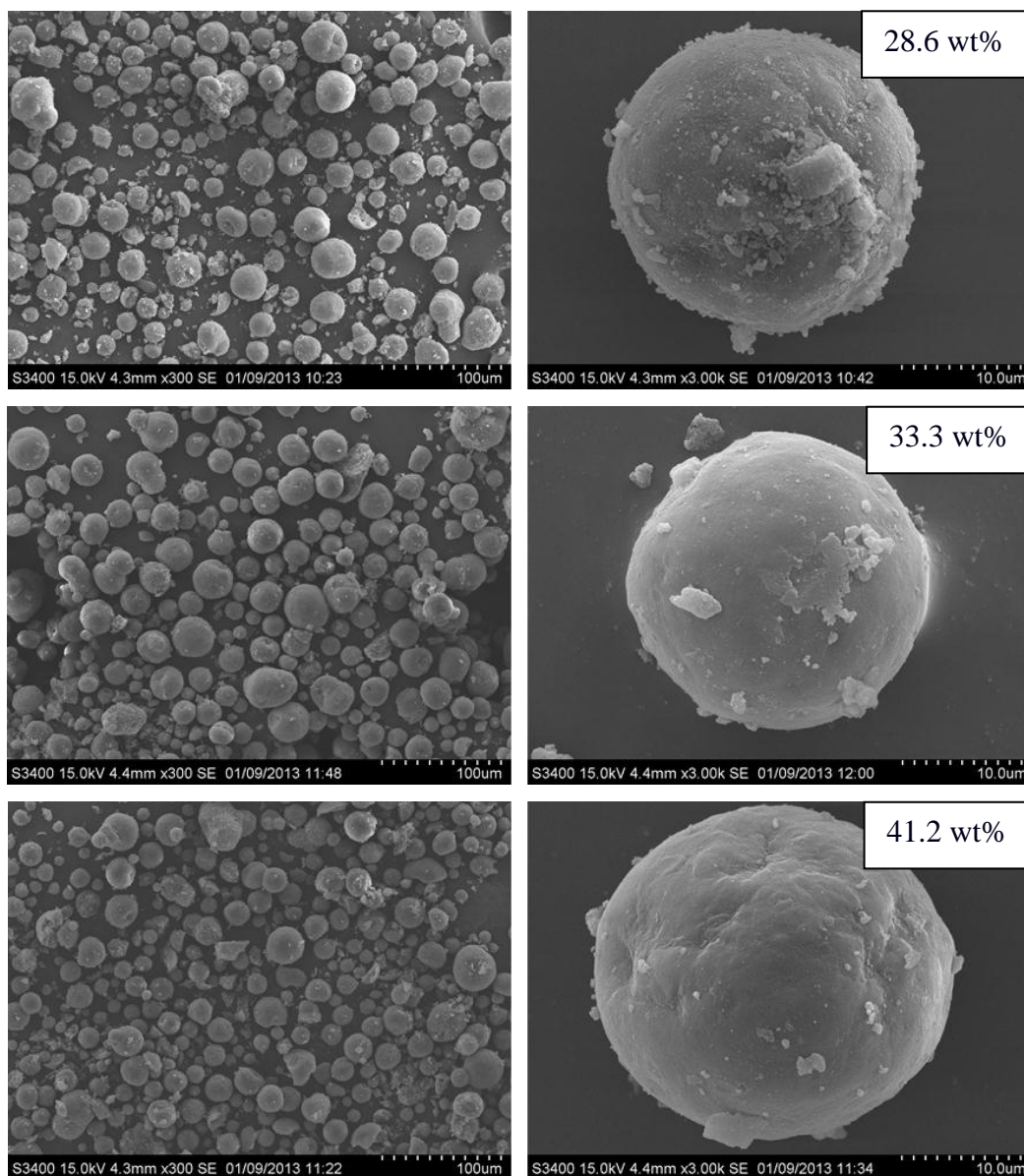
Figure 4.12 SEM micrographs of silica-supported dMAO+TMA at different residual TMA (continue)

Figure 4.13 Al EDX mappings of silica-supported dMAO+TMA at
different residual TMA
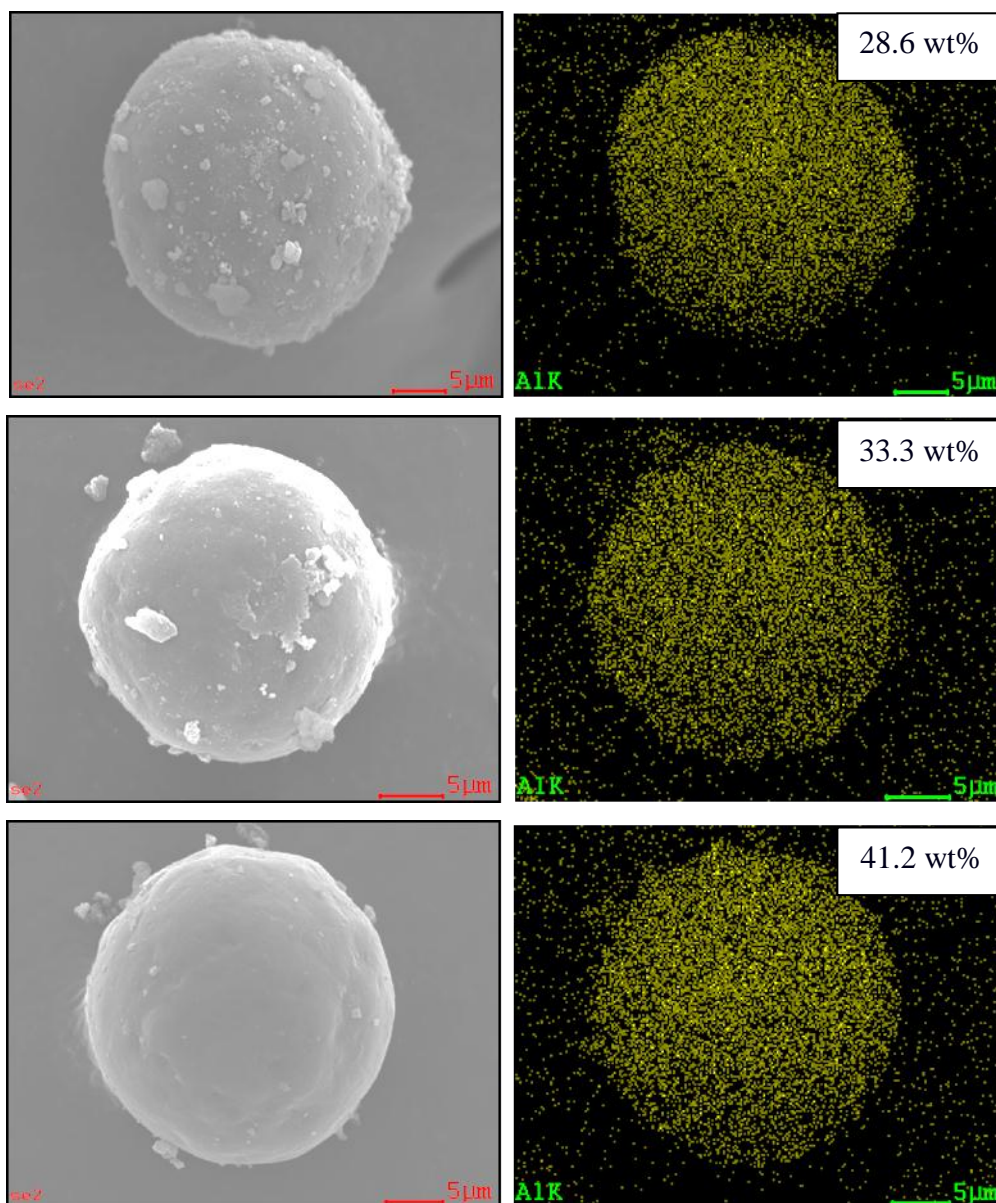
Figure 4.13 Al EDX mappings of silica-supported dMAO+TMA at
different residual TMA (continue)

The EDX analysis of a cross section of silica-supported dMAO+TMA particle
was considered the Al distribution of cross section support/dMAO+TMA particle as
shown in Figure 4.14. The Al mappings EDX showed the homogeneously distributed
of MAO on the support for all of the silica-supported MAO which means that the
cocatalyst was completely penetrated into the porous silica support without the
formation of concentration gradient.

Figure 4.14 Al EDX mappings of cross section silica-supported dMAO+TMA at different residual TMA

Figure 4.14 Al EDX mappings of cross section silica-supported dMAO+TMA at different residual TMA (continue)

4.2.3 Characterization of SiO₂-supported zirconocene/dMAO+TMA

The metallocene catalyst was reacted with support/dMAO+TMA solid to form silica-supported zirconocene/dMAO+TMA and it was characterized the morphology and distribution of species by SEM and EDX, respectively. The SEM showed that there is no difference from the effect of TMA through the morphology of particles as shown in Figure 4.15.

The EDX analysis of a silica-supported zirconocene/dMAO+TMA particle was considered the Al and Zr distribution. The mapping of Al and Zr (Figure 4.16) presented the homogeneously distributed of dMAO+TMA and metallocene catalyst on support surface.
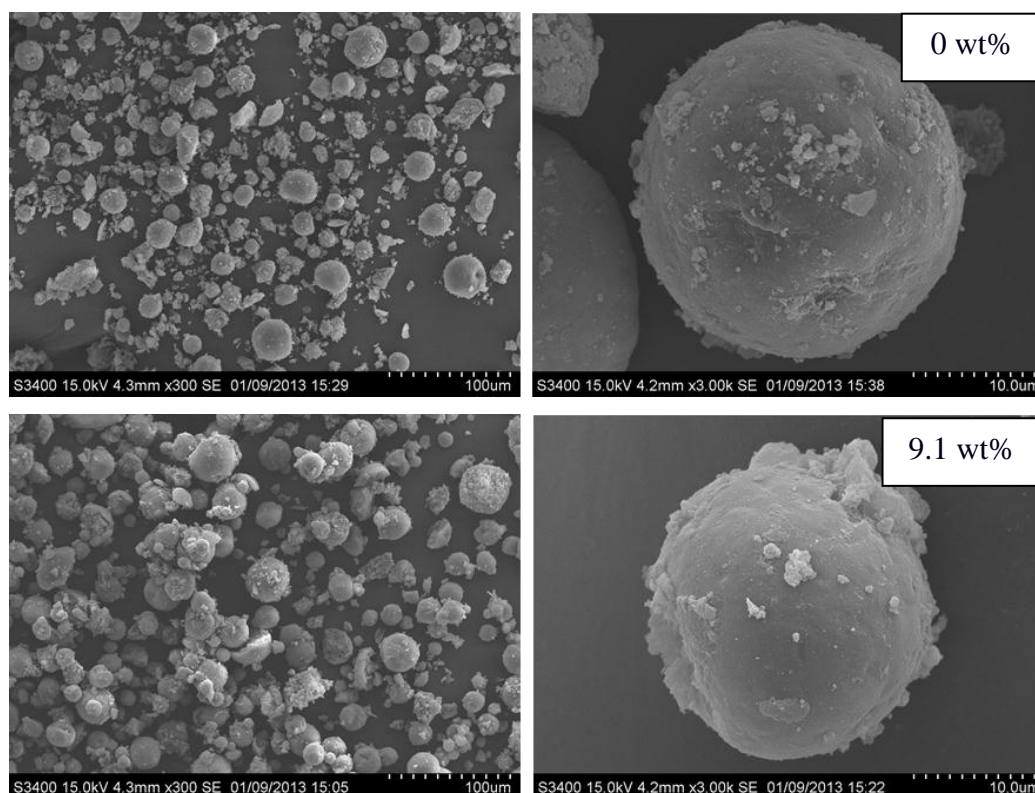
Figure 4.15 SEM micrographs of silica-supported zirconocene/dMAO+TMA at different residual TMA

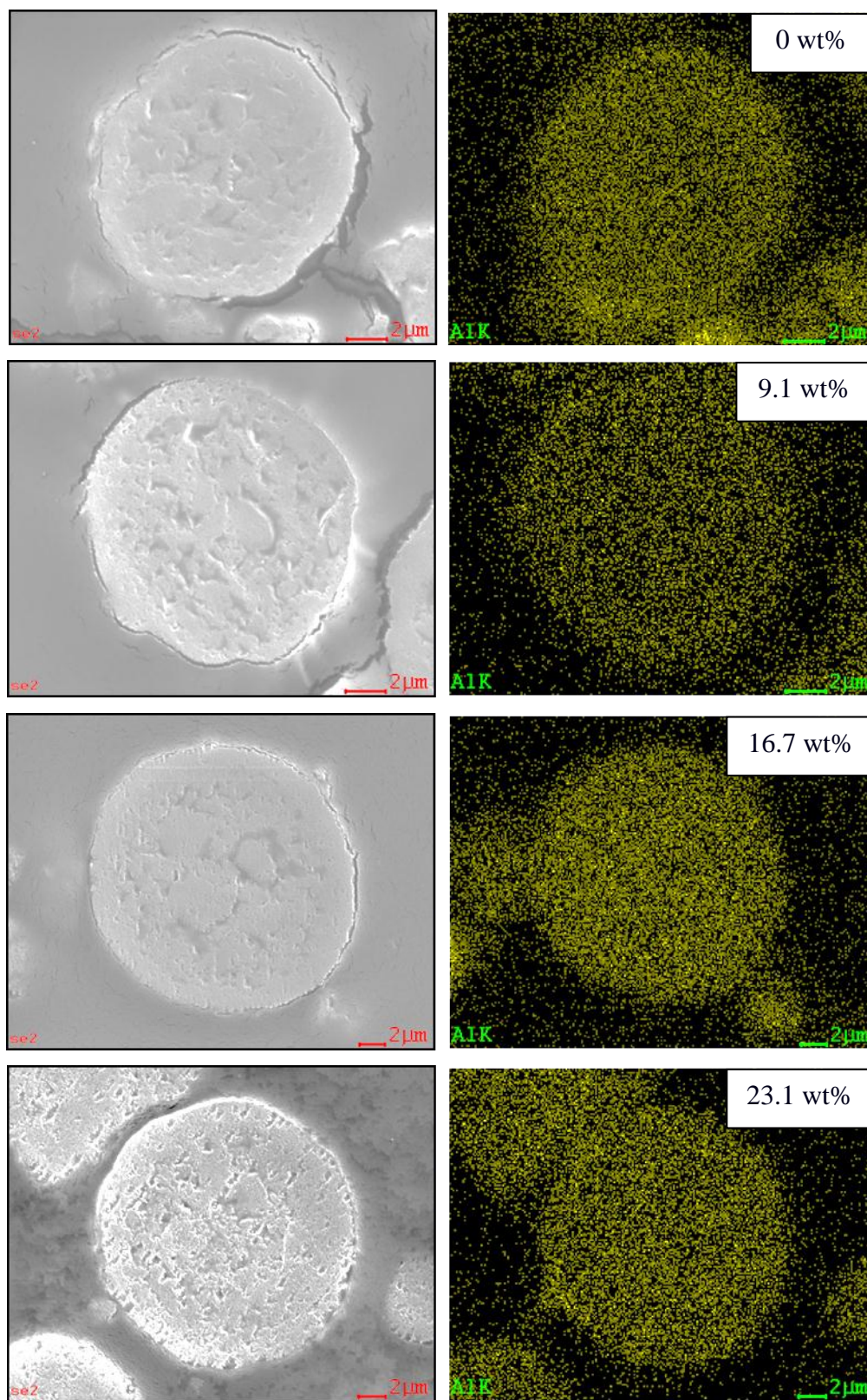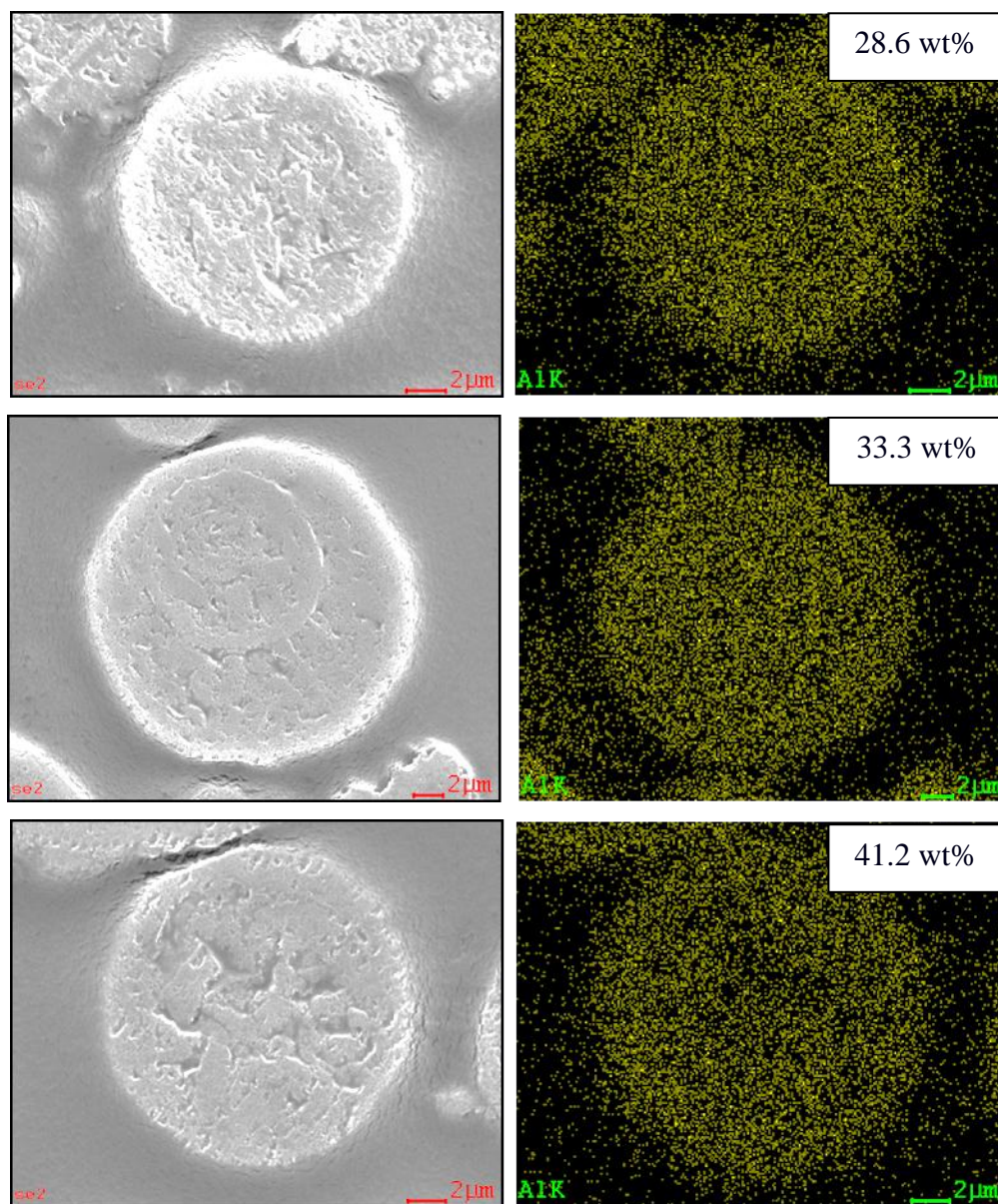**Figure 4.15** SEM micrographs of silica-supported zirconocene/dMAO+TMA at different residual TMA (continue)

41.2 wt%

Figure 4.15 SEM micrographs of silica-supported zirconocene/dMAO+TMA at different residual TMA (continue)

0 wt%
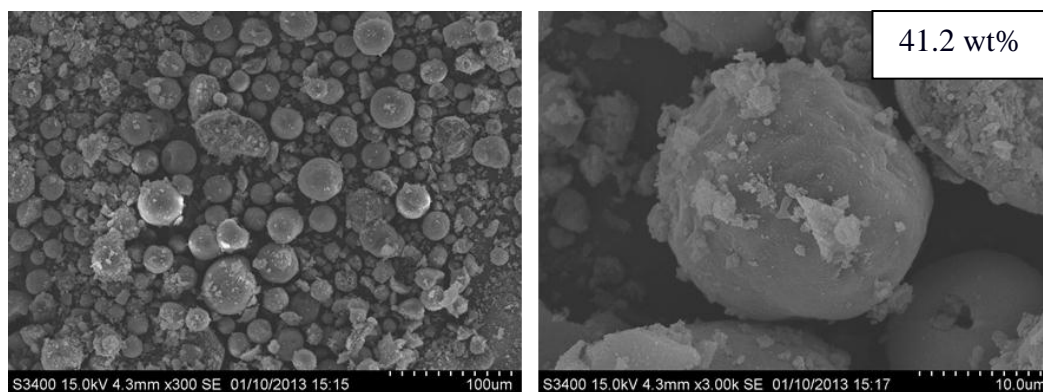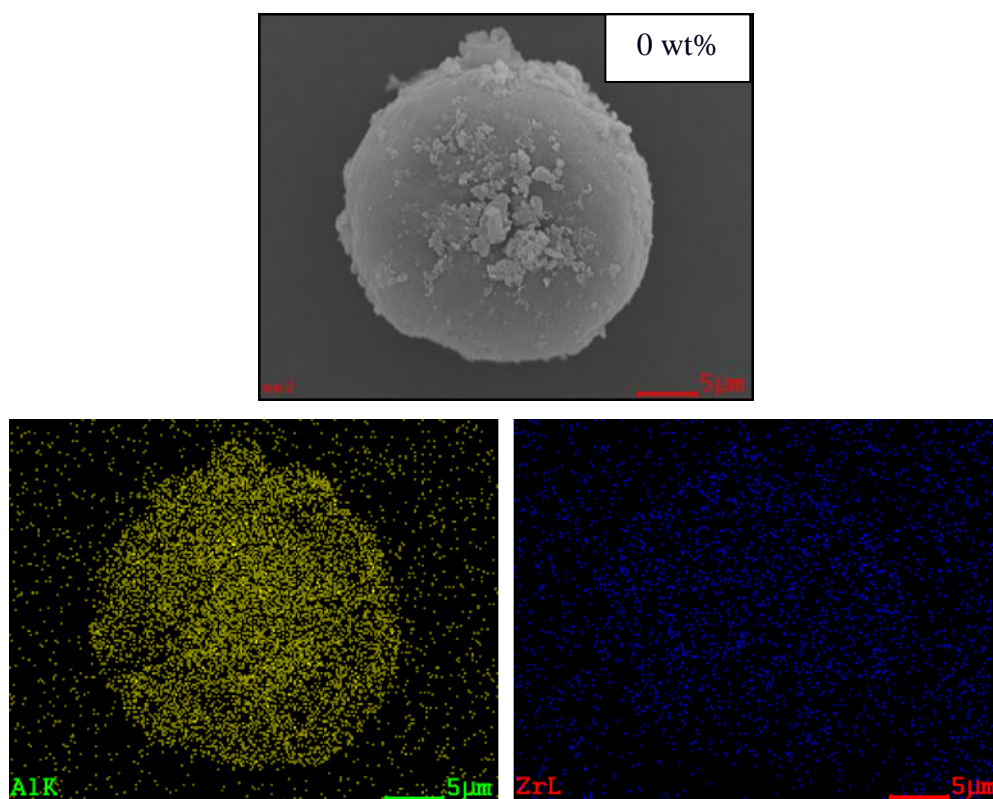
Figure 4.16 Al and Zr EDX mappings of silica-supported zirconocene/dMAO+TMA at different residual TMA
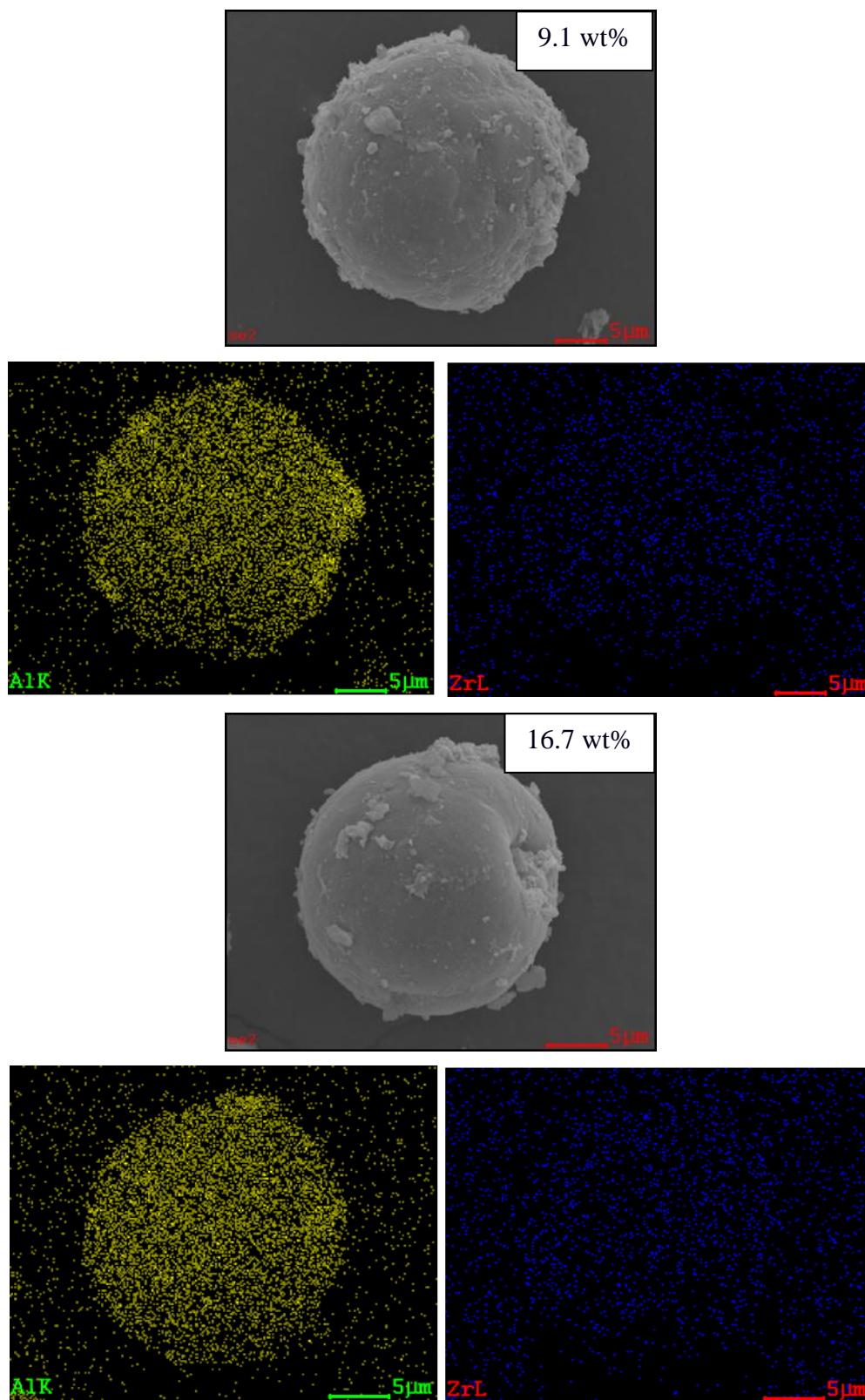
Figure 4.16 Al and Zr EDX mappings of silica-supported zirconocene/dMAO+TMA
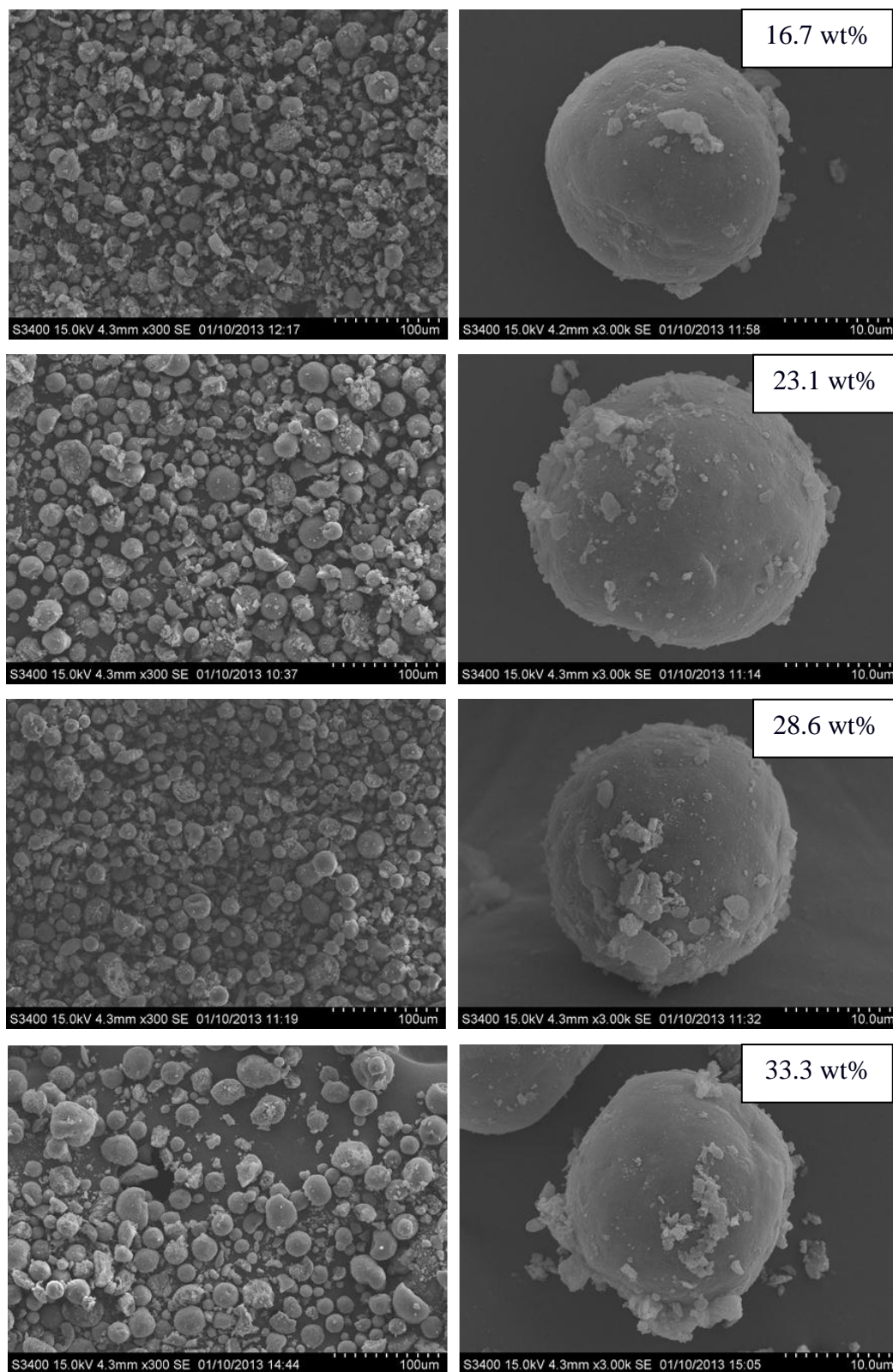
at different residual TMA (continue)

Figure 4.16 Al and Zr EDX mappings of silica-supported zirconocene/dMAO+TMA

at different residual TMA (continue)

Figure 4.16 Al and Zr EDX mappings of silica-supported zirconocene/dMAO+TMA
at different residual TMA (continue)

4.2.4 Catalytic activity and polymer properties of ethylene homopolymerization

The *ex situ* heterogeneous catalyst system of ethylene polymerization was performed to study the effect of residual TMA in MAO solution over the catalytic activity of silica-supported zirconocene/dMAO+TMA as provided in Table 4.4 and Figure 4.17. The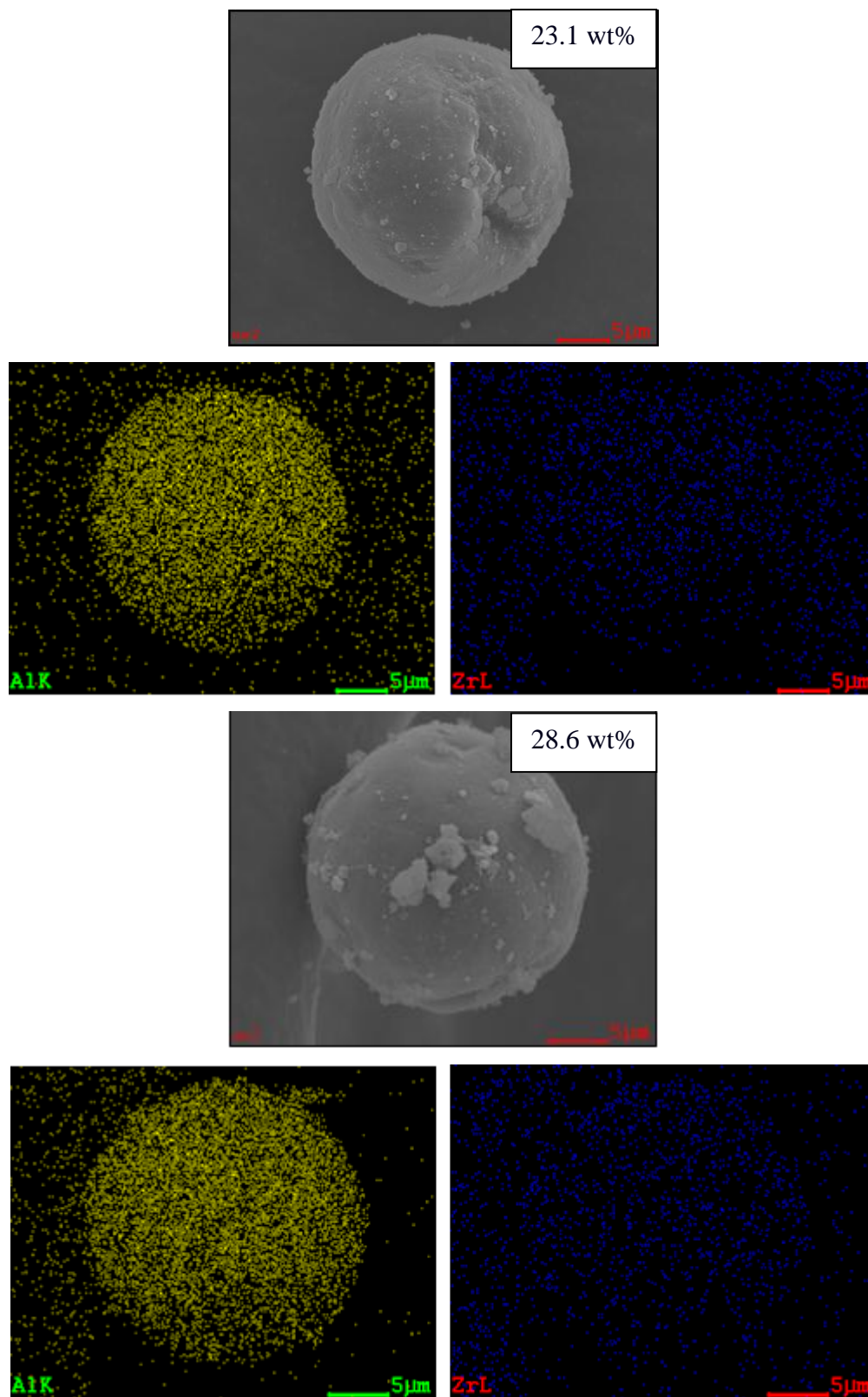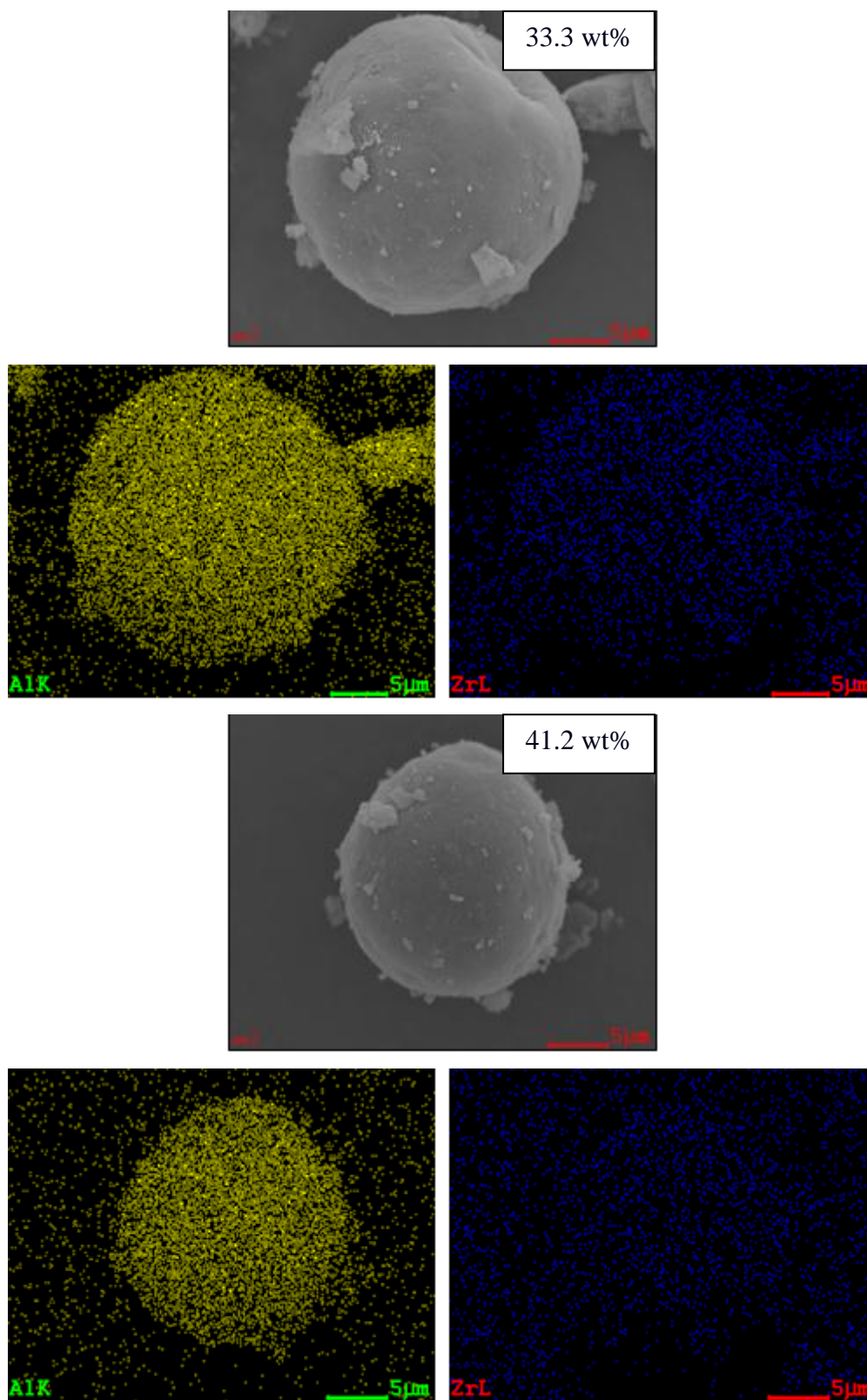 result showed that the 40 wt% of residual TMA provided the highest catalytic activity. At 0 wt% to 30 wt%, the FT-IR spectra of silica-supported dMAO+TMA revealed a band of isolated silanol group which this free hydroxyl group would react with metallocene complex during the preparation of SiO_2-supported zirconocene/dMAO+TMA. The reaction between isolated silanol group and metal complex is formed the catalyst poison; HCl, that affected on the activity of ethylene polymerization.

Table 4.4 Catalytic activity and polymer properties of silica-supported zirconocene/dMAO+TMA

	wt% TMA[a]	Activity[b] (kg PE/g cat.h)	T_m (ºC)	% crystallinity	MW[c]
Polyethylene	0 wt%	0.036	134.78	44.19	606331
	9.1 wt%	0.042	134.41	45.11	491821
	16.7 wt%	0.044	133.33	43.25	417738
	23.1 wt%	0.054	134.76	43.45	380287
	28.6 wt%	0.124	133.70	45.63	294964
	33.3 wt%	0.018	133.84	44.98	275759
	41.2 wt%	0.006	133.98	45.36	289364

[a] The amount of dMAO is constant at 1.2876 g or 0.02219 mol
[b] Slurry ethylene polymerization was performed at 70ºC (Al/Zr = 200) for 30 minutes
[c] Molecular weight of polymer was characterized by GPC
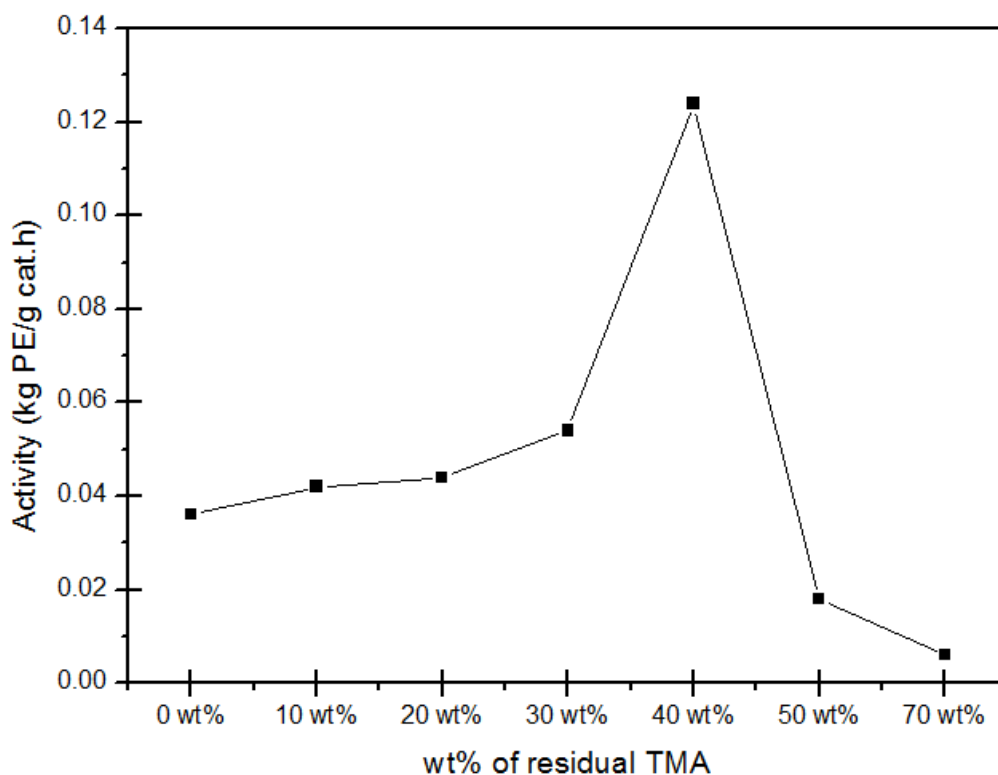
Figure 4.17 Catalytic activity of silica-supported zirconocene/dMAO+TMA

At 50 wt% and 70 wt%, the high TMA in MAO solution can form an inactive species between TMA and metallocene catalyst. The metallocene catalyst was firstly activated by TMA or MAO. After that, the TMA with shown a high amount was alkylated the active species and provided the formation of $Cp_2Zr(-CH_2AlMe_2)_2$ species (side reaction) which known as inactive species in ethylene polymerization which provided in Scheme 4.2 [54].

Then, the result can be implied that the high content of retained TMA, 50 wt% and 70wt%, in MAO may produce the inactive species of metallocene catalyst system that affected to the reduction of catalytic activity.

$$Cp_2Zr-Me + TMA \longrightarrow Cp_2Zr-CH_2-AlMe_2$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad\quad Cl \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Cl$$

Scheme 4.1 The reaction of TMA with activated metallocene [54]

$$Cp_2Zr-CH_2-AlMe_2 + TMA$$
$$\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad Cl$$

$$\longrightarrow Cp_2Zr-CH_2-AlMe_2$$
$$\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad Me$$

$$\longrightarrow Cp_2Zr(CH_2-AlMe_2)_2$$

Scheme 4.2 The alkylation reaction of TMA [54]

The polyethylene obtained was characterized its properties to study the effect of residual TMA contained in cocatalyst through the morphology, melting temperature (T_m), percentage of crystallinity (% X_c), and molecular weight of polymer as shown in table 4.4. The results from DSC technique provided that the melting temperature of samples gives the similar number of T_m and also of % X_c. Consequently, the residual TMA did not effect on the polymer properties of melting temperature and percentage of crystallinity.

The molecular weight of polyethylene was characterized to determine the influence of residual TMA. The result shows that the molecular weight of polyethylene was reduced in order to increase of TMA. It can be conclude that the TMA act as chain transfer agent in metallocene catalyst system [55].

The polymer morphology was obtained by SEM analysis. The results provided the similar in shape of polyethylene which can be concluded that the morphology of polymer was not affected by the amount of residual TMA as shown in Figure 4.18.
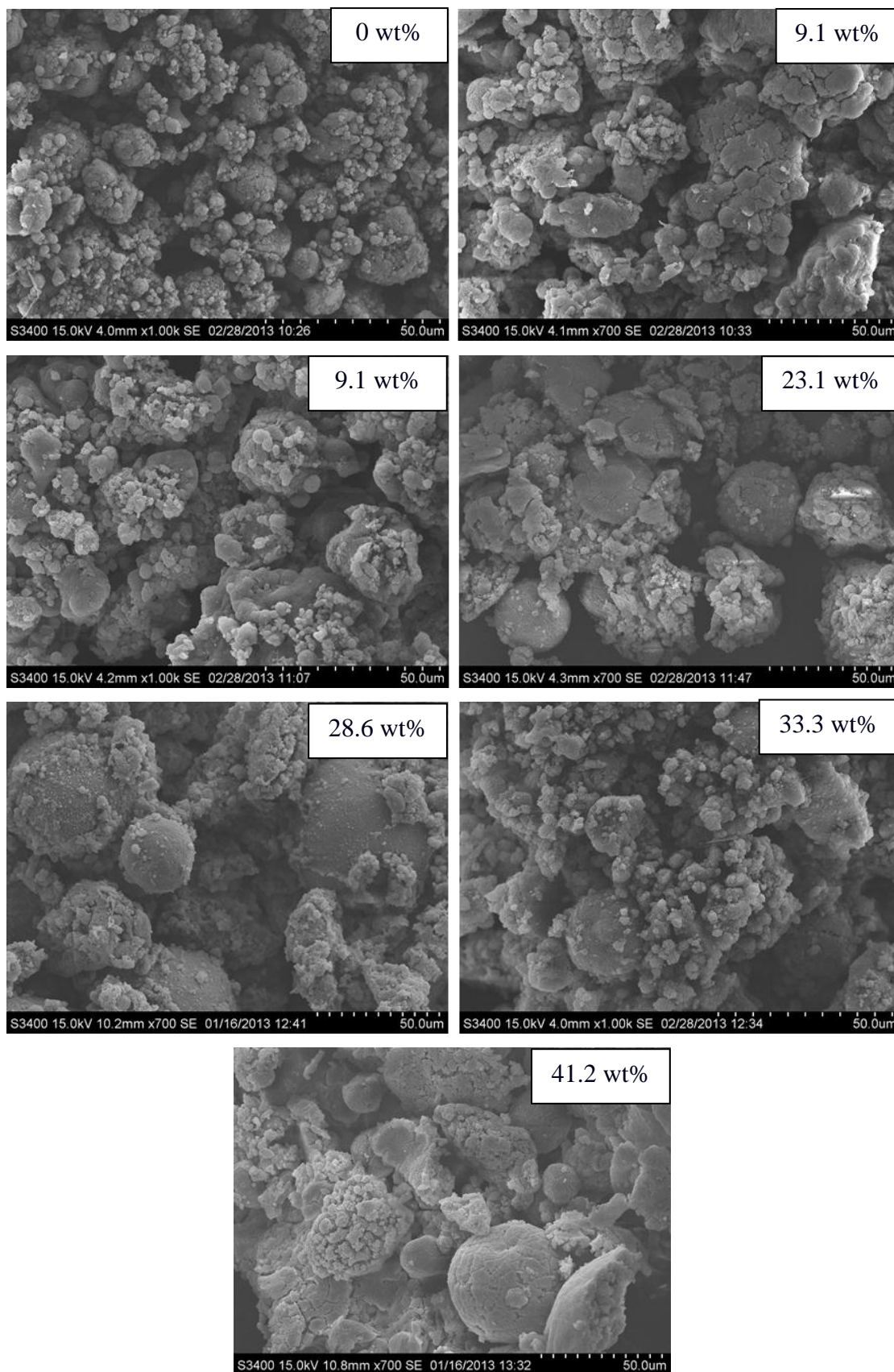
Figure 4.18 SEM micrographs of polymer at different residual TMA

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research was focused on the metallocene catalyst in the heterogeneous catalyst system for ethylene homopolymerization. The support used in this study is the commercial silica support with further treated with thermal at 400 ℃, 600 ℃, and 800 ℃ under argon atmosphere. Then, it was characterized by BET analysis and FT-IR technique. From nitrogen physisorption, the physical properties (BET surface area, average pore size diameter, and pore volume) of calcined silica at 600 ℃ provided the highest values of properties. FT-IR spectroscopy described the hydroxyl species of different calcination temperatures. The calcined silica contained a high amount of adsorbed water. But for calcined silica, vicinal and geminal hydroxyl groups was observed in silica with calcined at 400 ℃ which difference from silica with heating temperatures at 600 ℃ and 800 ℃. After that, the silica-supported MAO was prepared to study the effect of SiO_2:MAO ratios. The Al content was detected by ICP-OES and provided that the SiO_2:MAO ratio at 1.5 offering a highest amount and the amount of Al. It can be concluded that the suitable condition for the preparation of support/MAO system is the calcination temperature of silica support at 600 ℃ and the SiO_2:MAO ratio at 1.5.

The influence of residual TMA contained in MAO for ethylene polymerization was focused. Firstly, the MAO solution has to remove of residual TMA to the formation of dried-MAO which can be characterized using ^{1}H NMR method. Then, dMAO was prepared with the various amount of TMA (0 wt% to 41.2 wt% compared to dMAO) and it was reacted with silica support. The silica-supported dMAO+TMA was characterized by FT-IR spectroscopy and found that only of silica-supported dMAO+TMA of residual TMA from 0 wt% to 23.1 wt% observed a sharp band at 3746 cm^{-1} which assigned to isolated silanol groups. Then, the silica-supported

zirconocene/dMAO+TMA (Al/Zr molar ratio of 200) was prepared and performed an ethylene polymerization. The activity result showed the 28.6 wt% of residual TMA provided the highest catalytic activity. Moreover, the effect of residual TMA was studied on polymer properties. The SEM micrographs, melting temperature and crystallinty were not changed with the different amounts of TMA.

5.2 Recommendations

1. The silica-supported MAO was performed and characterized by FT-IR spectroscopy. The bonding from the reaction between support and MAO, -O-Al-, cannot be observed by FT-IR spectrum. But, this characterization can be provided only the stretching vibrations of the methyl groups in MAO or the -Al-CH$_3$ fragments of surface alkylaluminum compounds formed in the reaction between TMA and silica isolated silanol group. Then, the other characterization's method should be discussed to confirm the bonding between silica support and cocatalyst.

2. It can be observed that the silica, calcination temperature of 800 ℃, provided the higher amount of hydroxyl group than calcined silica at 600 ℃ by the ICP-OES of silica-supported MAO. This existence should be considered and discussed further in more details.

3. The preparation of silica-supported dMAO+TMA at the percent weight of TMA at 0 wt% to 23.1 wt% showed the isolated hydroxyl group by FT-IR spectroscopy. This characterization method offered only the quantitative analysis data, in more detail the qualitative method to determine the amount of hydroxyl group should be considered.

4. The high amount, 33.3 wt% and 41.2 wt%, of residual TMA in cocatalyst provided the poor catalytic activity which it could be form inactive species between TMA and metallocene catalyst. The method to determine of this species should be defined. Moreover, the mechanism of this reaction should be studied in more detail.

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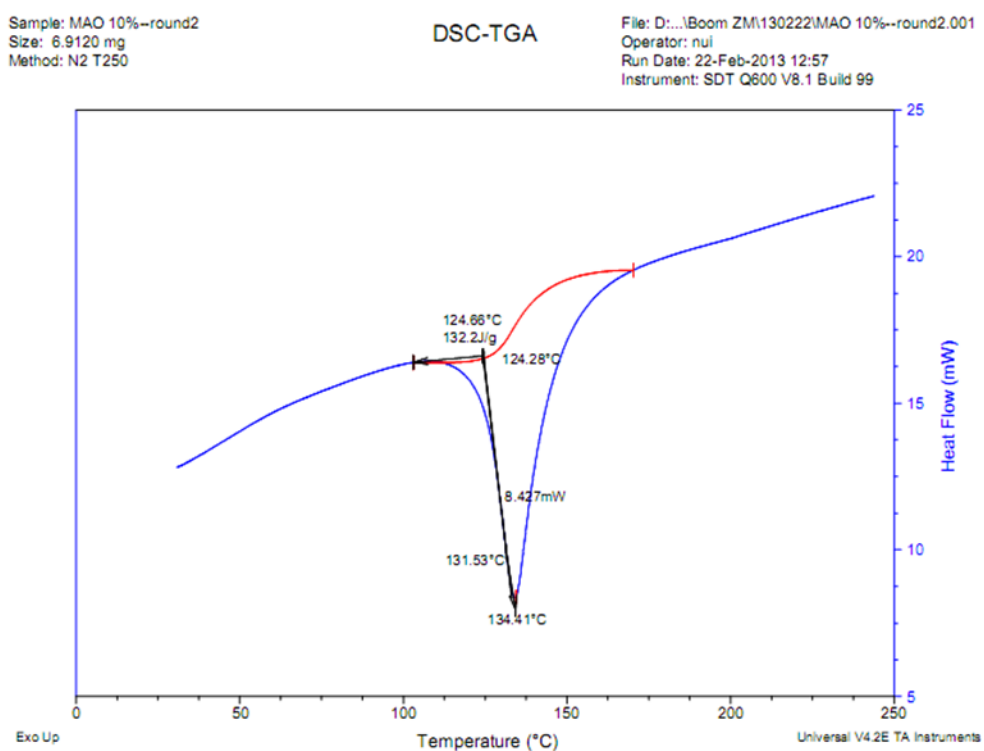
APPENDICES

APPENDIX A

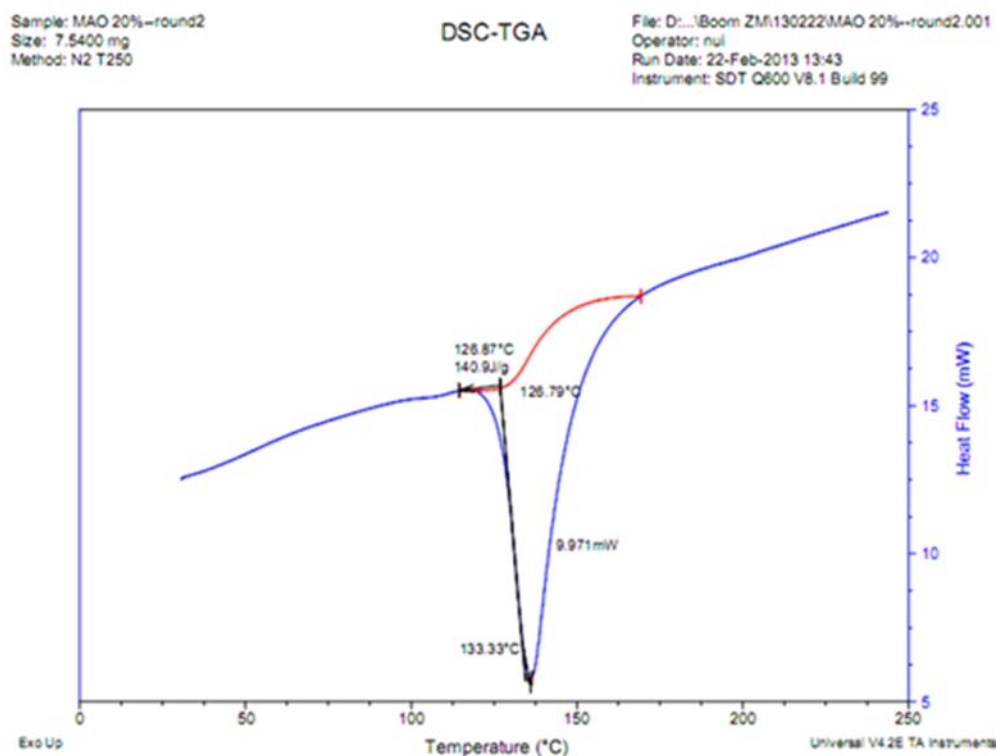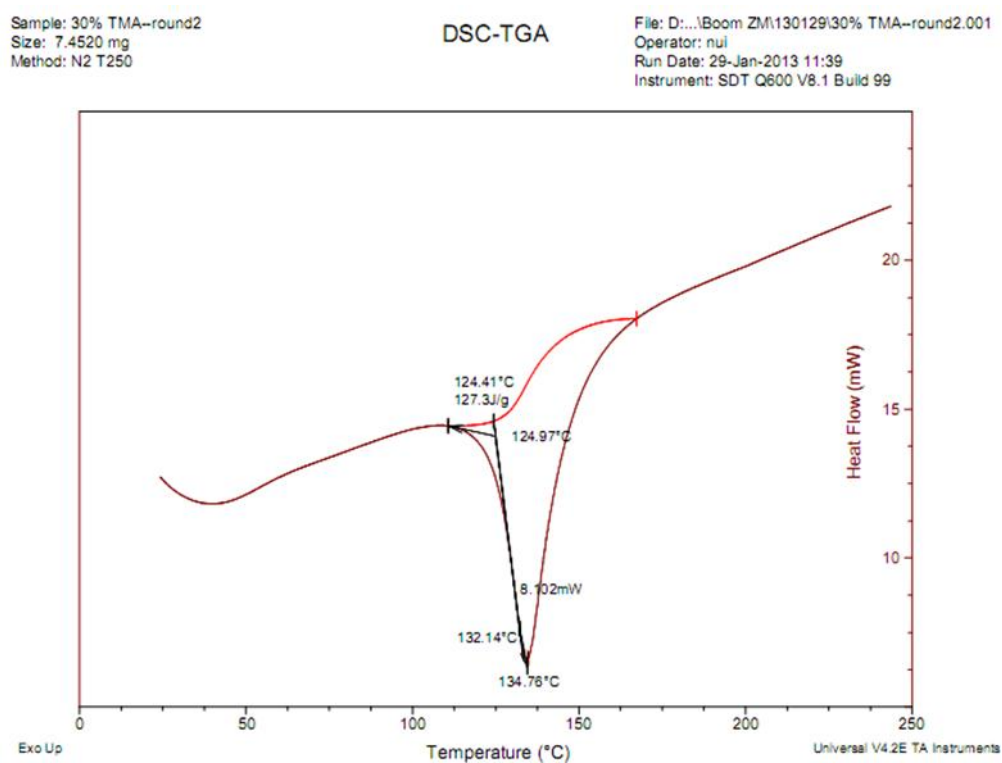**DIFFERENTIAL SCANNING CALORIMETRY**
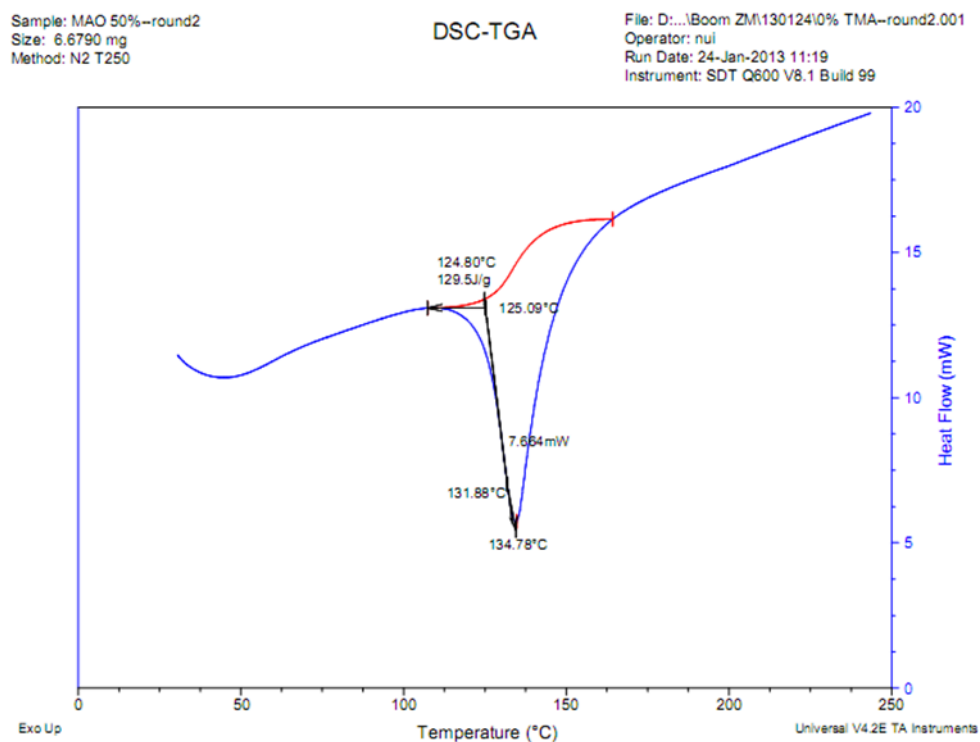
Figure A.1 DSC curve of polyethylene produced from silica-supported zirconocene/dMAO
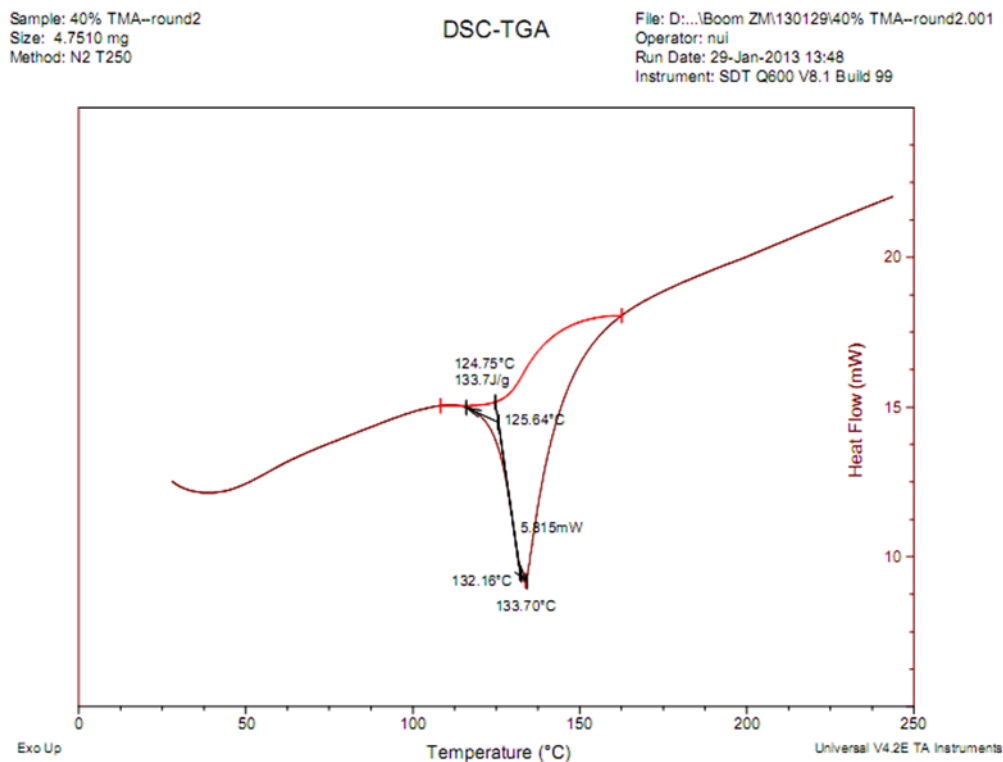

Figure A.2 DSC curve of polyethylene produced from silica-supported zirconocene/dMAO+TMA(9.1 wt%)
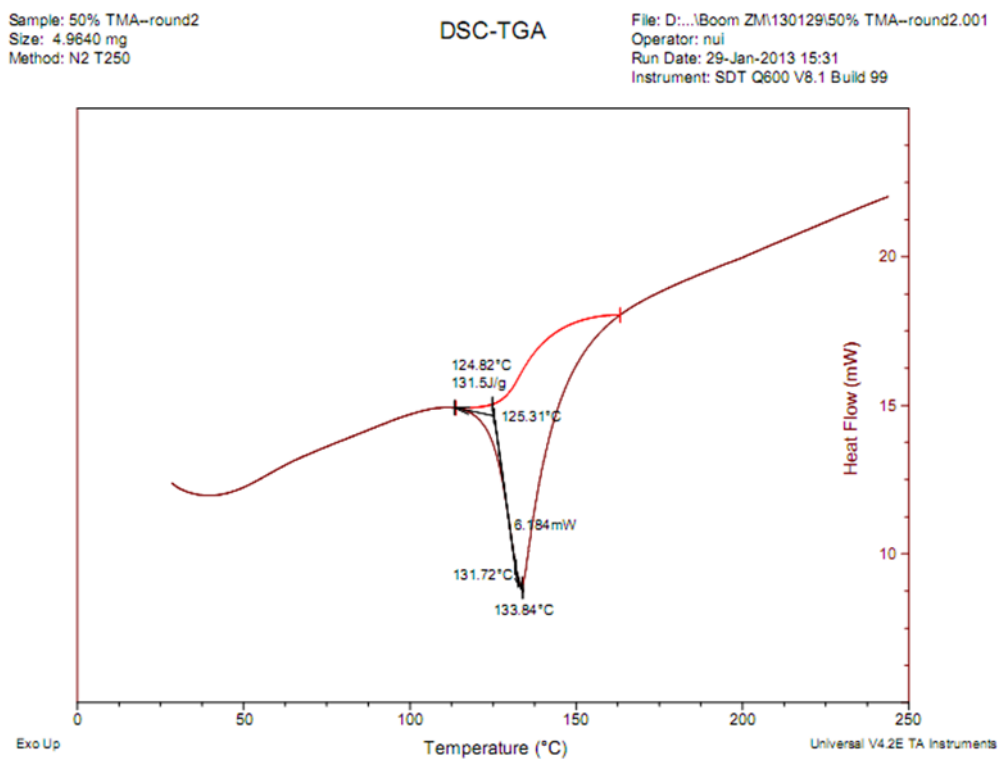
Figure A.3 DSC curve of polyethylene produced from silica-supported

zirconocene/dMAO+TMA(16.7 wt%)

Figure A.4 DSC curve of polyethylene produced from silica-supported

zirconocene/dMAO+TMA(23.1 wt%)

Figure A.5 DSC curve of polyethylene produced from silica-supported
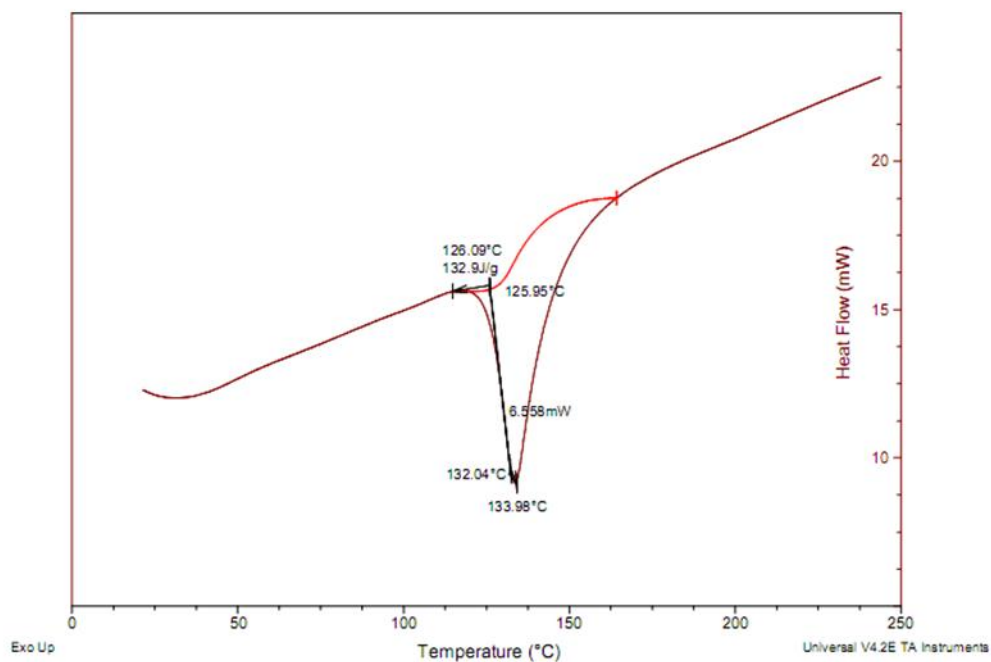zirconocene/dMAO+TMA(28.6 wt%)

Figure A.6 DSC curve of polyethylene produced from silica-supported
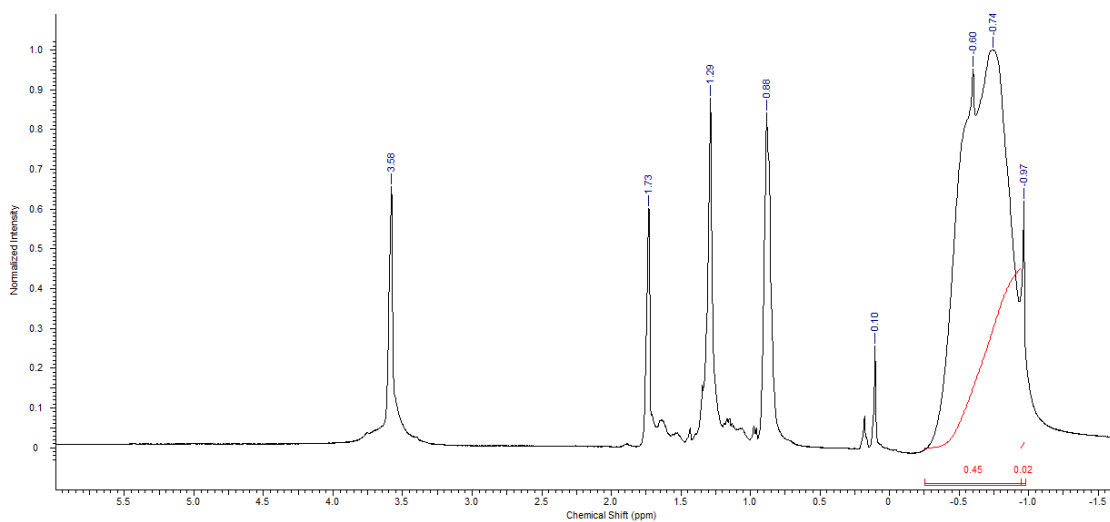zirconocene/dMAO+TMA(33.3 wt%)

Figure A.7 DSC curve of polyethylene produced from silica-supported
zirconocene/dMAO+TMA(41.2 wt%)

APPENDIX B
^{1}H-NMR SPECTROSCOPY
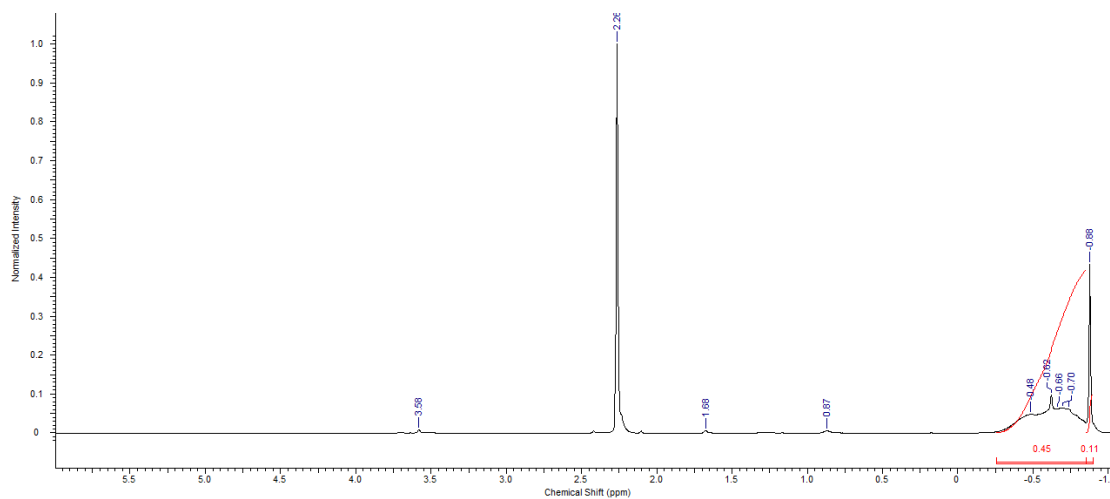
Figure B.1 ^{1}H NMR spectra of MAO solution

Figure B.2 ^{1}H NMR spectra of dMAO

APPENDIX C
CALCULATION OF POLYMER PROPERTIES

The percentage of crystallinity of polyethylene was determined by differential scanning calorimeter (DSC). The overall crystallinity of polymers is calculated from equation

$$\% \ X_C = (H_m/H_p)*100$$

where H_m is the enthalpy of the sample

H_p is the enthalpy of a totally crystalline PE (293 J/g)

APPENDIX D
LIST OF PUBLICATION

Chayut Chintanapatumporn, Saovalak Sripothongnak, Bunjerd Jongsomjit, and Piyasan Praserthdam "Effect of calcination temperature on SiO_2-supported zirconocene/MAO catalyst for ethylene polymerization". (The proceeding of the 2nd TIChE International Conference (TIChE 2012), Nakornratchasima, Thailand.

VITA

Mr. Chayut Chintanapatumporn was born on May 28, 1989 in Bangkok, Thailand. After graduated from Saint Gabriel's College in 2005, he spent his 4 years for study in a Bachelor of Science in Applied Chemistry at Chulalongkorn University with a 2nd class honor. Afterward, he continued his Master's degree at Department of Chemical Engineering at Chulalongkorn University and joined the Center of Excellence on Catalysis and Catalytic Reaction Engineering in 2010.