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COPOLYMERIZATION OF ETHYLENE /1-OCTENE OVER GALLIUM-MODIFIED
SILICA-SUPPORTED METALLOCENE CATALYST



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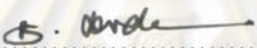
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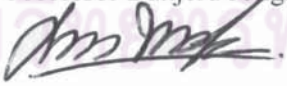
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อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. บรรเจิด จงสมจิตร, 96 หน้า

ในการผลิตพอลิเอทิลีน ตัวเร่งปฏิกิริยาที่นำมาใช้ได้แก่ ตัวเร่งปฏิกิริยาซีเกลอร์-นาคดา
ตัวเร่งปฏิกิริยาเมทัลโลซีน และตัวรองรับโลหะออกไซด์ โดยตัวเร่งปฏิกิริยาเมทัลโลซีนมัก
นำมาใช้ควบคู่กับตัวเร่งปฏิกิริยาร่วมเมทิลอะลูมิเนียมออกเซน ซึ่งจะให้ความว่องไวสูงมาก สำหรับการ
นำตัวเร่งปฏิกิริยาไปใช้ในอุตสาหกรรมได้มีการพัฒนาและปรับปรุงตัวเร่งปฏิกิริยาเมทัลโลซีนที่มี
ตัวรองรับอย่างจริงจัง เพื่อให้สามารถใช้ได้ในกระบวนการผลิตที่เป็นวัฏภาคแก๊สและวัฏภาค
ของเหลว แก้ปัญหาการเกิดการขีดยึดตัวของเนื้อพอลิเมอร์ในเครื่องปฏิกรณ์ สำหรับงานวิจัยนี้จะ
มุ่งเน้นพัฒนาตัวเร่งปฏิกิริยาเรซิมิก-เอทิลีนบีสอินดีนิลเซอร์โคเนียมไดคลอไรด์ [$\text{rac-Et(Ind)}_2\text{ZrCl}_2$]
ที่มีตัวรองรับเป็นซิลิกาที่ถูกปรับปรุงด้วยแคลเซียมเพื่อสังเคราะห์โคพอลิเมอร์ของเอทิลีนกับ
หนึ่งออกทีน การศึกษาจะแบ่งออกเป็น 2 ส่วน ในส่วนแรกจะทำการศึกษาผลของการปรับปรุงตัว
รองรับด้วยแคลเซียมและผลของวิธีการขีดยึดตัวเร่งปฏิกิริยาร่วม ซึ่งพบว่าการปรับปรุงด้วย
แคลเซียมทำให้ความว่องไวในการเกิดพอลิเมอร์เพิ่มขึ้น และวิธี *in situ* จะให้ความว่องไวในการเกิด
ปฏิกิริยาสูงกว่าระบบ *ex situ* อิมเพกเนชัน ในส่วนที่สองจะทำการศึกษาผลของการปรับปรุง
แคลเซียมบนตัวรองรับซิลิกาทั้งนี้ตัวรองรับจะมีโครงสร้างของรูพรุนต่างกัน ผ่านวิธี *in situ*
อิมเพกเนชัน จากการทดลองพบว่าตัวรองรับซิลิกาทั้งซิลิการูพรุนขนาดใหญ่และขนาดเล็กต่างให้
ความว่องไวในการเกิดปฏิกิริยาสูงขึ้นเมื่อมีการปรับปรุงด้วยแคลเซียม ทั้งนี้เมื่อพิจารณาผลของ
โครงสร้างรูพรุนพบว่าซิลิการูพรุนใหญ่ให้ความว่องไวในการเกิดปฏิกิริยาค่ากว่าการใช้ตัวรองรับ
ซิลิการูพรุนขนาดเล็ก โคพอลิเมอร์ที่ได้ทั้งหมดจะนำมาวิเคราะห์ เพื่อวัดคุณสมบัติและโครงสร้าง
ย่อยของพอลิเมอร์ด้วยเครื่องดีฟเฟอเรนเทียลสแกนนิ่งแคลอริมิเตอร์ (DSC) และเครื่องนิวเคลียร์
แมกเนติกเรโซแนนซ์ (^{13}C NMR)

ภาควิชา.....วิศวกรรมเคมี..... ลายมือชื่อนิสิต.....

สาขาวิชา.....วิศวกรรมเคมี..... ลายมือชื่อ.ที่ปรึกษาวิทยานิพนธ์หลัก.....

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SUPPORTED METALLOCENE CATALYST.

ADVISOR: ASST. PROF. BUNJERD JONGSOMJIT, Ph.D., 96 pp.

Nowadays, for polyethylene production, Ziegler-Natta catalysts, metallocene catalysts, and supported metal oxide (Philips process) all are capable of producing linear polyethylene. Metallocene catalysts activated by methylaluminoxane show very high activity in ethylene polymerization. The development of supported metallocenes is crucial for industrial application because it enables their use in gas- and slurry-phase processes and prevent reactor-fouling problems. This research proposed the development and improvement of metallocene catalyst, such as the $[rac\text{-Et(Ind)}_2\text{ZrCl}_2]$ catalyst system, by using gallium- modified silica support for ethylene/1-octene copolymerization. These studies were divided in two parts. In the first part, in this research, the effect of gallium modification and impregnation method was studied. It was found that an addition of gallium into support can improve activity and the in situ impregnation exhibited higher catalytic activity than the ex situ method. In the second part, the impact of gallium modification on silica-supported metallocene catalyst via in situ impregnation on the different pore sizes of silica was investigated. It was found that the catalytic activity of the large pore silica was lower than the small pore system. All the obtained polymers were characterized by DSC, and ^{13}C NMR to determine the polymer properties and polymer microstructure. All the obtained polymers were characterized by DSC, and ^{13}C NMR to determine the polymer properties and polymer microstructure.

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CHAPTER I

INTRODUCTION

Since 1950, polymer materials have experienced a rapid development from cheap, low-quality surrogates to materials that allow for new applications or replace established materials such as metal, wood or glass because of their better properties. Otherwise the demands for the plastics increase in huge quantities every year [Soga and Shiono, 1997]. Among synthetic polymers, polyethylene is the major polymer and the largest of production in plastic industry [Robinson, 2001]. Thus, it has chemical stability and great range of physical properties, polyethylene is the large usage polymer in many kind of industry such as from the strong flexible films and coating to rigid containers. It is the variation in molecular structure that results in this range of physical properties. The first step of development occurred in the ability to control the molecular weight in the commercial scale of ethylene production in 1930s [Bert *et al.*, 1983]. In 1970s, the industry scale of linear low density polyethylene (LLDPE) was commercialized [Staub, 1983]. The development of industrial LLDPE has the largest going rate in all type of polyethylene production until present [Phillip, 2001; Buckalew and Schumacher, 2000].

Research and development of high-performance olefin polymerization catalysts has contributed significantly to the advancement of organometallic chemistry and polymer chemistry and has made a dramatic impact on the polyolefin industry. More than 40 million tons of polyolefins are produced every year using catalytic olefin polymerization. Historically, the discovery of highly active catalysts results in the commercialization of new polyolefins. A recent example is the discovery of group 4 metallocene catalysts, which display very high ethylene polymerization activity [Sinn and Kaminsky, 1980; van der Heijden *et al.* 1998; Shapiro *et al.*, 1994]. These high-performance olefin polymerization catalysts have made possible the industrial production of linear low-density polyethylene, isotactic and syndiotactic polypropylene, syndiotactic polystyrene, etc.

Several studies comparing different group 4 metallocene structures in ethylene/ α -olefin copolymerization have been reported [Coevoet *et al.*, 1996; Yang *et al.*, 2005; Forlini *et al.*, 2002;]. Nevertheless, the homogeneous catalyst systems based on metallocene require high aluminum-to-transition metal molar ratios and extensive polymer washing, so as to remove residual aluminum. In addition, they are not suitable for industrial applications such as slurry and gas phase polymerization processes. Because most of the existing polymerization plants use these processes with heterogeneous catalyst systems, these soluble catalysts are unsuitable for the production of polyolefins on an industrial scale. To overcome this problem, metallocenes can be immobilized on inert or inorganic carriers such as aluminas, silicas and titanias, and zeolites [Nishii *et al.*, 2004; Kaminsky *et al.*, 2001; Soga *et al.*, 1993]. These carriers have been extensively studied for supported cocatalyst for years. This approach should permit the replacement of conventional Ziegler–Natta catalysts in existing processes. Remarkably, using immobilized metallocenes should result in the formation of uniform polymer particles with narrow size distribution and high bulk density compared to those provided by Ziegler–Natta-supported catalysts [Hasan *et al.*, 2002]. The heterogeneous metallocene system is necessary to produce polymer particle of desired morphology to avoid reactor fouling with finely dispersed swelling of polymers [JAMES *et al.*, 1994].

In many inorganic supports, SiO₂ is perhaps the most attractive support so far. However, the properties of silica itself may not be completely satisfied for all purposes based on the polymerization activity and properties of the obtained polymers, [Greco *et al.*, 2003] since some intrinsic undesirable properties, such as the acidity of various surface OH groups can lead to the formation of the multiple active sites. Therefore, a modification of the support properties is required.

In a previous study, the use of silane-modified silica-supported MAO with Et[Ind]₂ZrCl₂ catalyst for ethylene/ α -olefin copolymerization was investigated [Jongsomjit *et al.*, 2004]. It was found that silane modification resulted in increased activities for ethylene/1-hexene copolymerization. In addition the copolymerization of ethylene/1-octene via zirconia modification on the silica-supported metallocene catalyst was also studied [Jongsomjit *et al.*,

2008]. It was found that the zirconia modification on the silica support apparently resulted in increased polymerization activity. However, to the best of our knowledge only one study exists regarding its use in combination with olefin polymerization catalysts [Joao *et al.*, 2008].

The objectives of this investigation was synthesis of various SiO₂-based supports having gallium with various weight ratios such as SiO₂-0% , SiO₂-0.2% , SiO₂-1% and investigate on catalytic activities during the copolymerization of ethylene with 1-octene using various SiO₂-based supported MMAO with zirconocene catalysts.

This thesis was divided into five chapters. Chapter I involved an overview of the use of metallocene catalyst for the polyolefin industry. In Chapter II, knowledge and open literature dealing with metallocene catalysis for olefin polymerization were presented. The literature review was accentuated metallocene catalyst system used for copolymerization of ethylene with 1-octene. The experimental procedure as well as the instrument and techniques used for characterizing the resulting polymers were also described in Chapter III.

In Chapter IV, the results on ethylene and 1-octene copolymerization using gallium-modified silica-supported zirconocene/dMMAO catalysts were presented. The influences of introduction of gallium in the silica support on the catalytic activity and polymer properties were investigated. The characteristics support and catalyst precursors using N₂ physisorption, X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Raman spectroscopy, Scanning electron microscopy (SEM), and Energy-dispersive x-ray spectrometer (EDX) and obtained copolymer using Differential scanning calorimetry (DSC) and ¹³C-nuclear magnetic resonance (¹³C -NMR).

Finally, conclusions of this work and some recommendations for future research work were provided in Chapter V.

CHAPTER II

LITERATURE REVIEWS

2.1 Polymerization of olefins

Until 1950, processes for olefin polymerization were based on a radical process at high pressure and high temperature. Polymerization of ethylene under this condition (2000-3000 bars; 423-503 K) yields low-density polyethylene, a low melting, highly branched polyethylene, containing both long and short chain branches (Smedberg *et al.*, 2003). With propylene only atactic, low molecular weight material can be obtained. Ziegler found that ethylene could also be polymerized using TiCl_4 and alkylaluminium. The process yields linear polyethylene with a high molecular weight. Natta proved that the same type of catalysts also polymerized propylene (Natta *et al.*, 1995). The resulting polymer mixture is predominantly isotactic with addition polymer fractions that are of a lower stereoregularity or atactic. Copolymerization of ethylene with 1-hexene/1-octene with the titanium Ziegler catalysts result in copolymers in which the degree of incorporation of the alpha-olefin varies over molecular weight distribution. Upon reaction of a vanadium compound, e.g. $\text{V}(\text{acac})_3$ (acac = acetylacetonato) or VCl_4 , with and alkylaluminium cocatalysts a catalyst for the production of EP (copolymerization of ethylene and propylene) and EPDM (ethylene-propylene-diene elastomer) are obtained [Gambarotta *et al.*, 2003]. The (homogeneous) system shows high (initial) activity, but is deactivated rapidly [Milione *et al.*, 2002]. An important advantage is that the comonomers are randomly incorporated in the polymer over the full range of the molecular weight distribution. The heterogeneity of Ziegler Natta system and Phillip/Union Carbide type catalysts make them very attractive for industrial application, and most polyolefin materials are still produced by means of heterogeneous catalysts [Kashiwa *et al.*, 2004]. These heterogeneous systems combine high activity with an easy processability of the resulting product mixture and good polymer particle morphology. The catalyst system contain various type of active sites with different geometries and activities, which often leads to polymers with broad or polymodal molecular weight distribution or to mixtures of different type of polymers (e.g. mixture of atactic and isotactic


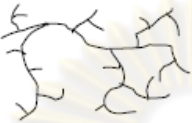

propylene [Kissin *et al.*, 2003]. Many improvements on the classical Ziegler Natta type catalysts have been made over the last 30 years, and modern Ziegler Natta system allow a much better control of polymer properties. Most of these improvements were achieved by empirical method [Hlatky, 2002]. In 1957, the first article on homogeneous titanium-based olefin polymerization were published by Brselow and Newburg, (1957) and by Natta and Pino (1957). When reacting Cp_2TiCl_2 with Et_2AlCl (DEAC) under conditions similar to those used with Ziegler Natta system, a catalyst that polymerizes ethylene is obtained. The first homogeneous system showed a low activity, when compared to classical Ziegler Natta system and was also not active in polymerization of higher olefin. In contrast to heterogeneous system, homogeneous catalysts have a single type of well-defined active sites. Although heterogeneous catalysts are in general industrially more practical, a higher control of properties of the catalyst, and more detailed kinetic and mechanistic studies are possible with well-defined molecular catalysts ("single site" catalysts) [Krentsel, Nekhaeve and Russ, 1990].

2.2 Classification of polyethylene

Polyethylene (PE) is the most important material in plastic and polymer type. Normally, polyethylene is classified to three type according to its density and structure, high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). The numerous studies show that the global market of LLDPE was increased in very interesting rate about 10 % per annum [Richards, 1998].

Table 2.1 summarized the characteristic of three type of polyethylene. The different in structure of polymer affects to the physical properties of polymer i.e. density of polymer and hence the application of polymer. HDPE is the polymer that has very less or does not have any branch in the polyethylene backbone. From this microstructure HDPE has very high crystalline phase in polymer morphology and highest density about 0.96 g/cm^3 . Polyethylenes which have many long and short chains branching formed by radical process are LDPE. The amount of long chain branching (LCB) and short chain branching (SCB) also affect the crystalline and others physical properties too.

Table 2.1 Density range, molecular structure, synthesis, and applications of various type polyethylenes [Richards, 1998].

Type of PE	Density (g/cm ³)	Molecular structure	Synthesis	Common uses
HDPE	0.945-0.965		Polymerization of ethylene on Philips, Ziegler-Natta and metallocene catalyst	Gas pipe, car gas tanks, bottles rope and fertilizer bag
LDPE	0.890-0.940		Free radical polymerization of ethylene at high temperature and high pressure	Packing film, bags, wire, sheathing, pipes, waterproof membrane
LLDPE (VLDPE,ULDPE)*	0.910-0.925		Copolymerization of ethylene with α -olefins on Ziegler-Natta and metallocene catalysts	Shopping bag, stretch wrap, greenhouse film

* A family of LLDPE with density of 0.87-0.915 g/cm³

Normally, long chain branching has the main effect on the polymer viscosity and melt rheology due to the molecular size and shape. On the other hands, short chain branching has the influence to polymer morphology and solid state properties of polyethylene. LLDPE was produced by the copolymerization of ethylene and α -olefins such as propylene, 1-butene, 1-hexene and 1-octene. Mostly, side chain in LLDPE distributed in short chain branching type by non-uniformly with linear microstructure of backbone polyethylene chain. The properties of LLDPE such as, thermal, physical and mechanical properties depend on the distribution of short chain in the copolymer and polymer microstructure (triad and dyad distribution). Thus, the several LLDPE grades are classified by the primarily result via microstructure of polymer and molecular weight of polymer

2.3 Catalyst System for Olefin Polymerization

In 1953 Karl Ziegler, who succeeded in polymerizing ethylene into highdensity polyethylene (HDPE) at standard pressure and room temperature, discovered of catalysts based on titanium trichloride and diethylaluminum chloride as cocatalyst, at Max-Planck-Institute in Mulheim. A little later, Natta, at the Polytechnical Institute of Milan, was able to indicate that an appropriate catalyst system was capable of polymerizing propene into semi-crystalline polypropene. Ziegler and Natta shared a Nobel Prize for Chemistry in 1963 for their work [Kaminsky and Laban, 2001] with this so-called Ziegler-Natta catalyst. Ziegler-Natta catalyst has been widely used in olefin polymerization; the coordination polymerization allows the catalyst geometry around the metal center to control the polymer structure. In homogeneous polymerization, the ligands of a catalyst largely controls the geometry of an active metal center on which the polymerization reaction occurs. However, when used the conventional Ziegler Natta catalysts, the molecular structure of the polymers cannot be controlled well because these catalysts have different nature types of catalytic sites.

Metallocene catalysts show in contrast to Ziegler-Natta systems, only one type of active site (single-site catalysts), which produces polymers with narrow molecular weight distribution and chemical composition distribution. The structural change of metallocene catalysts can possible to control polymer microstructure, comonomer incorporations and stereoregularity. These catalysts brought the way to expand possibilities of new olefin polymerization and good property of the resulting polyolefins [Yano *et al.*, 1999].

2.3.1 Metallocene Catalyst

Metallocene catalysts have been used to polymerize ethylene and α -olefins commercially. The structural change of metallocene catalysts can control composition distribution, incorporation of various comonomers, molecular weight distribution and stereoregularity [Sinclairand and Wilson, 1994]. One of the greatest challenges in organometallic complex is to synthesize the metallocene complex and apply for new polymerization technology with transition group IV metals. Metallocene complexes are become an important class of polymerization catalyst in the research and industrial area since it have many advantage in polymerization such as [Helmut and Koppl, 2000],

1. The homogeneous nature of catalysts provides the active sites that have the great number of activity in olefin polymerization. Comparison to conventional Ziegler-Natta catalyst or Philips catalyst, it was found that metallocene complex gave the higher activity about 100 times.

2. Metallocene catalysts have ability to control the stereoregularity (isotactic, atactic, syndiotactic and hemitactic polypropylene) of the polymers produced from prochiral olefins, such as propylene.

3. According from the narrow molecular weight distribution of polymer about 1-2, we can call metallocene catalyst as single site catalysts.

4. Their potential for producing polyolefin with regularly distributed short and long chain branches in the polymer chain. These parameters determine the properties of new materials for applications i.e. LLDPE and thus generate new markets.

5. Heterogeneous catalyst provide the different active sites than those in solution and can have an enormous effect on catalyst activity and the properties of the produced polyolefins in term of molecular weights, branching and stereospecificity.

2.3.2 Structure of Metallocene Catalyst

Metallocene catalysts are the organometallic coordination compounds in which one or two π -carbocyclic ligands such as cyclopentadienyl ring, substituted cyclopentadienyl ring, or derivative of cyclopentadienyl ring (such as fluorenyl and indenyl etc.) are bonded to central transition metal atom. The cyclopentadienyl ring of metallocene singly bonded to the ring-metal bond is not centered on any one of the five carbon atoms in the ring but equally on all of them [Gupta, Satish and Bhardwaj, 1994]. The typical structure of a metallocene catalyst is represented by **Figure 2.1**

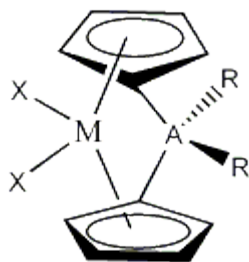


Figure 2.1 Typical chemical structure of a metallocene catalyst [Natta, 1957].

Where M = Group 4, 5 or 6 transition metal (e.g. Zr, Ti or Hf)

A = an optional bridging unit consisting of 1-3 atoms in the backbone

R = hydrocarbyl substituents or fused ring system (indenyl, fluorenyl, and substituted derivatives)

X = chlorine or other halogens from group 7 or an alkyl group

Compositions and types of metallocene have several varieties. When the two cyclopentadienyl (Cp) rings on either side of the transition metal are unbridged, the metallocene is non-stereorigid and it is characterized by C_{2v} - symmetry. The Cp_2M (M = metal) fragment is bent back with the centroid-metal-centroid angle θ about 140° due to the interaction with the other two σ bonding ligands (Pasynkiewicz, 1990). When the Cp rings are bridged (two Cp rings arranged in the chiral array and connected together with chemical bonds by a bridging group), the stereorigid metallocene, called ansa-metallocene, could be characterized by either a C_1 , C_2 or C_s symmetry depending upon the substitutions on two Cp rings and the structure of the bridging unit as schematically illustrated [Gupta, 1994] in the **Figure 2.2**.

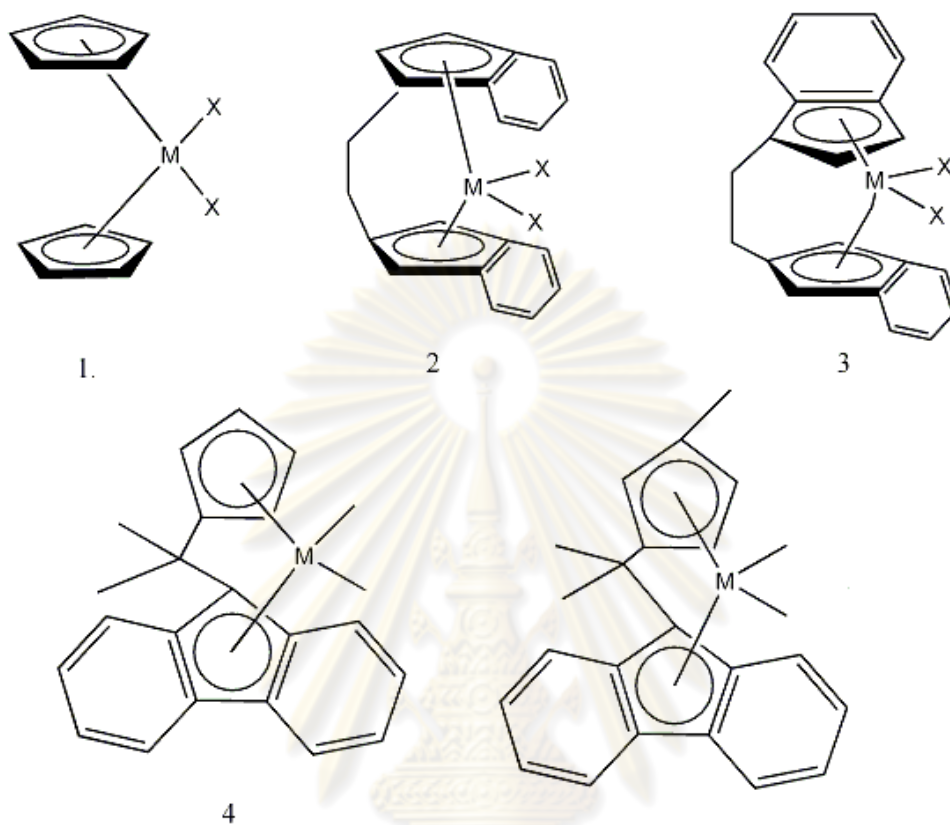


Figure 2.2 Schematic representations of metallocene symmetry (Type 1: C_{2v} -symmetric, Type 2: C_2 -Symmetric, Type 3 and Type 4: C_s -symmetric, Type 5: C_1 -symmetric) (C, italic. It is better to draw all the structures in a similar way) [Gupta *et al.*, 1994].

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2.3.3 Cocatalysts

Aluminoxane, especially methylaluminoxane (MAO) plays the very important role to activate metallocene catalyst. Before the MAO was discovered, in Ziegler- Natta catalyst alkylaluminumchloride was used to activate Cp_2TiCl_2 but it exhibited the very poor activity. Using of MAO as cocatalyst can promote the productivity of polymerization by several order of magnitude. Otherwise usin of MAO, the other aluminoxanes such as, ethylaluminoxane (EAO) or iso-buthylaluminoxane (iBAO) or modified methylaluminoxane was employed to use as cocatalyst too. (Structure of MAO, EAO, iBAO and MMAO was shown in **Figure 2.3**).

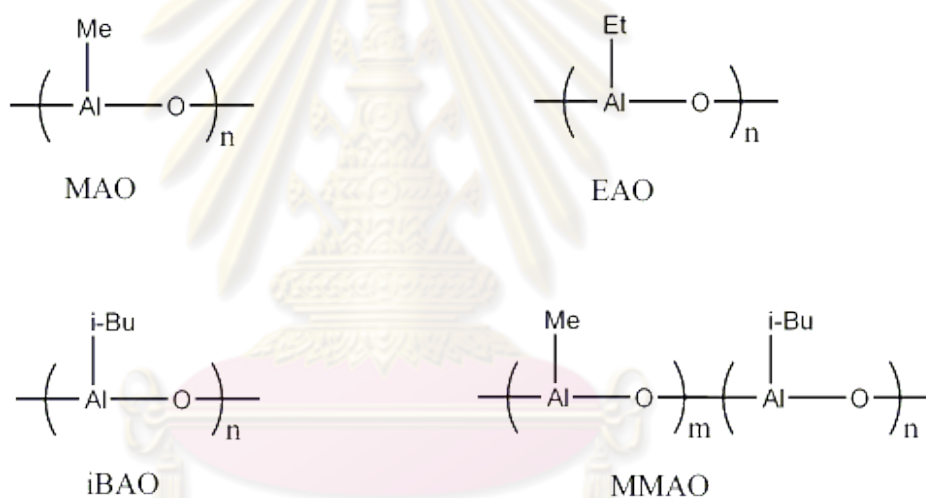
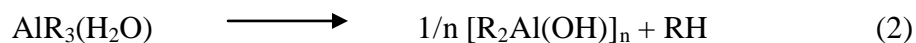
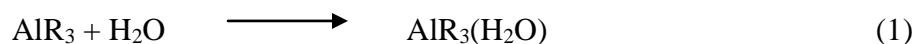


Figure 2.3 Several kinds of MAO [Pasykiewicz, 1990; Chien, 1976].

A metallocene catalyst precursor can be activated with organoalumoxanes, especially methylaluminoxane (MAO), which provides maximum activity. Methylaluminoxane is a compound in which aluminum and oxygen atoms are arranged alternately and free valances are saturated by methyl substitutions. It is prepared by carefully controlled partial hydrolysis of trimethylaluminum (TMA) and according to investigations [Pédeutour *et al.*, 2002]. The hydrolysis of AlR_3 ($R = Me, Et, iBu$) has been shown to proceed via the formation of an alkylaluminum water complex shown in Equation 1 [Scheirs *et al.*, 2000], which subsequently

eliminates an alkane to form a dialkylaluminum hydroxide complex. This rapidly associates to give dimers or larger oligomers in solution as shown in Equation 2.



The structure of MAO consists mainly of units of the basic structure $[\text{Al}_4\text{O}_3\text{Me}_6]_4$, which contains four aluminum, three oxygen atoms and six methyl groups. Although very extensive research has been carried out in both academia and industry, the exact composition and structure of MAO are still not entirely clear or well understood. The proposed structures for MAO in the open literature (Chen and Marks, 2000) shown in **Figure 2.4** include: (1) one-dimensional linear chains, (2) cyclic rings, which contain three-coordinate Al centers, (3) two-dimensional structures, and (4) three-dimensional clusters is based on structural similarities with *tert*-butylaluminoxanes, which form isolable and X-ray crystallographically characterizable cage structures (5) (Sinn, 1995).

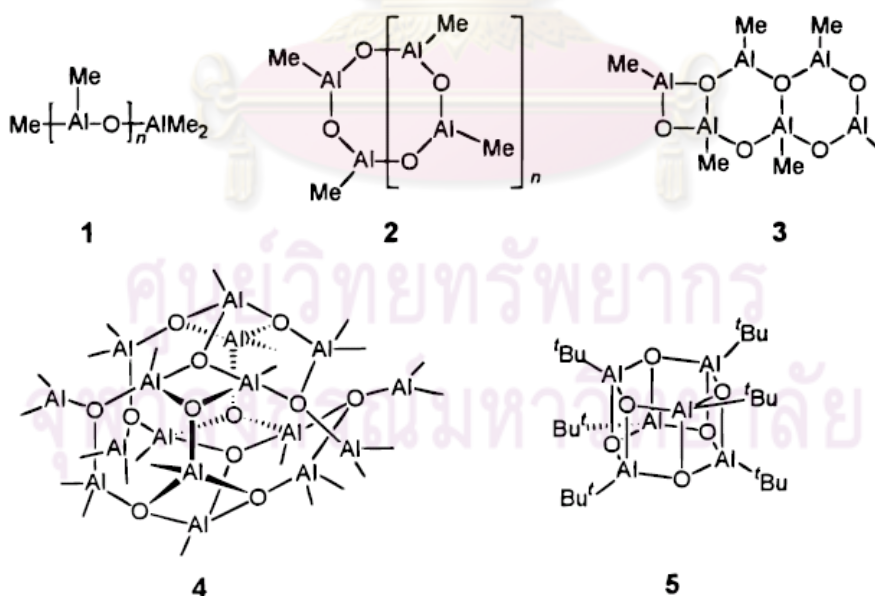


Figure 2.4 The general proposed structure of MAO [Sinn, 1995].

Depending on the nature of the hydrated salt (the H₂O source) used for the MAO synthesis and the exact MAO synthetic reaction conditions; MAO activated metallocenes may exhibit widely differing activities in olefin polymerization. The MAO structure can hardly be elucidated directly because of the multiple equilibria present in MAO solutions, and residual trimethylaluminum in MAO solutions appears to participate in equilibria that interconvert various MAO oligomers [Giannetti *et al.*, 1985].

Cryoscopy MAO molecular weight decrease after AlMe₃ addition according to a linear relationship, which is caused by disproportionate reactions [Tritto, 1997]. However, recent in-situ FTIR spectroscopy investigations do not indicate any obvious reaction between TMA and MAO. Nevertheless, in light of its complicated, unresolved structural features, MAO is usually represented for the sake of simplicity as having linear chain or cyclic ring structures $[-Al(Me)-O-]_n$, containing three-coordinate aluminum centers [Chen *et al.*, 2000]. However, conventional MAO has very low solubility in aliphatic solvents as well as poor storage stability in solution. To solve these limits, MAO can be modified. Commercial modified methylaluminoxanes (MMAO), which prepared by controlled hydrolysis of mixture of trimethylaluminum and triisobutylaluminum, exhibit improved solution storage stability and improved solubility in aliphatic solvents and can be produced at lower cost while providing good polymerization efficiency [Chen *et al.*, 2000]. Recently, the modification by evacuated MAO was studied. Dried methylaluminoxane (MAO) which was free of Me₃Al, was more active than the standard MAO system, resulting in a steady polymerization rate and giving higher Mw polypropylenes. Additive effects of trialkylaluminum on the dried MAO system showed that the polymer yield was increased by the addition of *i*-Bu₃Al and Oct₃Al and decrease by Me₃Al and Et₃Al [Ioku, 2002].

Cam and Giannini [1992] investigated the role of TMA present in MAO by a direct analysis of Cp₂ZrCl₂/MAO solution in toluene-d₈ using ¹H-NMR. Their observation indicated that TMA might be the major alkylating agent and that MAO acted mainly as a polarization agent. However, in general it is believed that MAO is the key cocatalyst in polymerizations involving metallocene catalysts. The role of MAO included 1) alkylation of misallocate, thus forming catalyst active species, 2) scavenging impurities, 3) stabilizing the cationic center by ion-pair interaction and 4) preventing bimetallic deactivation of the active species. Ethylene/ α -

olefins copolymers with bimodal CCD were produced with homogeneous Cp_2ZrCl_2 with different co catalysts such as MAO and mixture of TEA/borate or TIBA/borate. It seemed that the active species generated with different co catalysts have different activities and produce polymers with different molecular weights. Haricot *et al.* [2004] have investigated the relationship between the supporting effects of MMAO in the living polymerization of propylene, and investigated the additive effect of trialkylaluminiums in the $[\text{ArN}(\text{CH}_2)_3\text{NAr}]\text{TiMe}_2$ metaloxide supported MMAO systems. It was found that the activity and the molecular weight values in the presence of trialkylaluminiums were slightly smaller than that of the corresponding MMAO/ SiO_2 system due to the induction period. Because of a small amount of trialkylaluminium hindered the initiation reaction. On the one hand, not only the aluminoxane has effect to the polymerization behavior but the trialkylaluminum has the influence too. Shiono, T. *et al.* [2000] have studied on the effect of trialkylaluminum type to the characteristic of polymerization. For example, the addition of Oct3Al and Et3Al increased the propagation rate of living polymerization with $[t\text{-BuNSiMe}_2\text{Flu}]\text{TiMe}_2 / \text{B}(\text{C}_6\text{F}_5)_3$ system at 223 K.

On the one hand, not only the aluminoxane has effect to the polymerization behavior but the trialkylaluminum has the influence too. Liu *et al.* [2006] have studied on the effect of trialkylaluminum type to the characteristic of polymerization, are investigated for ethylene polymerization without MAO or $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$. The effects of alkylaluminums, Al/Zr molar ratio, polymerization temperature and time as well as the comonomer 1-hexene on polymerization performance are examined. In appropriate range of Al/Zr molar ratio, the catalyst system bis(phenoxy-imine)Zr complex/trialkylaluminum shows high activity for ethylene polymerization, which approximates to bis(phenoxy-imine)Zr complex/MAO system. Their catalytic activities depend on not only the nature, but also the amount, of the trialkylaluminum. Both the molecular weights and the polydispersities (M_w/M_n) of polyethylene produced by bis(phenoxy-imine)Zr complex with Et_3Al , He_3Al , or Me_3Al are higher than those with MAO. The nature, rather than the amount, of alkylaluminum determines the M_w and the polydispersity of polymer in polymerization with the same complex. Unexpectedly, M_w of the polyethylenes produced with bis(phenoxyimine) Zr complex/triethylaluminum increases with polymerization time. The catalyst system bis(phenoxy-imine)Zr complex/trialkylaluminum has low capacity of copolymerization.

2.4 Metallocene Catalysts

2.4.1 Classification of metallocene catalyst systems

Polymerization with metallocene catalyst can be arranged to 2 major types, the supported system and non-supported system. For the non-supported system, the cocatalyst was a mobile phase in the polymerization medium. On the other hands, the supported metallocene catalyst system, the co-catalyst mostly was immobilized on the organic or inorganic support. In the early category, the activity was very high and easy to control the molecular weight. These systems still can divide to 2 subcategories, aluminoxane system and cationic metallocene system. To study the metallocene catalyst behavior by changing the substitute bridge or effect of activator are very famous to pick the homogenous metallocene catalyst system to study, because it did not have effect of interaction between inorganic support (silica or alumina) and metallocene catalyst systems.

2.4.2 Homogeneous metallocene catalyst with aluminoxane systems

At the first generation of this system, metallocene catalyst was a simple model which assembled from the cyclopentadienyl or substituted cyclopentadienyl ligands were π -bonded to the central metal atom. The development of metallocene catalyst was going on the synthesis of metallocene compounds. Breslow and Newbreg were the first researchers who apply the metallocene catalyst for polymerization [Newburg *et al.*, 1957]. They used the soluble bis(cyclopentadienyl)titanium derivative and alkylaluminum for ethylene polymerization. However, it was found that the productivity of these catalyst system was very low and the low molecular weight of polymer too. Moreover, these catalysts systems did not show activity when propylene was chosen to be a monomer for olefin polymerization. The breakthrough step of this typical metallocene occurred when Kaminsky and co-workers observed that the addition of water to trialkylaluminum in molar ratio 1:1 during the polymerization of ethylene could improve the productivity rate in significance [Sinn *et al.*, 1980]. It was known that the improved activity in the event above came from the reaction between water and trialkylaluminum to produce

alkylaluminum in the system. Thus, Kaminsky and his group decided to use the alkylaluminum as the cocatalyst coupling with the metallocene compound. From this combination, the next generation of metallocene catalyst was born.

It brought to the development in olefins polymerization because Metallocene/aluminum system showed the activity higher than conventional Ziegler-Natta catalyst. In addition, the produced polymer from metallocene system gave the narrower polymer distribution than the traditional system.

2.4.3 Heterogeneous Metallocene Catalysts

Since Kaminsky discovered the high activity $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ ethylene polymerization system, metallocene catalysts have slowly evolved as procedures push to commercialize the technology. In order to achieve the high activities, the metallocene catalyst required excessive molar Al to transition metal ratio (Al:M) of between 1000- 15000 : 1. Such ratio are commercially unacceptable in terms of the cost and the amount of residues left in the polymer. A significant effort has been put into reducing the amount of MAO required and this has led to the development of many systems with nonaluminum cocatalysts. Significant effort has also gone into heterogenizing the catalyst system by supporting the metallocene and cocatalyst onto an inorganic support such as silica, alumina, magnesium chloride, starch, zeolite, cyclodextrin and polymers [Chu *et al.*, 2000]. Therefore, heterogeneous catalysts offer several additional advantages important to industry, they improved product morphology and the ability to be used in gas and/or slurry phase synthesis methods more than their corresponding homogeneous metallocene systems. To overcome the preparation complexities of traditionally supported metallocene catalysts, metallocene can be supported in situ, which eliminates the need for a supporting step before polymerization. These systems have a good catalytic activity, produce polymers with a good morphology and high bulk density and do not cause reactor fouling [Chu *et al.*, 1997].

2.5 Heterogeneous System

2.5.1 Supported metallocene catalyst

Metallocene catalysts in dissolved form are in most cases unsuitable for the application in an industrial scale. In order to use them in existing technical processes (drop-in technology) by exchanging the conventional Ziegler-Natta catalysts, metallocenes have to be supported. Different methods are possible by using MAO as cocatalyst (Kaminsky and Winkelbach, 1999; Kaminsky and Laban, 2001).

(1) In the method of direct heterogenization, the metallocene or a mixture of the metallocene and MAO is anchored via physisorption or chemisorption onto the support. In the first case, the metallocene must be activated by external MAO.

(2) The metallocene can be supported by covalent bonding of its ligand environment to the support followed by activation with external MAO. The metallocene can be synthesized gradually as a covalent bonded species direct on the supporting material.

(3) Initial impregnation of MAO onto the support followed by adsorption and simultaneous activation of the metallocene (indirect heterogenization). In analogy to the homogeneous metallocene catalysis, the bonding between the active species $[\text{Cp}_2\text{ZrCH}_3]^+$ and the supported MAO is ionic. When performing the method of indirect heterogenization, no further MAO has to be added.

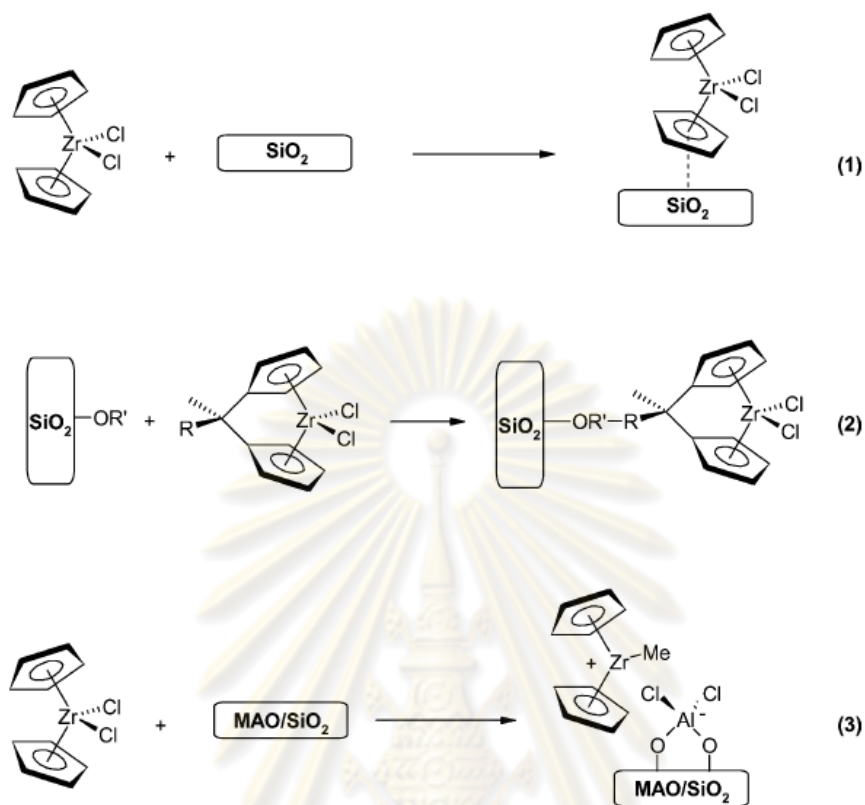


Figure 2.5 Supporting methods of metallocenes: (1) direct heterogenization, (2) covalent bonding on the support, (3) indirect heterogenization [Kaminsky and Laban, 2001]

Metallocenes supported according to the method of direct heterogenization have been known to produce polymers with higher molecular weight than those afforded by the homogeneous catalysts. However, direct heterogenization has also been known to change the polymerization characteristics of the metallocene, possibly by the interaction with surface hydroxyl groups. Sacchi *et al.* [1995] carried out propylene polymerization in the presence of the isospecific $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$ and the aspecific $[\text{Ind}]_2\text{ZrCl}_2$ complexes in solution and anchored to SiO_2 and SiO_2/MAO supports. From the stereochemical analysis of the polypropylene samples obtained it can be deduced that the same active species is formed when a metallocene is in solution and when it is anchored to the SiO_2/MAO support and a completely different active species is formed when the metallocene is anchored to the silica. Difficulties can also be encountered in the covalent bonding of metallocene complexes. If they are successively

synthesized on the support, chemically non- uniform anchor groups, such as vicinal and geminal silanol group, can lead to a mixture of different active species. The most promising method of supporting is indirect heterogenization as the chemical nature of the metallocene is changed, if at all, only to a small degree. The polymers obtained by the method of indirect heterogenization are very similar to those obtained by the homogeneous system. Each metallocene on the support forms an active center and the starting point for the growth of a polymer chain. The improvements a supported catalyst needs to achieve in order to be accepted in existing manufacturing facilities are the following (Chien, 1988):

(a) The supported catalyst system should have activity approaching those of the homogeneous catalysts.

(b) The supported system needs to be more stable.

(c) The amount of methylaluminumoxane has to be greatly reduced for economic viability of the supported catalysts.

(d) The supported catalyst should produce higher Mw polymers at high temperature of polymerization compared to those produced by homogeneous system.

(e) Polyolefins obtained in homogeneous processes have a very low particle size, as well as a broad size distribution and low bulk density. Supported catalysts must be able to control the polymer morphology.

(f) The supported systems should have the capability of producing polymers having desired broad or bimodal MWD for good rheological and physical properties.

(g) Some supported metallocenes catalysts have been reported to cause fouling of gas-phase reactors. Corrective measures must be found.

(h) The steric control of metallocene catalysts is determined by molecular structure. It would be advantageous if this can be controlled or even altered by the support.

2.5.2 Supporting Methods

In the case of carriers like silica or other inorganic compounds with OH group on the surface, the resulting catalyst displayed very poor activities even combined with MAO. The reaction of metallocene complexes with the Si-OH groups might cause the decomposition of active species. Such decomposition could be suppressed by fixing MAO on the silica surface and then reacting with metallocenes [Ferreira *et al.*, 2000]. Therefore, silica must be pretreated before the interaction with metallocene, to reduce the OH concentration and to prepare an adequate surface for metallocene adsorption and reaction in a non-deactivating way [Ferreira *et al.*, 2000]. Metallocene immobilization methods can be divided into three main groups. The first method is the direct support of catalyst onto an inert support. The second method involves the pretreatment of the inert support with MAO or other alkylaluminum followed by metallocene supporting. The third method, the catalyst is chemically anchored to the support, which often involves in-situ catalyst synthesis. These methods produce catalysts with distinct activities, comonomer reactivity ratios, and stereospecificities.

2.5.2.1 Direct Supporting of Inert Material

[Collins *et al.*, 1992] reported that $\text{Et(Ind)}_2\text{ZrCl}_2$, when supported on partially dehydrated silica, reacted with surface hydroxyl groups during adsorption to form inactive catalyst precursors and free ligands (**Figure 2.6**). Therefore, the activity is lower compared to the case of using dehydrated silica. **Figure 2.7** shows the proposed structure $\text{Et(Ind)}_2\text{ZrCl}_2$ supported on alumina. For the case of alumina, the activity of catalyst supported on dehydrated alumina is lower than the one supported on partially dehydrated alumina. The high Lewis acidity of aluminum sites on dehydrated alumina facilitates the formation of Al-Cl bonds and Zr-O bonded species when the metallocene compound is adsorbed on these sites. However, the metal sites in this case remain inactive even after MAO addition.

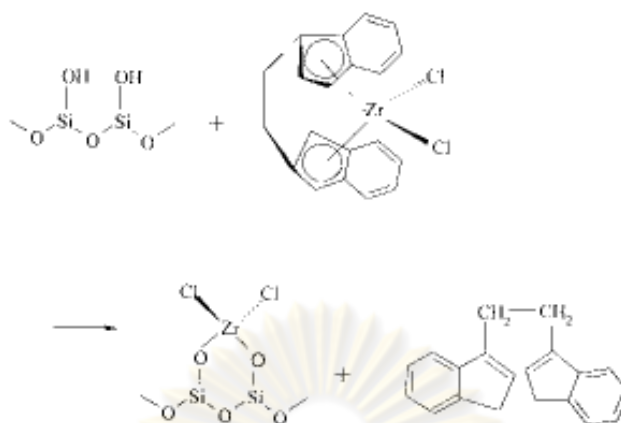


Figure 2.6 Structure of $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ supported on silica [Shan *et al.*, 2002]

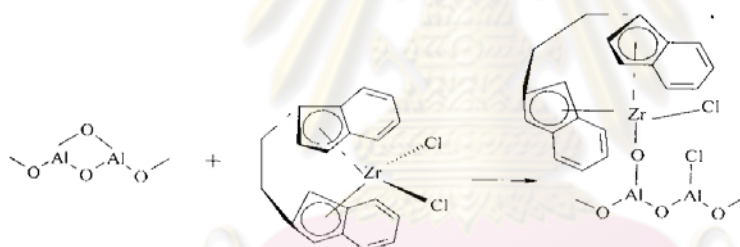


Figure 2.7 Structure of $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ supported on alumina [Shan *et al.*, 2002]

[Kaminsky *et al.*, 1994] proposed a possible explanation for the different behavior of metallocene supported directly on to silica, homogeneous systems, or supported onto MAO-pretreated silica. It is assumed that the supporting of metallocenes on silica takes place in three stages. First, the metallocene reacts with OH groups of the silica as shown in **Figure 2.8**.

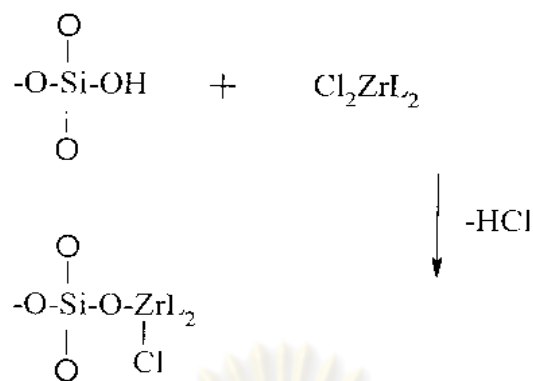


Figure 2.8 Reaction of silica and metallocene during catalyst supporting [Kaminsky *et al.*, 1994], where L is a ligand (Cp, Ind).

The second step is the alkylation by MAO as shown in **Figure 2.9**

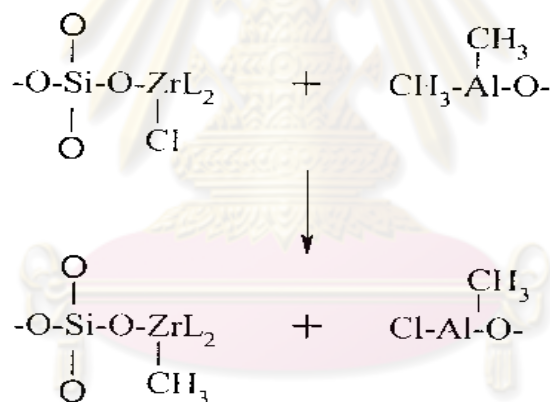


Figure 2.9 Alkylation of supported metallocene by MAO [Kaminsky *et al.*, 1994]

The third step is the dissociation of the $-\text{SiO}_2\text{-O-Zr-}$ bond to an ion pair to form the cation active center $(\text{SiO})\text{-(Zr)}^+$. The polydispersity of polymers produced with these supported metallocenes are reported to be relatively high ($5 \approx 8$) due to different electronic and steric interactions between the silica surface and the metal active sites. The immobilization of the zirconocene on silica inhibits bimolecular deactivation processes because the active sites are separated from each other. As a consequence less use of MAO is required, increased molecular

silica was ca. 10 wt%. Depending on silica types, saturation of MAO supported on silica can occur at lower MAO contents. [Harrison *et al.*, 1998] compared a variety of silica and alumina supports with different degrees of surface hydroxylation as the supports. It was shown that as the concentration of OH groups on the surface of the support increased, more MAO could be impregnated and thus catalyst with more metallocene content could be produced. The most obvious benefit of supported catalyst with more metallocene was increased activities compared to catalysts with lower concentration of surface hydroxyl groups (increased activities both in kg PE/mol Zr/hr and kg PE /gsupport/ h). However, at high polymerization temperatures, leaching of catalyst from the support was observed. In lower polymerization temperatures, leaching was less significant, however, the morphology and bulk density of the polymer formed were still unsuitable for use in gas-phase polymerization. For the case of propylene polymerization, a decrease in syndiotacticity was observed by [Xu *et al.*, 2000] when the metallocene catalyst was supported on pretreated silica.

2.5.2.3 Chemically Anchoring Catalyst on Support

[Soga *et al.*, 1994] described a method to support zirconocenes more rigidly on SiO₂. The supporting steps are as follows: 1) Silica was treated with SiCl₄ to substitute the OH groups with chlorine atoms. 2) The resulting silica was filtered and washed with tetrahydrofuran (THF). 3) The solid was re-suspended in THF and a lithium salt of indene, dissolved in THF, was added drop-wise. 4) The resulting solid was filtered and washed again with THF. And to re-suspended solid in THF, ZrCl₄ 2THF dissolved in THF was added. The final solid part was separated by filtration, washed with THF and diethyl ether, and dried under vacuum. The supported catalyst produced in this way showed higher isospecificity than the corresponding homogenous system for propylene polymerization. MAO or ordinary alkylaluminums were used as cocatalysts. The yield was higher when MAO was used as the cocatalyst, but the molecular weight of the polypropylene was half of the molecular weight obtained when TIBA was used as the cocatalyst (3.4×10^5 g/mol and 7.2×10^5 g/mol, respectively). **Figure 2.11** shows the structure of the silica supported metallocenes.

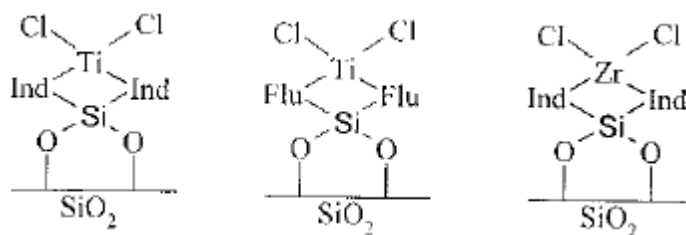


Figure 2.11 Structure of some silica supported metallocene catalysts [Soga *et al.*, 1994]

[Lee *et al.*, 1997] used spacer molecules in supporting metallocene catalysts onto silica to eliminate the steric hindrance near the active site caused by the silica surface (**Figure 2.12**).

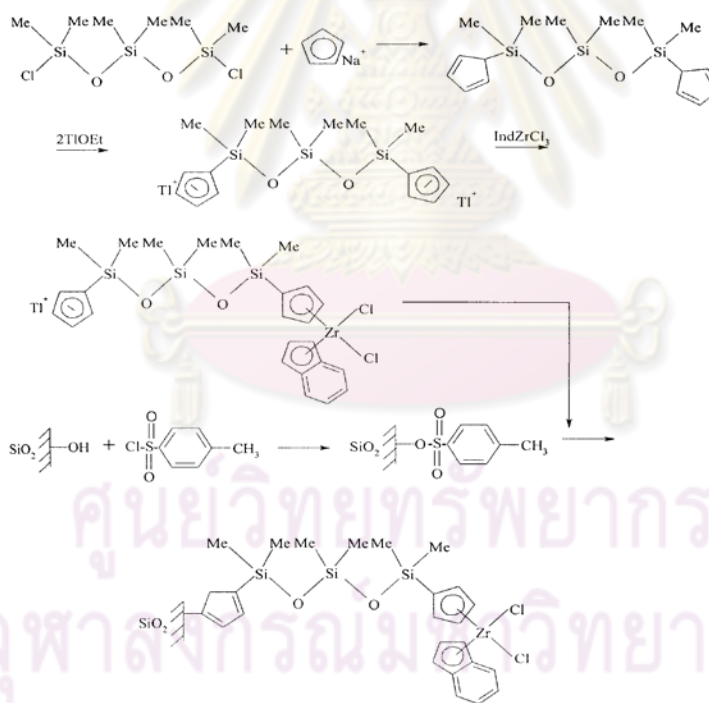


Figure 2.12 Mechanism for supporting metallocene catalysts on silica using spacer molecules [Lee *et al.*, 1995].

By distancing the active site from the silica surface, higher catalytic activities but lower polymer molecular weights were obtained in comparison with analogous silica-supported catalysts without spacer between silica and CpIndZrCl₂. [Iiskola *et al.*, 1997] treated the surface of partially dehydroxylated silica with a silane coupling agents, Cp(CH₂)₃Si(OCH₂CH₃)₃, and then immobilized CpZrCl₃ onto cyclopentadienyl surface formed on the silica to obtain a highly active catalyst (**Figure 2.13**) for ethylene polymerization in the presence of MAO. Depending on the calcination temperature and the modification methods, the catalysts show different activities and produced polymers with different molecular weights. In general, when compared to homogeneous Cp₂ZrCl₂ systems, all the supported catalysts showed lower activities, but the polymers produced had higher molecular weights. On the other hand, when compared to homogeneous Cp₂ZrCl₂ systems, the activities of the supported catalysts were similar but molecular weights of polymer produced were lower and depended on the silica surface modification method used. The polydispersity index of the polymers ranged from 2.2 to 2.8.

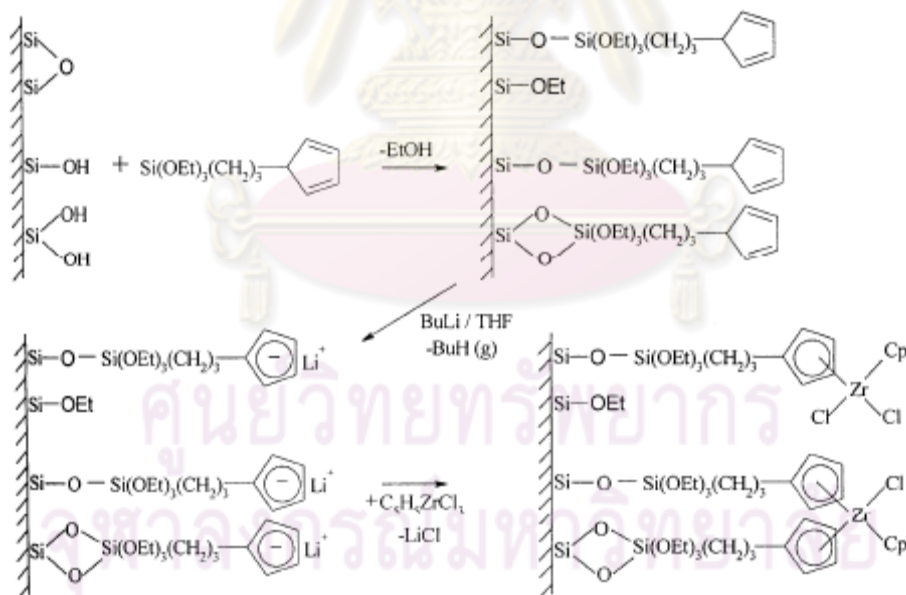


Figure 2.13 Modification of silica with Cp(CH₂)₃Si(OCH₂CH₃)₃ and preparation of supported metallocene catalysts [Iiskola *et al.*, 1997].

2.5.2.4. Supporting on other supports

The metallocene $n\text{-BuCp}_2\text{ZrCl}_2$ was grafted on partially dehydroxylated commercial silica Grace 948 whose surface had been chemically modified by wet impregnation of an organosilane Ph_3SiCl , Me_3SiCl , or Me_2SiHCl , aiming at supported catalyst systems with well spaced α -olefin polymerization active centers. These catalyst systems produced polyethylenes with narrow molecular weight distribution when methylaluminoxane was used as cocatalyst, with twice the activity of $n\text{BuCp}_2\text{ZrCl}_2$ supported on bare SiO_2 . [Joao *et al.*, 2000]

The effect of different catalyst support treatments in the 1-hexene/ethylene copolymerization with supported metallocene catalyst was investigated by [Soares *et al.*, 2004]. The catalysts in the study were supported catalysts containing SiO_2 , commercial MAO supported on silica (SMAO) and MAO pretreated silica (MAO/silica) with Cp_2HfCl_2 , $\text{Et}(\text{Ind})_2\text{HfCl}_2$, Cp_2ZrCl_2 and $\text{Et}(\text{Ind})_2\text{ZrCl}_2$. All the investigated supported catalysts showed good activities for the ethylene polymerization.

The silica-supported MAO was in situ- and ex situ immobilized with zirconocene catalyst to produce ethylene copolymers [Jongsomjit *et al.*, 2004]. The in situ catalytic system exhibited higher activities compared with the ex situ one. The ethylene/1-hexene (EH) copolymerization showed the highest activities for both catalytic systems. In addition, the in situ system resulted in narrow molar mass distributions (MMD) for all copolymers indicating a uniform catalytic site present.

Li *et al.* [1999] investigated nano-sized and micro-sized silica particles. The particles were used to support $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst for ethylene polymerization. Nano-sized catalyst exhibited much better ethylene polymerization activity than micro-sized catalyst. At the optimum temperature of 60°C , nano-sized catalyst's activity was 4.35 times the micro-sized catalyst's activity, which was attributed to the large specific external surface area, the absence of internal diffusion resistance, and the better active site dispersion for the nano-sized catalyst.

Jongsomjit *et al.* [2005] were investigated role of titania in $\text{TiO}_2\text{-SiO}_2$ mixed oxides-supported metallocene catalyst during ethylene/1-octene copolymerization. This study showed enhanced activities of ethylene/1-octene copolymerization via $\text{TiO}_2\text{-SiO}_2$ mixed oxides-

supported MAO with a zirconocene catalyst. It was proposed that titania was decorated on silica surface and acted as a spacer to anchor MAO to the silica support resulting in less steric hindrance and less interaction on the support surface.

The catalytic system methylaluminoxane (MAO) and $(n\text{-BuCp})_2\text{ZrCl}_2$ was immobilized on commercial silica, silica–alumina and aluminophosphate calcined at different temperatures [Grieken *et al.*, 2007]. Catalysts supported on silica–alumina exhibited higher polymerization activity than those supported on silica and aluminophosphate. Besides, the activity of MAO/ $(n\text{BuCp})_2\text{ZrCl}_2$ catalytic system supported on silica–alumina and aluminophosphate decreased strongly with support calcination temperature, while remained almost constant when silica was employed as support. All these experimental features suggest a role of the support acid properties and hydroxyl group population in the generation of active polymerization species.

The use of silica and zirconia as a support for zirconocene/MAO catalyst for copolymerization of ethylene/1-olefin (1-hexene, 1-octene, and 1-decene) was investigated [Jongsomjit *et al.*, 2008]. It was found that the use of zirconia support showed promising activities compared to those of the silica. Increased activities can be attributed to higher amount of $[\text{Al}]_{\text{MAO}}$ present on the zirconia support coupled with strong interaction between the $\text{O}_{\text{support}}\text{--Al}_{\text{cocatalyst}}$ linkage.

2.5.2.5 Effect of gallium modified supports

Petre *et al.* [2002] investigated the effect of boria, gallia and india loadings on the surface acidities of $\text{Al}_2\text{O}_3\text{--M}_2\text{O}_3$ ($\text{M}=\text{B}, \text{Ga}, \text{In}$). In the case of $\text{Al}_2\text{O}_3\text{--Ga}_2\text{O}_3$, they were also found that the addition of Ga_2O_3 on alumina caused a decrease in the acidity of alumina and did not affect markedly the basicity, while depositing indium oxide on alumina decreased both the acidity and basicity. Moreover, alumina-supported Ga_2O_3 and In_2O_3 samples displayed a well-preserved amphoteric character.

Mathew *et al.* [2005] synthesized $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxides by sol–gel method on catalytic performances for steam reforming of dimethyl ether (DME). They suggested that Ga_2O_3 significantly affected the catalytic performance with respect to the DME conversion and H_2 yield. In addition, the catalytic activity increased with the gallium concentration in $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxides. It was very interesting that without the aid of an additional transition metal component, Ga_2O_3 and $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide system exhibited good activity in the reforming reaction.

Takahashi *et al.* [2006] synthesized $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions with aluminum isopropoxide and gallium acetylacetonate as precursor using glycothermal method. They were found that the reaction with a higher $\text{Al}/(\text{Ga}+\text{Al})$ charged ratio yielded the glycol derivative of boehmite as a by-product and increasing in the Al content in the solid solution increased the surface area and the thermal stability of the solid solution. The oxides system exhibited extremely high catalytic activity for selective catalytic reduction of NO_x with methane as a reducing agent. Moreover, the solid solution showed high durability under steaming conditions.



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CHAPTER III

EXPERIMENTAL

3.1 Objectives of the Thesis

The objective of this research is to investigate the effect of gallium-modified silica supported metallocene catalyst for ethylene/1-octene copolymerization was investigated. Besides the influence of Ga modification, the alternative method for in situ impregnation of MMAO on the modified support was also conducted. The comparative study between the conventional (ex situ) and in situ impregnation is further discussed.

3.2 Scopes of the Thesis

1. Preparation of Ga-modified silica supports with various weight ratio (0.2, 1%)
2. Preparation of modified-SiO₂ (LP) supports by impregnation with dried methylaluminoxane (dMMAO).
3. Study and characterization for the effects of Ga modification and impregnation method with zirconocene catalyst on catalytic and polymer properties during ethylene and ethylene/1-octene polymerization.
4. Study and characterization for the effects of Ga modification and different pore sizes support via in situ impregnation method with zirconocene catalyst on catalytic and polymer properties

3.3 Research Methodology

The flow diagram research methodology is shown in **Figure 3.1**.

All reactions were conducted under argon atmosphere using schlenk techniques and glove box.

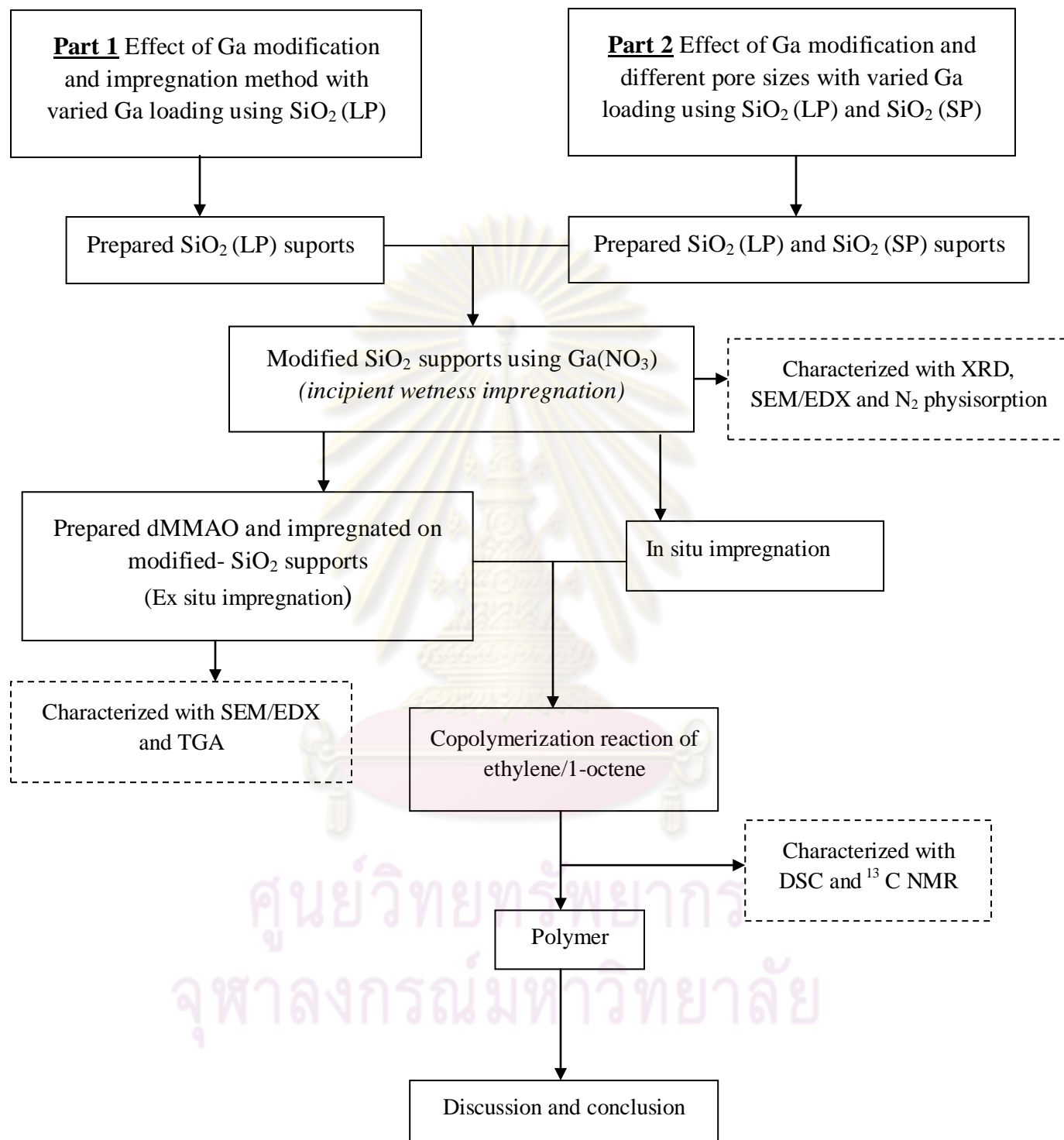


Figure 3.1 Flow diagram of research methodology

3.4 Experimental

3.4.1 Chemicals

The chemicals used in these experiments were analytical grade, but only major materials are specified as follows:

1. Silica gel from Fuji Silysia Chemical Ltd., Japan (Cariact Q-50) was calcined at 400 °C for 6 hours under vacuum.
2. Silica gel from Fuji Silysia Chemical Ltd., Japan (Cariact P-10) was calcined at 400 °C for 6 hours under vacuum.
3. Aluminium nitrate was purchased from Aldrich Chemical Company, Inc. and use as received
4. Polyethylene glycol (average mol wt. 200) was purchased from Aldrich Chemical Company, Inc. and use as received
5. Modified Methylaluminoxane (MMAO) 5.6% wt in hexane was donated from Tosoh Akso, Japan and used without further purification.
6. rac-Ethylenebis(indenyl)zirconium dichloride ($\text{Et(Ind)}_2\text{ZrCl}_2$) was supplied from Aldrich Chemical Company, Inc. and used without further purification.
7. Trimethylaluminum $[\text{Al}(\text{CH}_3)_3]$ 2.0 M in toluene was supplied from Nippon Aluminum Alkyls Ltd., Japan and used without further purification.
8. Ethylene gas (99.96%) was devoted from National Petrochemical Co., Ltd., Thailand and used as received.
9. Ultra high purity argon gas (99.999%) was purchased from Thai Industrial Gas Co., Ltd., and further purified by passing through columns packed with molecular sieve 3 A, BASF Catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentoxide (P_2O_5) to remove traces of oxygen and moisture.
10. Toluene was devoted from EXXON Chemical Ltd., Thailand. This solvent was dried over dehydrated CaCl_2 and distilled over sodium/benzophenone under argon atmosphere before use.
11. 1-Hexene (99%) was purchased from Aldrich Chemical Company, Inc. and purified by distilling over sodium under argon atmosphere before use.

12. 1-Octene (98%) was purchased from Aldrich Chemical Company, Inc. and used as received.

13. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma.

14. Methanol (Commercial grade) was purchased from SR lab.

3.4.2 Equipments

Due to the metallocene system is extremely sensitive to the oxygen and moisture. Thus, the special equipments were required to handle while the preparation and polymerization process. For example, glove box: equipped with the oxygen and moisture protection system was used to produce the inert atmosphere. Schlenk techniques (Vacuum and Purge with inert gas) are the others set of the equipment used to handle air-sensitive product.

3.4.2.1 Cooling system

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

3.4.2.2 Inert gas supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve 3×10^{-10} m to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at 300°C overnight before flowing the argon gas through all the above columns. The inert gas supply system is shown in **Figure 3.2**.

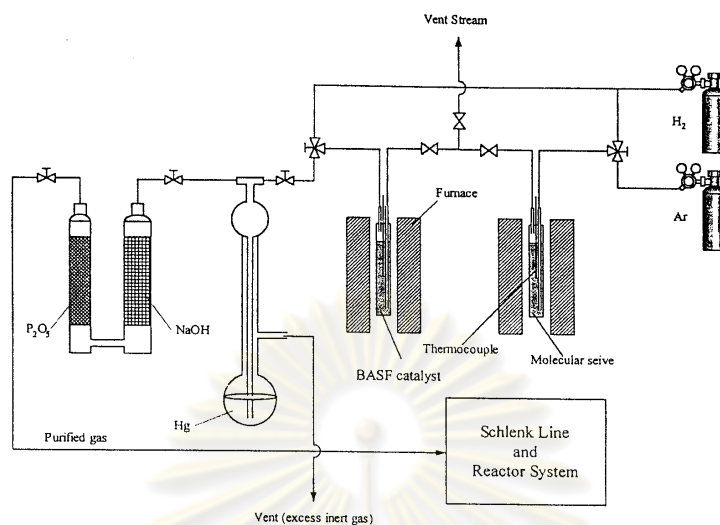


Figure 3.2 Inert gas supply system

3.4.2.3 Magnetic stirrer and heater

The magnetic stirrer and heater model RTC basis from IKA Labortechnik were used.

3.4.2.4 Reactor

A 100 ml glass flask connected with 3-ways valve was used as the copolymerization reactor for atmospheric pressure system and a 100 ml stainless steel autoclave was used as the copolymerization reactor for high pressure systems.

3.4.2.5 Schlenk line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with the trap and the mercury bubbler that was a manometer tube and contains enough mercury to provide a seal from the atmosphere when argon line was evacuated. The Schlenk line was shown in **Figure 3.3**.

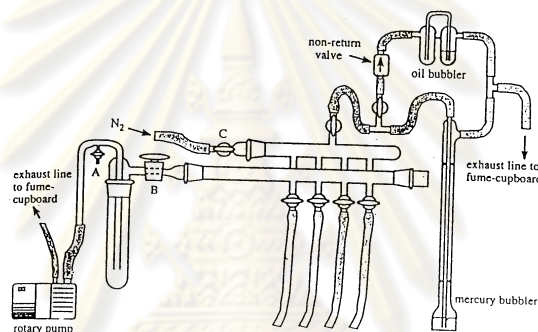


Figure 3.3 Schlenk line

3.4.2.6 Schlenk tube

A tube with a ground glass joint and side arm, which was three-way glass valve as shown in **Figure 3.4**. Sizes of Schlenk tubes were 50, 100 and 200 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture.

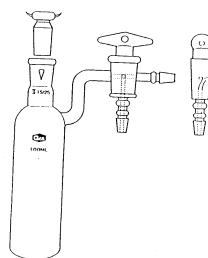


Figure 3.4 Schlenk tube

3.4.2.7 Vacuum pump

The vacuum pump model 195 from Labconco Corporation was used. A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

3.4.2.8 Polymerization line

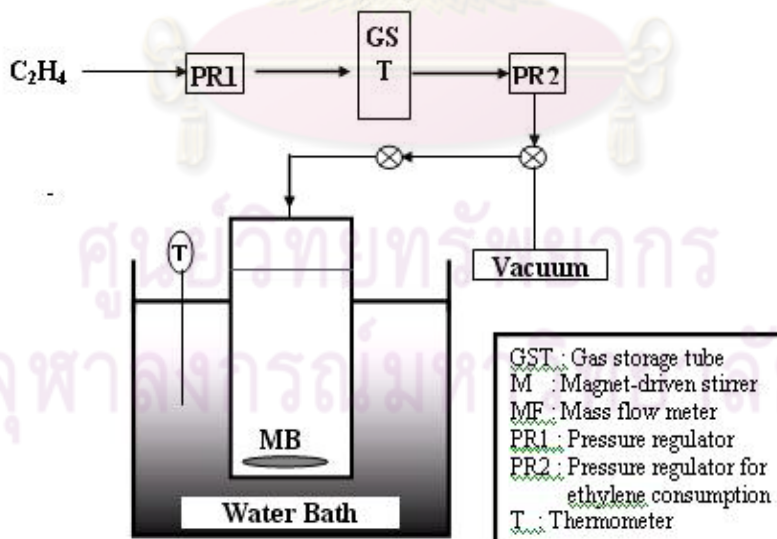


Figure 3.5 Diagram of system in slurry phase polymerization

3.4.3 Supporting Procedure

3.4.3.1 Preparation of gallium-modified silica supports

The gallium modification on the silica supports were prepared by the incipient-wetness impregnation method according to the procedure described previously [Jongsomjit *et al.*, 2008]. The Ga source in this case was $\text{Ga}(\text{NO}_3)_3$. Gallium was impregnated into silica gel (Cariact Q-50, P-10) with 0.2 and 1 wt % of Ga. The support was dried in oven at 110°C for 12 h and calcined in air at 500°C for 2 h.

3.4.3.2 Preparation of dried-MMAO (dMMAO)

Removal of TMA from MMAO was carried out according to the reported procedure [Hagimoto *et al.* 2004]. The toluene solution of MMAO was dried under vacuum for 6 h at room temperature to evaporate the solvent, TMA, and $\text{Al}(\text{iBu})_3$ (TIBA). Then, continue to dissolve with 100 ml of heptane and the solution was evaporated under vacuum to remove the remaining TMA and TIBA. This procedure was repeated 6-8 times and the white powder of dried MMAO (dMMAO) was obtained.

3.4.3.3 Preparation of MMAO/Modified support

1. Ex situ impregnation method

MMAO-modified silica was prepared by impregnating 0.1g of thermally treated silica (LP) (at 400°C under vacuum for 4 h) with the desired amount of dMMAO in 10 ml toluene at room temperature for 30 min. The solid part was separated and washed once with 20 ml of toluene and 3 times with 20 ml hexane, followed by drying in vacuum at room temperature. The white powder of supported cocatalyst (dMMAO/support) was then obtained.

2. In situ impregnation method and polymerization

0.2 g of the Ga-modified silica supports is allowed to contact with 1.14 ml of MMAO for 30 min, in reactor with magnetic stirring. After this period of time, the suspension was mixed with desired amount of zirconocene and TMA ($[Al]_{TMA}/[Zr]_{cat} = 1135$). Then toluene (to make a total volume of 30 ml) was introduced in to reactor. The reactor was frozen in liquid nitrogen to stop reaction and then 0.018 mol of 1-octene was injected into the reactor. The reactor was evacuated to remove argon. Then, it was heated up to polymerization temperature (70°C) and the polymerization was started by feeding ethylene gas (total pressure 50 psi in the reactor) until the consumption of ethylene at 0.018 mol (6 psi was observed from the pressure gauge) was reached. The reaction of polymerization was completely terminated by addition of acidic methanol. The time of reaction was recorded for purpose of calculating the activity. The precipitated polymer was washed with methanol and dried at room temperature.

3.4.4 Polymerization on the support with Ex situ impregnation

The ethylene/1-octene copolymerization reaction was performed in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. In the glove box, the desired amounts of *rac*-Et[Ind]₂ZrCl₂ and TMA were mixed and stirred for 5 min for aging. Then, toluene (to make a total volume of 30 ml) and 0.2 g of dMMAO/support were introduced into the reactor. After that, the mixture of *rac*-Et[Ind]₂ZrCl₂ (5×10^{-5} M) and TMA (3.75×10^{-3} mole corresponding to $[Al]_{TMA}/[Zr]_{cat} = 1135$) was mixed and stirred for 5 min aging at room temperature, separately, then were injected into the reactor. After this point, the similar procedure as mentioned in 2 was conducted.

3.4.5 Characterization of supports and catalyst precursor

3.4.5.1 N₂ physisorption

Measurement of BET surface area, average pore diameter and pore size distribution of silica support were determined by N₂ physisorption using a Micromeritics ASAP 2000 automated system.

3.4.5.2 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of sample. It was conducted using a SIEMENS D-5000 X-ray diffractometer with CuK_α($\lambda = 1.54439 \times 10^{-10}$ m). The spectra were scanned at a rate 2.4 degree/min in the range $2\theta = 20-80$ degrees.

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

SEM and EDX were used to determine the morphologies and elemental distribution throughout the sample granules, respectively. The SEM of JEOL mode JSM-6400 was applied. The EDX was performed using Link Isis series 300 program.

3.4.5.4 Thermogravimetric analysis (TGA)

TGA was performed to determine the interaction force of the supported dMMAO. It was conducted using TA Instruments SDT Q 600 analyzer. The samples of 10-20 mg and a temperature ramping from 25 to 600°C at 2 °C /min were used in the operation. The carrier gas was N₂ UHP.



Figure 3.6 Thermogravimetry

3.4.6 Characterization Method of Polymer

3.4.6.1 Differential scanning calorimetry (DSC)

The melting temperature of polymer products was determined with thermal analysis measurement. It was performed using a Perkin-Elmer DSC P7 calorimeter. The DSC measurements reported here were recorded during the second heating/cooling cycle with the rate of $20^{\circ}\text{C min}^{-1}$. This procedure ensured that the previous thermal history was erased and provided comparable conditions for all samples. Approximately 10 mg of sample was used for each DSC measurement.

3.4.6.2 ^{13}C NMR spectroscopy (^{13}C NMR)

^{13}C NMR spectroscopy was used to determine the α -olefin incorporation and copolymer microstructure. Chemical shift were referenced internally to the benzene-d₆ and calculated according to the method described by Randall [80]. Sample solution was prepared by dissolving 50 mg of copolymer in 1,2,4-trichlorobenzene and benzene-d₆. ^{13}C NMR spectra were taken at 60°C using BRUKER A400 operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

CHAPTER IV

RESULTS AND DISCUSSIONS

PART 1: Effect of Ga modification and impregnation method on SiO₂ (LP)-supported metallocene catalyst during ethylene/1-octene copolymerization

In this part, the catalytic activity during ethylene/1-octene copolymerization of Ga-modified SiO₂ (LP)-supported metallocene catalyst was investigated. In fact, the large pore SiO₂ support was prepared, and then sequentially modified with Ga having approximately 0.2 and 1.0 wt% of Ga in the support, named as, SiO₂-Ga-0.2% and SiO₂-Ga-1.0% respectively. The Ga-modified SiO₂ supports were then characterized using N₂ physisorption, XRD and SEM/EDX.

4.1 Characterization of supports and supported dMMAO

4.1.1 Characterization of supports with N₂ physisorption

The Ga- modified silica supports having different surface areas, such as SiO₂ and silica modified with Ga (SiO₂-Ga-0.2%, SiO₂-Ga-1.0%) were characterized before impregnation with dMMAO. It was observed that the SiO₂ support denoted as SiO₂ having the surface area of 70.9 m²/g was obtained as seen in **Table 4.1**. However, the surface area of Ga-modified silica supports is in the range of 68-70 m²/g as shown in **Table 4.1**. It can be observed that after modification with Ga, we obtained only little decrease of surface area.

Table 4.1 BET surface areas of Ga-modified silica supports with different Ga loading

Support	BET surface area (m ² /g)	Pore volume (cm ³)
SiO ₂	70.9	0.26
SiO ₂ -Ga -0.2%	70.6	0.25
SiO ₂ -Ga - 1.0%	68.8	0.23

4.1.2 Characterization of supports and catalyst precursors with x-ray diffraction (XRD)

The supports with various weight ratio of gallium were characterized before impregnation with dMMAO. The XRD patterns of these supports are shown in **Figure 4.1**. It can be seen that all supports exhibited the similar XRD patterns indicating only a broad peak between 20-30° as seen typically for the conventional amorphous silica. After modification with 0.2, 1.0 wt% of gallium, the support still exhibited the similar XRD patterns as seen for the unmodified one. It indicated that gallium was in the highly dispersed form or low amount of gallium, which was invisible by XRD.

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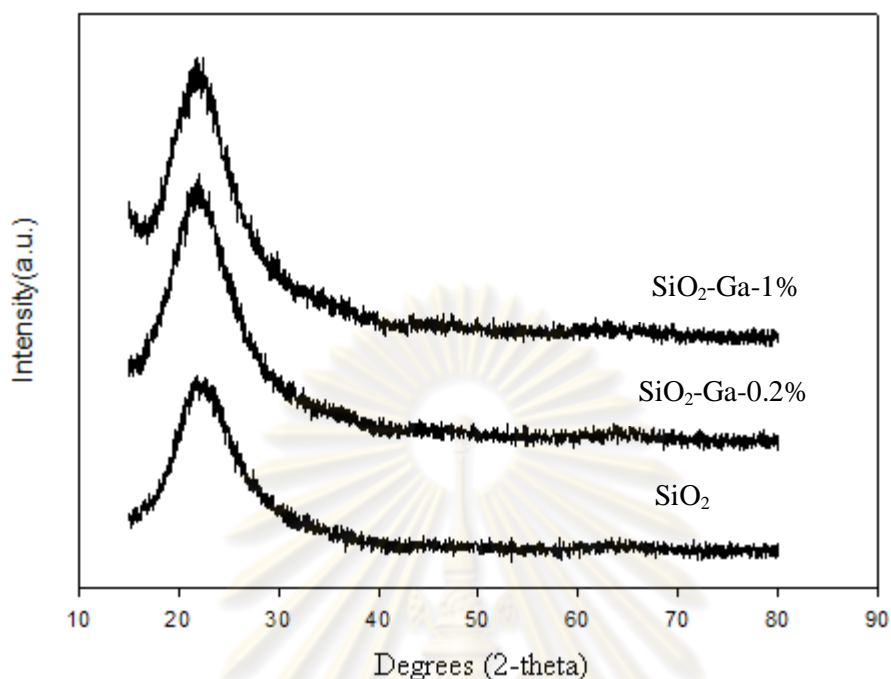


Figure 4.1 XRD patterns of different Ga-modified silica supports with different Ga loading

4.1.3 Characterization of supports and supported dMMAO with scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDX)

In order to determine the morphologies of the supports and elemental distributions of the supports after impregnation, SEM and EDX were performed, respectively. The SEM micrographs of various Ga-modified silica supports before impregnation with dMMAO are shown in **Figure 4.2**. The EDX mapping of the supports can provide more information about the distribution of elements on each supports and also used to determine the concentrations of $[Al]_{dMMAO}$ present on supports after impregnation. The EDX spectrum obtained is shown in **Figure 4.3** indicating good distribution of dMMAO. It was found that the average amount of $[Al]_{dMMAO}$ on were SiO_2 , SiO_2 -Ga -0.2% and SiO_2 -Ga -1.0% are 13.1, 15.2 and 17.7%, respectively as shown in **Figure 4.4**. The largest amount of $[Al]_{dMMAO}$ present in the SiO_2 -Ga-1.0% can be probably attributed to increased adsorption ability of dMMAO with Ga modification.

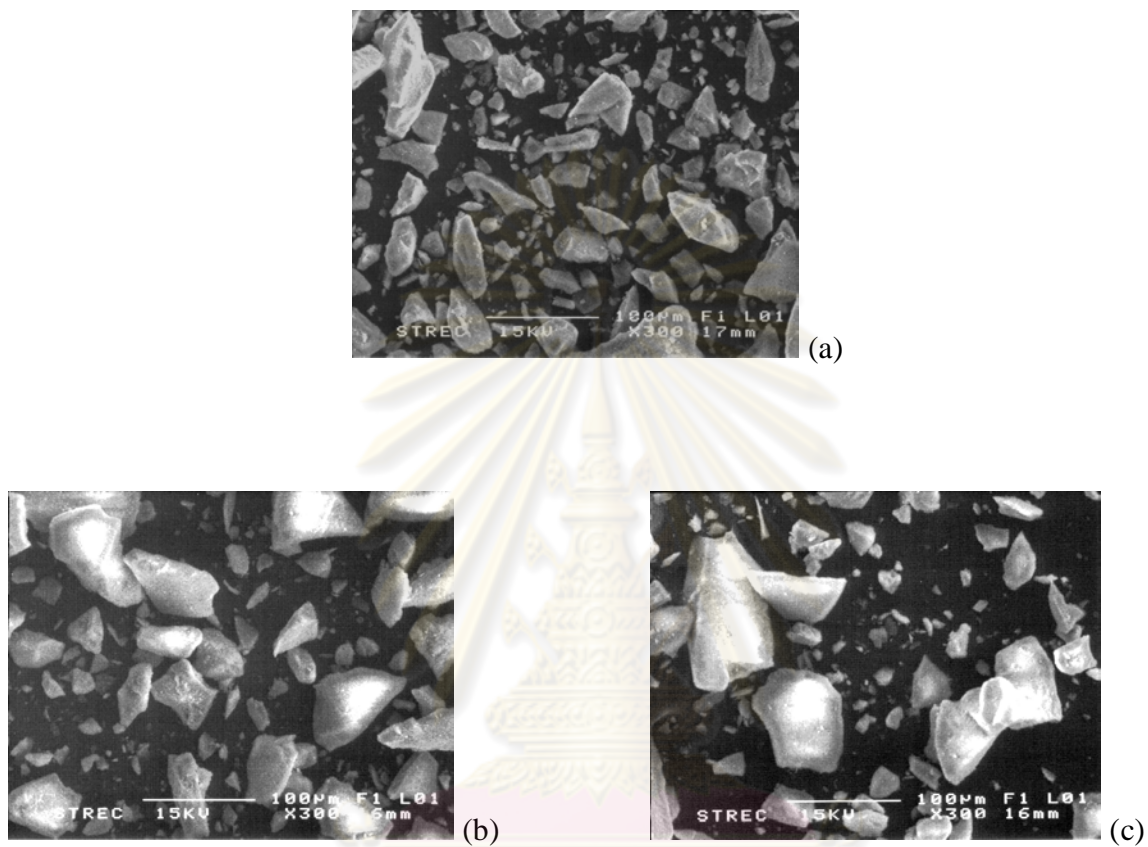


Figure 4.2 SEM micrograph of Ga-modified silica supports before dMMAO impregnation;

(a) SiO_2 (b) SiO_2 -Ga -0.2% (c) SiO_2 -Ga -1.0%

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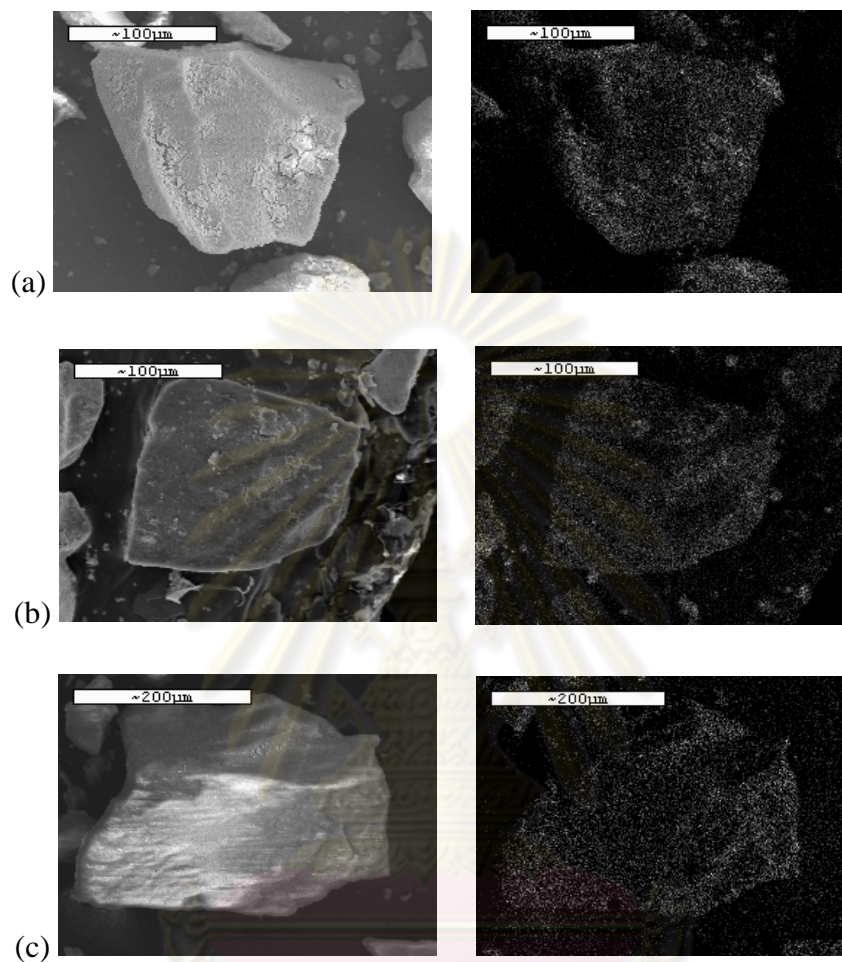
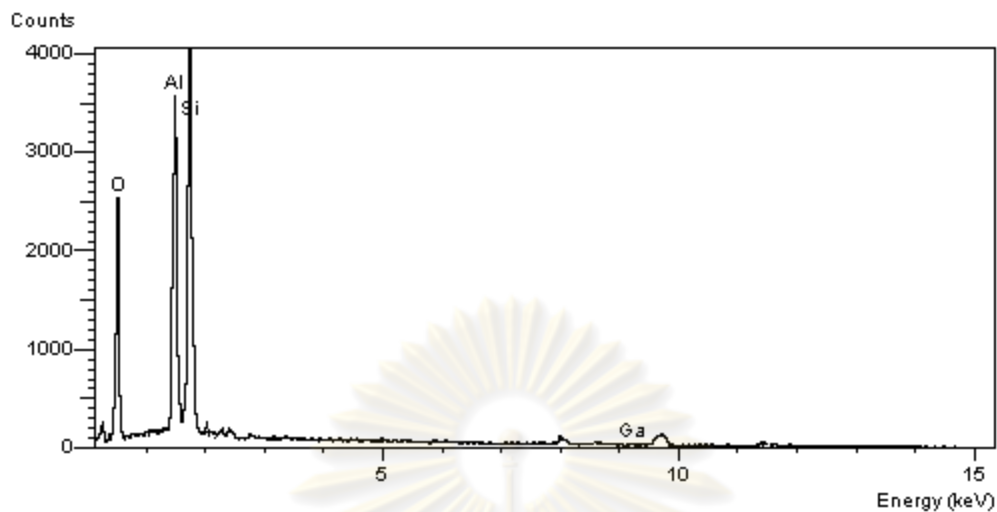


Figure 4.3 SEM/EDX mapping for Al distribution on Ga-modified silica supports with ex situ impregnation method (a) SiO_2 (b) SiO_2 -Ga -0.2% (c) SiO_2 -Ga -1.0%

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Catalyst precursor	[Al] _{dMMAO} (wt%) on the support
dMMAO/ SiO ₂	13.1
dMMAO/ SiO ₂ -Ga- 0.2%	15.2
dMMAO/ SiO ₂ -Ga- 1.0%	17.7

Figure 4.4 A typical spectrums of the supported/MMAO from EDX analysis used to measure the average [Al]_{dMMAO} concentration on Ga-modified silica supports with ex situ method

4.1.4 Characterization of supports and supported dMMAO with thermogravimetric analysis (TGA)

In order to identify the interaction of $[Al]_{dMMAO}$ on various modified supports. The TGA measurement was performed to prove the degree of interaction between the support and the cocatalyst (dMMAO). The TGA provide information on the degree of interaction for dMMAO bound to the supports in term of weight loss and removal temperature. The TGA profiles of $[Al]_{dMMAO}$ on various supports are shown in **Figure 4.5**. It was observed that the weight loss of $[Al]_{dMMAO}$ present on various supports were in the order of $SiO_2-Ga-1.0\% > SiO_2-Ga-0.2\% > SiO_2$. This indicated that $[Al]_{dMMAO}$ present on SiO_2 had the strongest interaction among other supports. The decomposition temperatures at 10% weight loss ($T_d 10\%$) were 420, 205 and 178 °C for SiO_2 , $SiO_2-Ga-0.2\%$ and $SiO_2-Ga-1.0\%$.

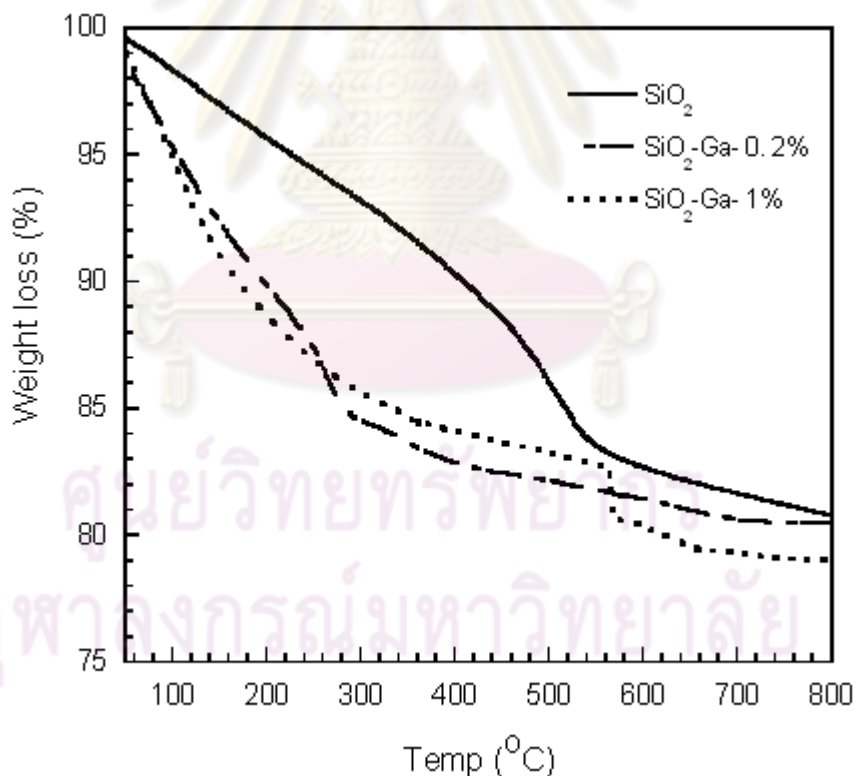


Figure 4.5 TGA profiles of supported dMMAO on different supports

4.2 Characteristics and catalytic properties of ethylene/1-octene copolymerization

4.2.1 The effect of Ga modification on the catalytic activity

Table 4.2 Catalytic activities of Ga modification and impregnation method during ethylene/1-octene copolymerization

Samples	Impregnation method ^a	Polymerization yield (g)	Polymerization times (s)	Catalytic Activity ^b (kg of pol /mol Zr h)
Homogeneous	n.a.	1.486	130	27,433 ^c
	n.a.	1.534	123	29,803 ^d
SiO ₂	EI	1.225	184	15,978 ^c
	II	1.495	88	40,405 ^d
SiO ₂ -Ga -0.2%	EI	1.298	176	17,700 ^c
	II	1.666	90	44,426 ^d
SiO ₂ -Ga -1.0%	EI	1.375	162	20,370 ^c
	II	1.756	76	55,329 ^d

^a EI: Ex situ, II: in situ

^b Activities were measured at polymerization temperature of 70°C, [ethylene] = 0.018 mole, [1-octene] = 0.018 mole, [Al]_{MMAO} / [Zr]_{cat} = 1135, [Al]_{TMA} / [Zr]_{cat} = 2500, in toluene with total volume = 30 ml and [Zr]_{cat} = 5 × 10⁻⁵ M.

^c with dMMAO ^d with MMAO

The effect of Ga modification on ethylene/1-octene copolymerization was investigated. Both in situ and ex situ impregnation were observed to exhibit increases in activity with Ga modification and impregnation method increased amount of Ga as shown in **Table 4.2**. It was proposed that Ga possibly acts as a spacer group to anchor metallocene catalyst and support and limit the disadvantages of highly attachment. Moreover, an addition of Ga into support can increase Lewis acid centers in the system, which can interact with zirconocene. As a result there are more active species for polymerization. In order to give a better understanding, the effect of Ga in polymerization activity can be proposed based on the work reported by Joao *et al.* [2008]. They revealed that the introduction of Ga, even in small amounts, strongly improves the ability of these supports to immobilize metallocene catalysts. The interaction between zirconocene and the Lewis acid centers derived from the introduction of Ga in the support seems to play an important role in the formation of the active species and the optimization of Ga of the MCM-41 support. It is possible to prepare heterogeneous metallocene catalysts that exhibit high polymerization activity.

4.2.2 The effect of impregnation method on the catalytic activity

Table 4.2 presents the impregnation method for each support and the corresponding polymerization activities. It can be seen that for the in situ impregnation method of Ga-modified silica support, the activity is higher than that of the ex situ method. This can be explained as the following; (i) for the ex situ method, partial MMAO can reach into the pore of support and lead to loss of active species. Thus, the 1-octene co monomer cannot adsorb on active site present in the pore, and (ii) for the in situ method, MMAO can be present in the bulk, which differs from the ex situ one that is only present inside the support. This makes, the in situ impregnation similar to homogeneous system, and hence enhances the polymerization activity. Moreover, by comparison of different systems for the in situ method, the heterogeneous gives better activity than the homogeneous one due to the following reasons; (i) the heterogeneous system exhibits higher bulk density than homogeneous system. Good bulk density can improve distribution of active site. In addition, it can reduce reactor fouling, which is resulted from the adhesion polymer to the reactor [Koltzenburg *et al.*, 1997]., and (ii) the SiO₂ support might

prohibit the formation of $ZrCH_2CH_2Zr$ species, which is formed via bimolecular process and minimize steric hindrance effect of the system. Therefore, ethylene/1-octene can adsorb on active site easier.

4.2.3 The effect of various supports on the melting temperatures of copolymers

The melting temperatures (T_m) of copolymer evaluated by the differential scanning calorimeter (DSC) are shown in **Table 4.3**. DSC curves of the copolymer are also shown in Appendix B.

Table 4.3 Melting temperatures of copolymers obtained different SiO_2 -based supports

System	Impregnation method	T_m ($^{\circ}C$)	Crystallinity (%)
Homogeneous	EI	n.o.	n.o.
	II	n.o.	n.o.
SiO_2	EI	n.o.	n.o.
	II	n.o.	n.o.
SiO_2 -Ga-0.2%	EI	n.o.	n.o.
	II	n.o.	n.o.
SiO_2 -Ga- 1.0%	EI	n.o.	n.o.
	II	n.o.	n.o.

n.o. refers to not observe

From the characterization of copolymer in **Table 4.3**, it revealed that no melting temperature was found indicating non-crystalline polymer produced in this specified polymerization system. The non-crystalline polymers were attributed to the high degree of 1-octene insertion, which can be confirmed by ^{13}C NMR.

4.2.4 The effect of various supports on the incorporation of copolymers

The quantitative analysis of triad distribution for all copolymers was conducted on the basis assignment of the ^{13}C NMR spectra of ethylene/1-octene (EO) copolymer and calculated according to the method of Randall *et al.* [1989]. The characteristics of ^{13}C NMR spectra (as shown in appendix C) for all copolymers were similar indicating the copolymer of ethylene/1-octene. The triad distribution of all polymers is shown in **Table 4.4**. Ethylene incorporation in all systems gave copolymers with similar triad distribution. No triblock of OOO in the copolymers was found. Only the random copolymers can be produced in all systems. It showed that Ga modification trended to slightly increase % octene incorporation.

Table 4.4 ^{13}C NMR analysis of ethylene/1-octene copolymer

System	Impregnation method	Triad distribution of copolymer						1-octene insertion (mol %)
		OOO	EOO	EOE	EEE	OEO	OEE	
Homogeneous	EI	0.000	0.100	0.146	0.481	0.045	0.228	25
	II	0.000	0.237	0.077	0.468	0.092	0.126	31
SiO_2	EI	0.000	0.025	0.107	0.700	0.012	0.156	14
	II	0.020	0.214	0.034	0.486	0.118	0.128	27
SiO_2 -Ga-0.2%	EI	0.000	0.113	0.136	0.519	0.053	0.179	25
	II	0.022	0.238	0.031	0.408	0.145	0.156	29
SiO_2 -Ga-1.0%	EI	0.000	0.105	0.135	0.488	0.041	0.236	24
	II	0.000	0.195	0.019	0.477	0.218	0.091	21

E refers to ethylene monomer and O refers to 1-octene comonomer

PART 2: The effect of Ga-modified silica-supported zirconocene /MMAO catalyst via in situ impregnation on the different pore sizes of silica supports

In this part, the catalytic activity during ethylene/1-octene copolymerization of Ga-modified silica-supported zirconocene /MMAO catalyst via in situ impregnation on the different pore sizes of silica supports was investigated. In fact, the silica supports employed were in both large pore and small pore, then sequentially Ga having approximately 0.2 and 1.0 wt% of Ga in the support was produced, named as SiO₂(LP) , SiO₂(LP)-Ga-0.2% and SiO₂(LP)-Ga-1.0% for large pore silica and SiO₂(SP) , SiO₂(SP)-Ga-0.2% and SiO₂(SP)-Ga-1% for small pore silica, respectively. The Ga-modified silica supports were, then characterized using N₂ physisorption, XRD and SEM.

4.3 Characterization of supports

4.3.1 Characterization of supports with N₂ physisorption

The Ga-modified silica supports having different surface areas, such as SiO₂ (LP), SiO₂ (SP) and silica modified with gallium were characterized. It was observed that SiO₂ (LP) having the surface of 70.9 m²/g was obtained as seen in **Table 4.5**. In the same way, SiO₂ (SP) exhibited the surface of 216.8 m²/g. As seen, BET surface areas of SiO₂ (LP) supports were smaller than SiO₂ (SP) support. However, the surface area of Ga-modified silica supports for both large and small pore silica decreased upon increasing the amounts of Ga loading.

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Table 4.5 BET surface areas of Ga-modified silica supports with different Ga loading

Support	BET surface area (m ² /g)
SiO ₂ (LP)	70.9
SiO ₂ (LP) - Ga-0.2%	70.6
SiO ₂ (LP) -Ga-1.0%	68.8
SiO ₂ (SP)	216.8
SiO ₂ (SP) -Ga- 0.2%	176.7
SiO ₂ (SP) -Ga- 1.0%	169.7

4.3.2 Characterization of supports with X-ray diffraction (XRD)

The various supports with different pore structure were characterized. The XRD patterns of supports with different pore structure are shown in **Figure 4.6 and 4.7**. With Ga modification, the silica supports for both large pore and small pore exhibited the similar of XRD peaks between 20-30°. The characteristic peaks associated with Ga were not found due to low amount of Ga or Ga was highly dispersed on silica.

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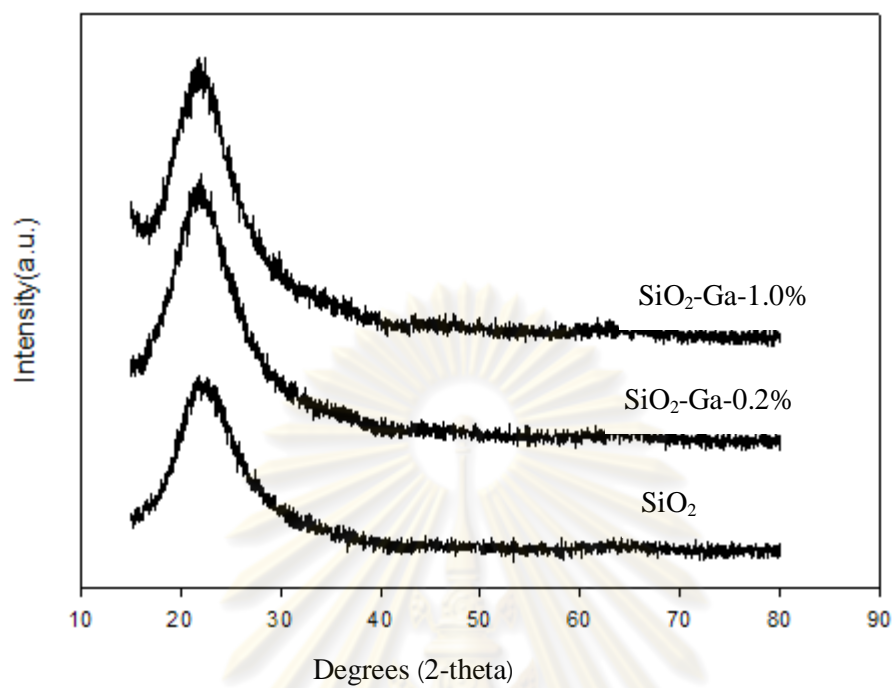


Figure 4.6 XRD patterns of different Ga-modified silica (LP) supports with different Ga loading

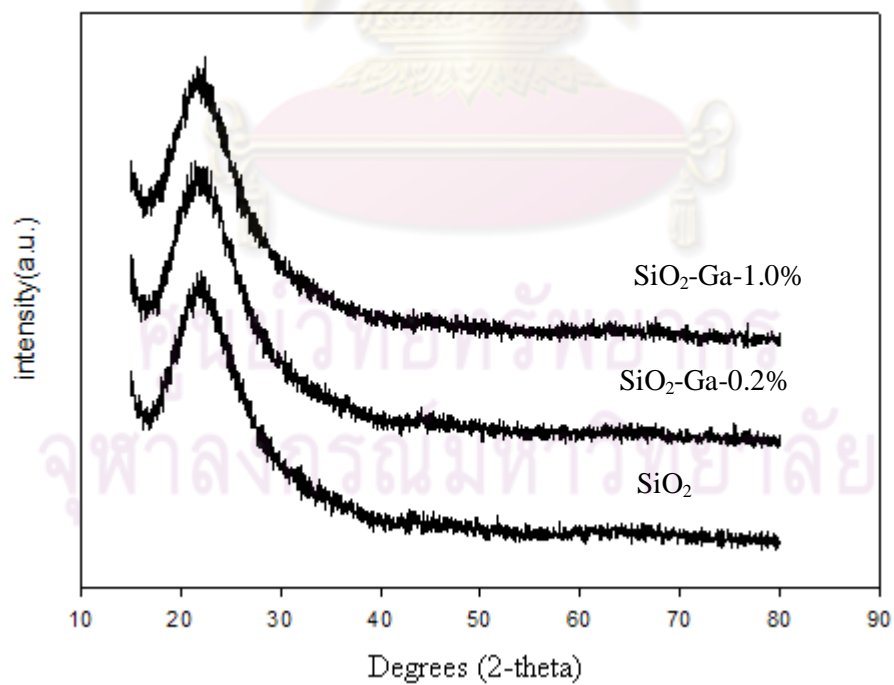


Figure 4.7 XRD patterns of different Ga-modified silica (SP) supports with different Ga loading

4.3.3 Characterization of supports with scanning electron microscope (SEM)

Scanning electron microscopy was also used to determine the morphology of SiO_2 . **Figure 4.8** is the SEM micrograph of large pore SiO_2 and **Figure 4.9** is the SEM micrograph of small pore SiO_2 . The image reveals that the SiO_2 (SP) particles have the spheroidal structure.

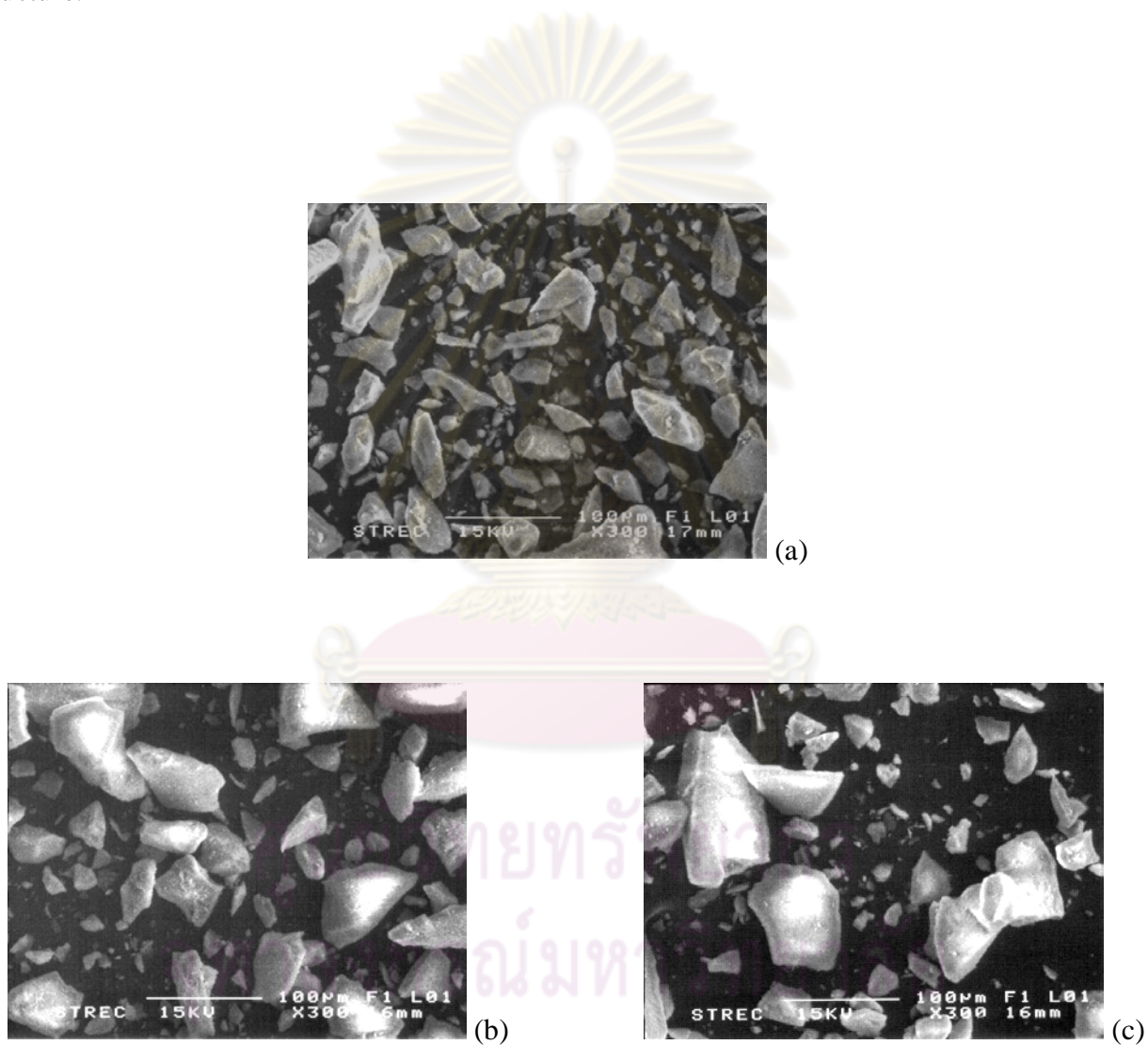


Figure 4.8 SEM micrograph of Ga-modified silica (LP) supports with different Ga loading;

(a) SiO_2 (LP), (b) SiO_2 (LP) - Ga- 0.2%, (c) SiO_2 (LP) - Ga- 1.0%

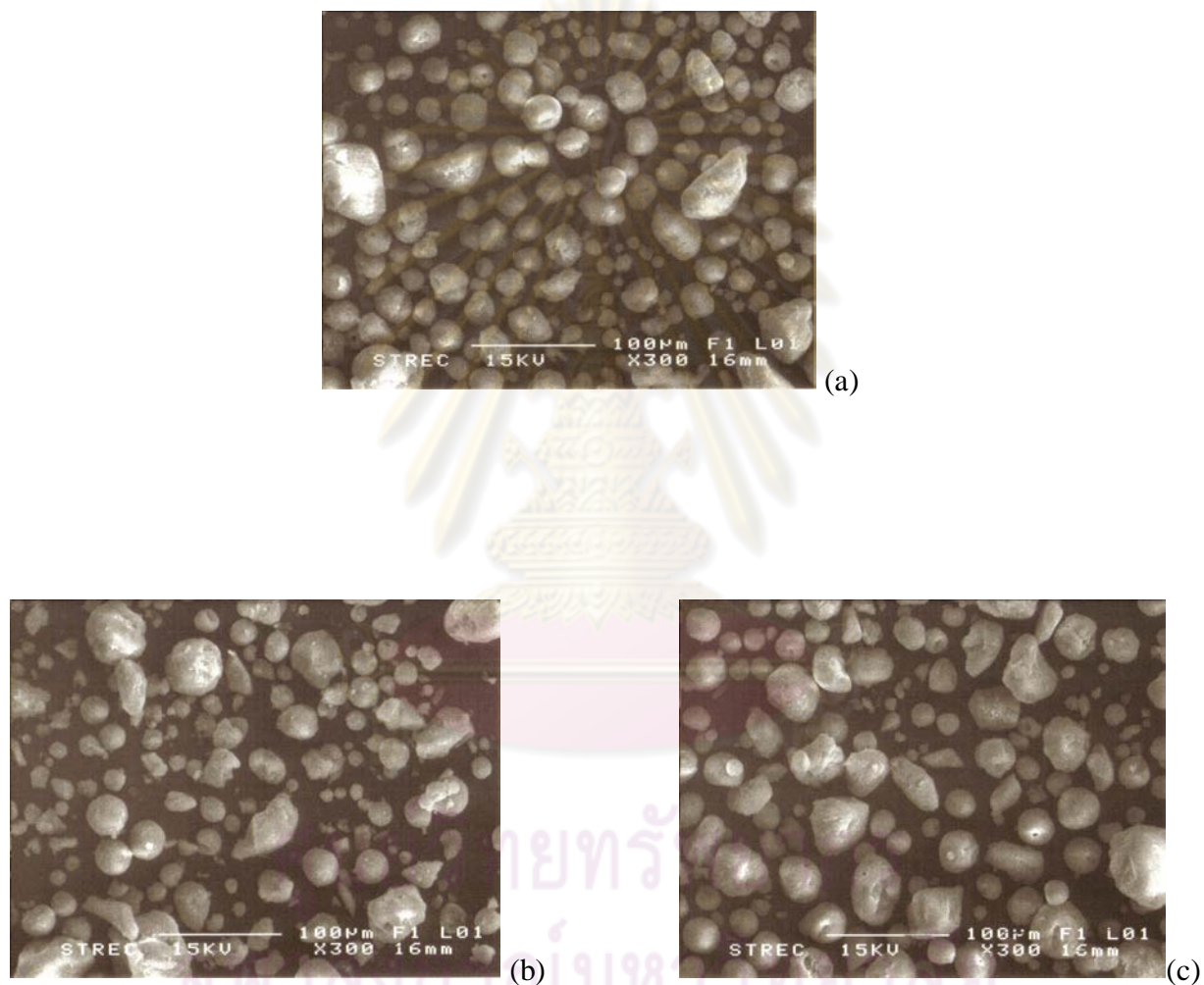


Figure 4.9 SEM micrograph of Ga-modified silica (SP) supports with different Ga loading;

(a) SiO_2 (SP), (b) SiO_2 (SP) -Ga- 0.2%, (c) SiO_2 (SP) -Ga-1.0%

4.4 Characteristics and catalytic properties of ethylene/1-octene copolymerization

4.4.1 The effect of Ga-modified silica supports with the different pore sizes via in situ impregnation method on the catalytic activity

Table 4.6 Catalytic activities of various silica-supported zirconocene/MMAO catalyst via in situ impregnation method

Samples	Polymerization ^a	Polymerization	Catalytic Activity ^b (kg of pol /molZr h)
	Yield (g)	times (s)	
Homogeneous	1.534	123	29,803
SiO ₂ (LP)	1.495	88	40,405
SiO ₂ (LP) -Ga-0.2%	1.666	90	44,426
SiO ₂ (LP) -Ga- 1.0%	1.756	76	55,329
SiO ₂ (SP)	1.798	80	53,411
SiO ₂ (SP) -Ga- 0.2%	1.989	74	64,708
SiO ₂ (SP) -Ga- 1.0%	2.036	74	66,214

^a The polymer yield was fixed [limited by ethylene fed and 1-octene used (0.018 mole equally)].

^b Activities were measured at polymerization temperature of 70 °C , [ethylene]= 0.018 mole, [1-octene]= 0.018 mole, [Al]_{MMAO}/[Zr] = 1135, [Al]_{TMA}/[Zr] = 2500, in toluene with total volume = 30 ml, and [Zr]= 5x10⁻⁵ M

The ethylene/1-octene copolymerization with *rac*-Et[Ind]₂ZrCl₂ catalyst was performed for a comparative study of the catalytic activities derived from different supports. The activities of catalyst using various supports are listed in **Table 4.6**. It was obvious that, for the support with both large and small pore, the presence of Ga increased the catalytic activity as already mentioned in 4.2.1. For the Ga-modified silica (LP) support, the polymerization activities were lower than Ga-modified silica (SP) support because MMAO cocatalyst can reach into its pore , leading to lower MMAO present in bulk and lesser of active species. Therefore, catalytic activity decreased. On the contrary, MMAO can extend into the pore in lower content when using silica small pore. This makes MMAO remain highly in the bulk and hence enhance the activity of polymerization. Considering, the polymerization activity of supported metallocene system, it was higher than homogeneous system as explained in 4.2.2. This result was due to higher bulk density and more distribution of active sites in heterogeneous system.



4.4.2 The effect of various supports on the melting temperatures of copolymers

The melting temperatures (T_m) of copolymer evaluated by the differential scanning calorimeter (DSC) are shown in **Table 4.7**. DSC curves of the copolymer are also shown in Appendix B.

Table 4.7 Melting temperatures of copolymers obtained different SiO₂-based supports

System	T_m (°C)	Crystallinity (%)
Homogeneous	n.o.	n.o.
SiO ₂ (LP)	n.o.	n.o.
SiO ₂ (LP) – 0.2%	n.o.	n.o.
SiO ₂ (LP) – 1.0%	n.o.	n.o.
SiO ₂ (SP)	n.o.	n.o.
SiO ₂ (SP) – 0.2%	n.o.	n.o.
SiO ₂ (SP) – 1.0%	n.o.	n.o.

n.o. refers to not observe

From the characterization of copolymer in **Table 4.7**, it revealed that no melting temperature was found indicating non-crystalline polymer produced in this specified polymerization system. The non-crystalline polymers were attributed to the high degree of 1-octene insertion, which can be confirmed by ¹³C NMR.

4.4.3 The effect of various supports on the incorporation of copolymers

The quantitative analysis of triad distribution for all copolymers was conducted on the basis assignment of the ^{13}C NMR spectra of ethylene/1-octene (EO) copolymer and calculated according to the method of Randall *et al.* [1989]. The characteristics of ^{13}C NMR spectra (as shown in appendix C) for all copolymers were similar indicating the copolymer of ethylene/1-octene. The triad distribution of all polymers is shown in **Table 4.8**. It revealed that Ga modification did not cause specific effects over 1-octene insertion via in situ impregnation method. Moreover, by comparison of different pore sizes, large pore SiO_2 gives higher insertion than small pore SiO_2 due to 1-octene can extend into the pore in higher content when using silica large pore and minimize steric hindrance effect [Shan *et al.*, 2002].

Table 4.8 ^{13}C NMR analysis of ethylene/1-octene copolymer

System	Triad distribution of copolymer						1-octene insertion (mol %)
	OOO	EOO	EOE	EEE	OEO	OEE	
Homogeneous	0.000	0.237	0.077	0.468	0.092	0.126	31
SiO_2 (LP)	0.020	0.214	0.034	0.486	0.118	0.128	27
SiO_2 (LP) – 0.2%	0.022	0.238	0.031	0.408	0.145	0.156	29
SiO_2 (LP) – 1.0%	0.000	0.195	0.019	0.477	0.218	0.091	21
SiO_2 (SP)	0.000	0.203	0.034	0.482	0.180	0.101	24
SiO_2 (SP) – 0.2%	0.000	0.197	0.036	0.452	0.216	0.099	23
SiO_2 (SP) – 1.0%	0.000	0.180	0.026	0.516	0.192	0.086	21

E refers to ethylene monomer and O refers to 1-octene comonomer

CHAPTER V

CONCLUSIONS & RECOMMENDATIONS

5.1 CONCLUSIONS

The ethylene/1-octene copolymerization using silica supports with Ga modification was studied and divided into two parts: *part 1* studied the effect of Ga modification and impregnation method on silica supported metallocene catalyst during ethylene/1-octene copolymerization with varied Ga loading and *part 2* investigated the effect of Ga modification on silica-supported metallocene catalyst via in situ impregnation on the different pore sizes of silica supports and the amounts of Ga loading were also varied.

For the first part, this research showed that the activities for both in situ and ex situ impregnation increased with Ga modification. It was proposed that an addition of Ga into support can increase Lewis acid centers in the system, which can interact with zirconocene. As a result, there are more active species for polymerization. Ethylene/1-octene copolymerization under the in situ impregnation exhibited more catalytic activity than the ex situ method. This was due to the in situ method has good bulk density and no adhesion of polymer to the reactor.

In the second part, the copolymerization of Ga-modified SiO₂ support having small pore and large pore as the supports via in situ impregnation method was investigated. It was found that the catalytic activity of the small pore silica was higher than that of the large pore system due to MMAO can extend into the pore in lower content when using silica small pore. This makes MMAO remain highly in the external surface and hence enhance the activity of polymerization.

RECOMMENDATIONS

- Investigation of other supports should be further studied.
- Investigation of other modifier should be further studied.

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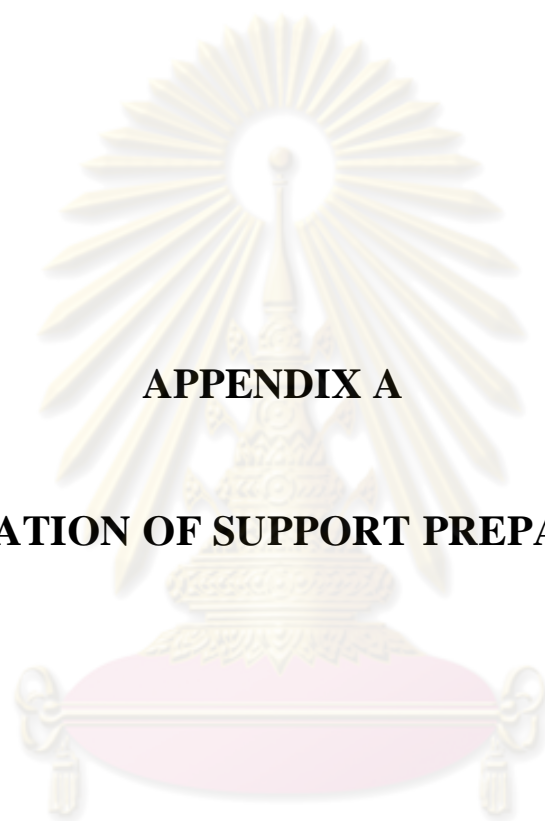


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APPENDICES

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APPENDIX A

(CALCULATION OF SUPPORT PREPARATION)

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A.1 Calculation of support composition (Ga-Modified SiO₂)

Calculation of gallium loading

Preparation of 0.2%Ga-modified SiO₂ by the incipient wetness impregnation method are shown as follows:

Reagent: - Gallium (III) nitrate hydrate Ga(NO₃)₃
 Molecular weight = 255.74 g/mol
 - Support: - large pore SiO₂, small pore SiO₂

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

Gallium = 0.2 g
 Silica = 100-0.2 = 99.8 g

For 1 g of SiO₂ support

Gallium required = $1 \times (0.2/99.8) = 0.002$ g

Gallium 0.002 g was prepared from Ga(NO₃)₃ and molecular weight of Ga is 69.72

$$\begin{aligned} \text{Ga(NO}_3)_3 \text{ required} &= \frac{\text{MW of Ga(NO}_3)_3 \times \text{gallium required}}{\text{MW of Ga}} \\ &= (255.74/69.72) \times 0.002 = 0.0073 \text{ g} \end{aligned}$$

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Preparation of 1%Ga-modified SiO₂ by the incipient wetness impregnation method are shown as follows:

Reagent: - Gallium (III) nitrate hydrate Ga(NO₃)₃
 Molecular weight = 255.74 g/mol
 - Support: - large pore SiO₂, small pore SiO₂

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

Gallium = 1.0 g
 Silica = 100-1.0 = 99 g

For 1 g of SiO₂ support

Gallium required = $1 \times (1/99)$ = 0.010 g

Gallium 0.010 g was prepared from Ga(NO₃)₃ and molecular weight of Ga is 69.72

$$\begin{aligned} \text{Ga(NO}_3)_3 \text{ required} &= \frac{\text{MW of Ga(NO}_3)_3 \times \text{gallium required}}{\text{MW of Ga}} \\ &= (255.74/69.72) \times 0.010 = 0.0367 \text{ g} \end{aligned}$$

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APPENDIX B
(NUCLEAR MAGNETIC RESONANCE)

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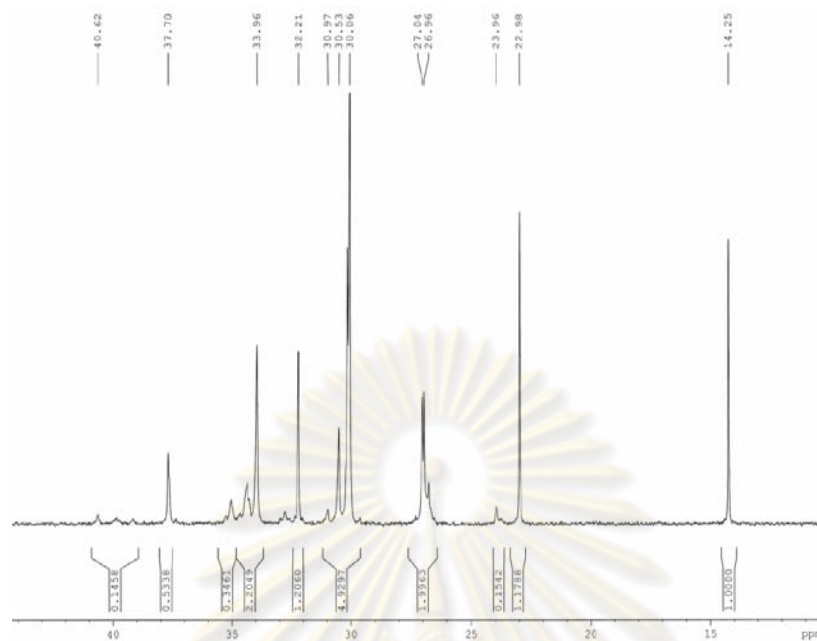


Figure B-1 ^{13}C NMR spectrum of ethylene/1-octene copolymer produces with homogenous via ex situ impregnation

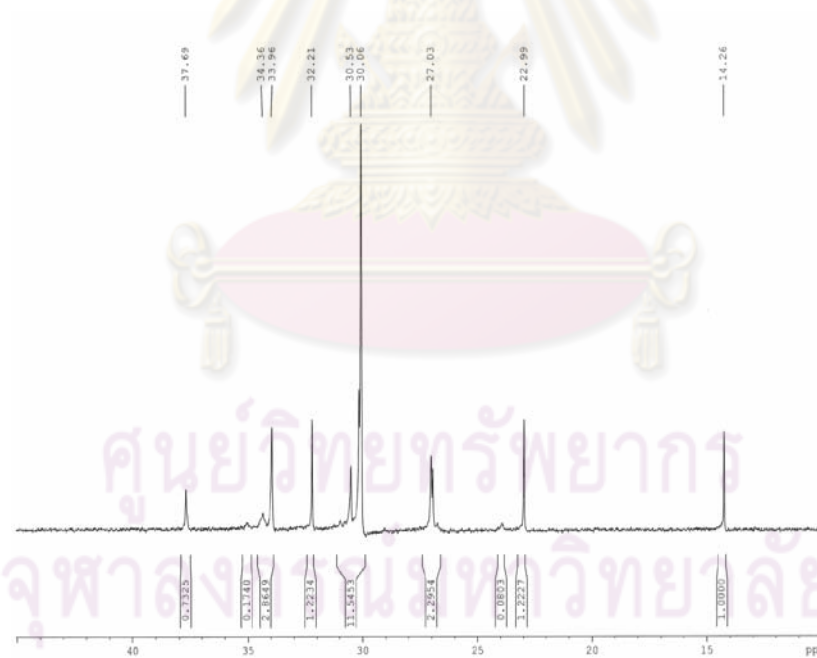


Figure B-2 ^{13}C NMR spectrum of ethylene/1-octene copolymer produces with SiO_2 (LP) via ex situ impregnation

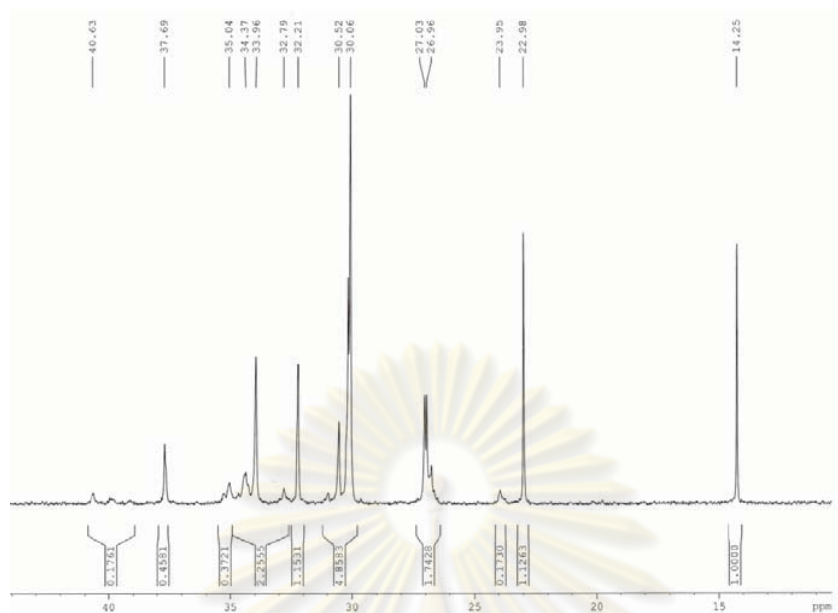


Figure B-3 ^{13}C NMR spectrum of ethylene/1-octene copolymer produces with $\text{SiO}_2(\text{LP})$ - 0.2% via ex situ impregnation

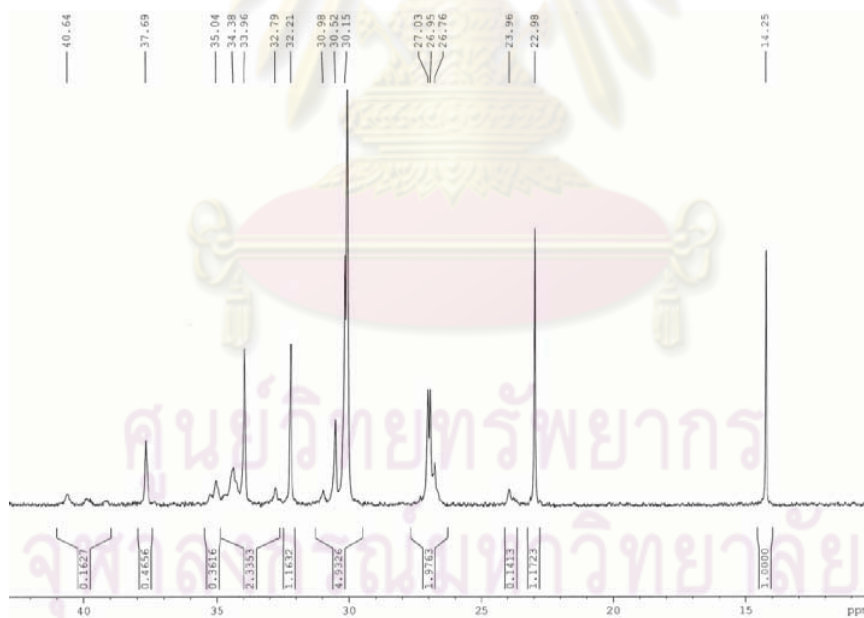


Figure B-4 ^{13}C NMR spectrum of ethylene/1-octene copolymer produces with $\text{SiO}_2(\text{LP})$ - 1% via ex situ impregnation

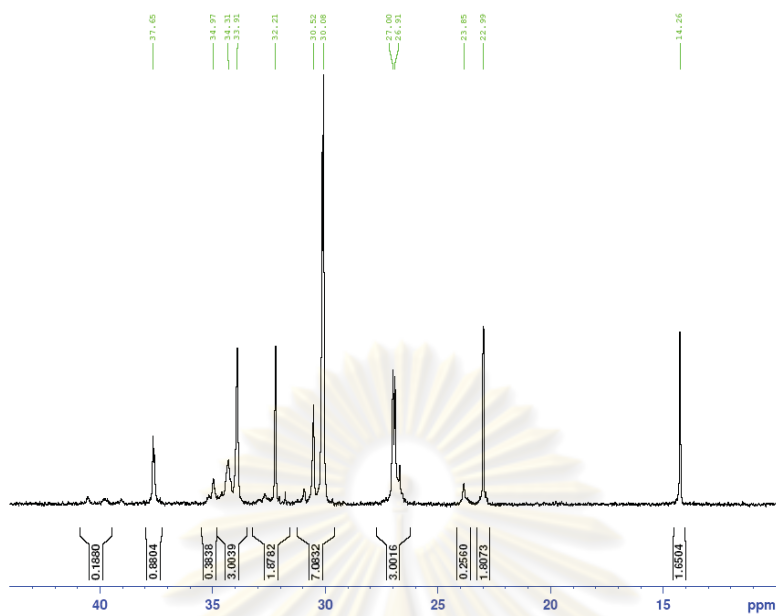


Figure B-5 ^{13}C NMR spectrum of ethylene/1-octene copolymer produces with homogenous via in situ impregnation

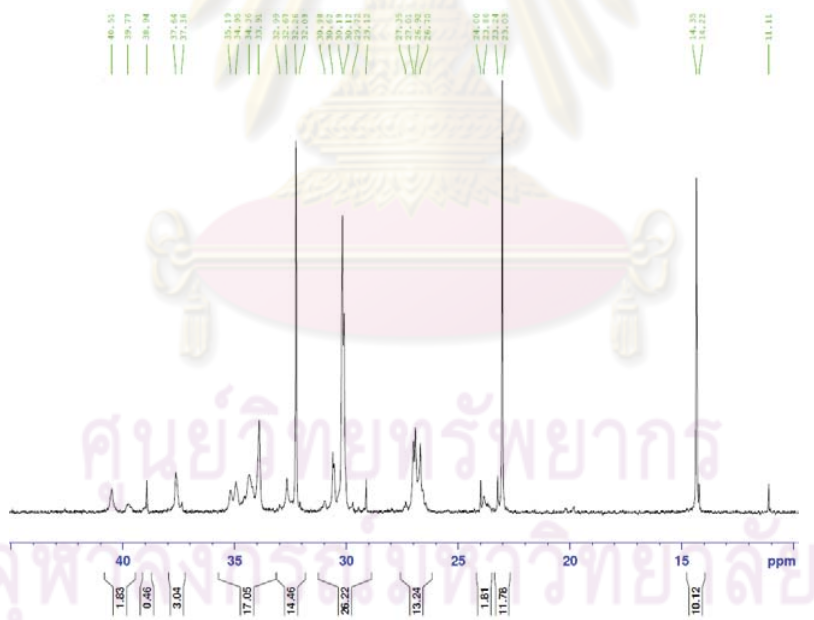


Figure B-6 ^{13}C NMR spectrum of ethylene/1-octene copolymer produces with SiO_2 (LP) via in situ impregnation

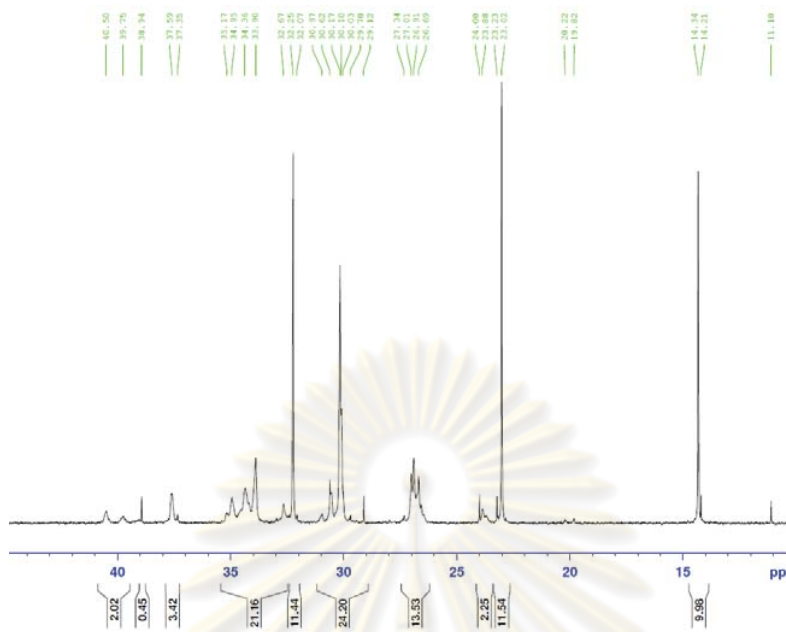


Figure B-7 ^{13}C NMR spectrum of ethylene/1-octene copolymer produces with SiO_2 (LP)-0.2% via in situ impregnation

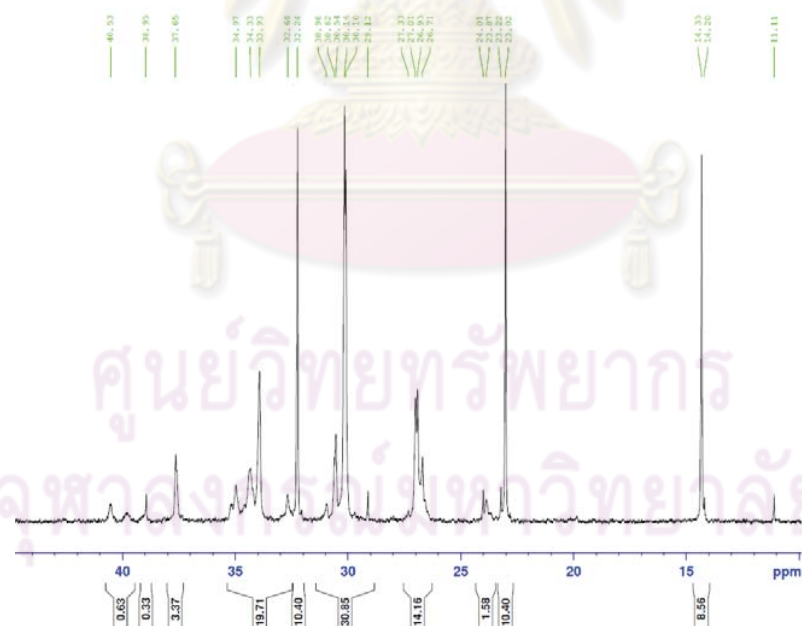


Figure B-8 ^{13}C NMR spectrum of ethylene/1-octene copolymer produces with SiO_2 (LP)-1% via in situ impregnation

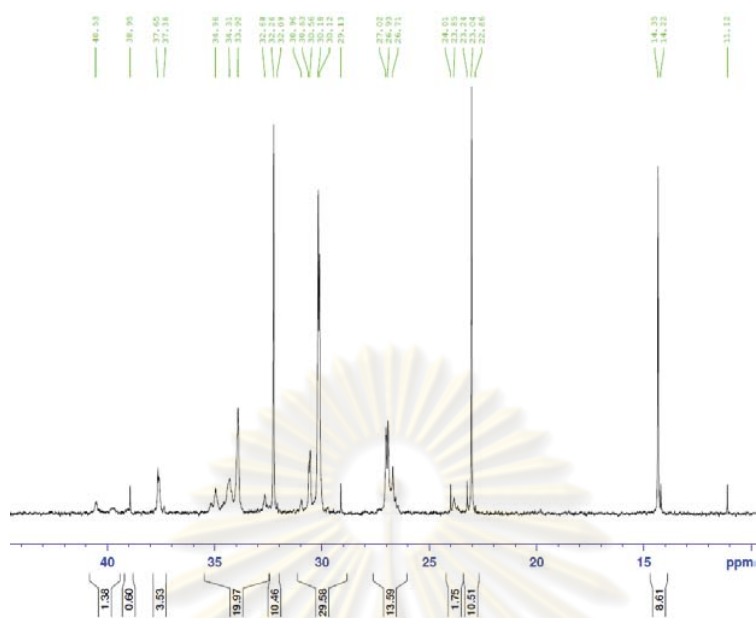


Figure B-9 ¹³C NMR spectrum of ethylene/1-octene copolymer produced with SiO₂ (SP) via in situ impregnation

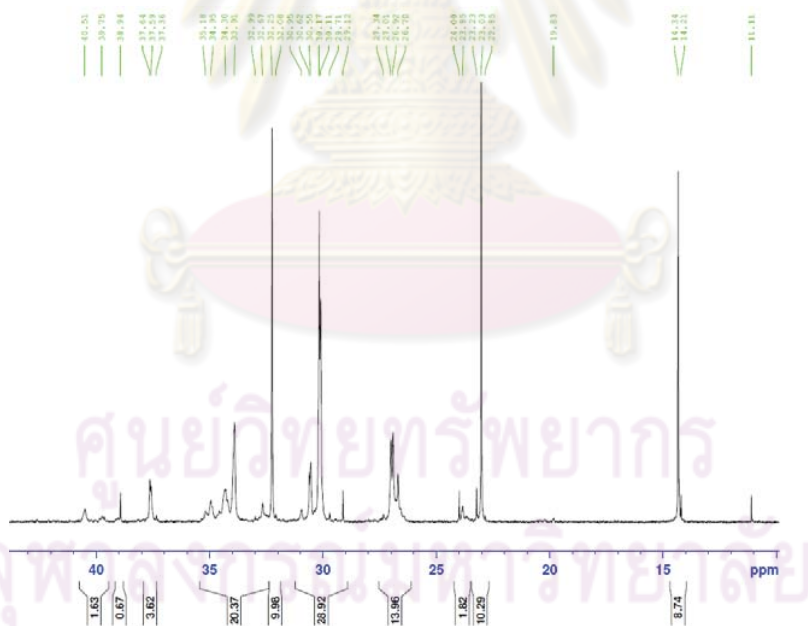


Figure B-10 ¹³C NMR spectrum of ethylene/1-octene copolymer produced with SiO₂ (SP)-0.2% via in situ impregnation

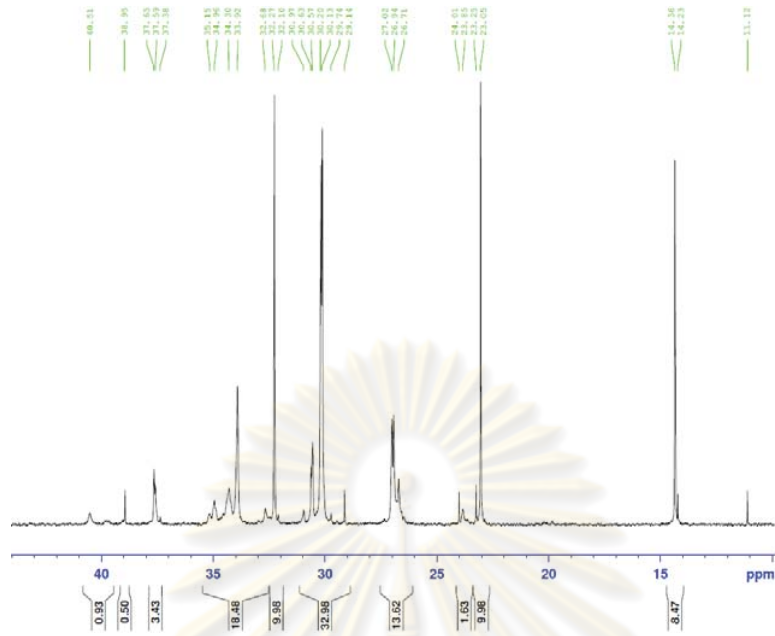


Figure B-11 ^{13}C NMR spectrum of ethylene/1-octene copolymer produced with SiO_2 (SP)-1% via in situ impregnation

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APPENDIX C
(DIFFERENTIAL SCANNING CALORIMETER)

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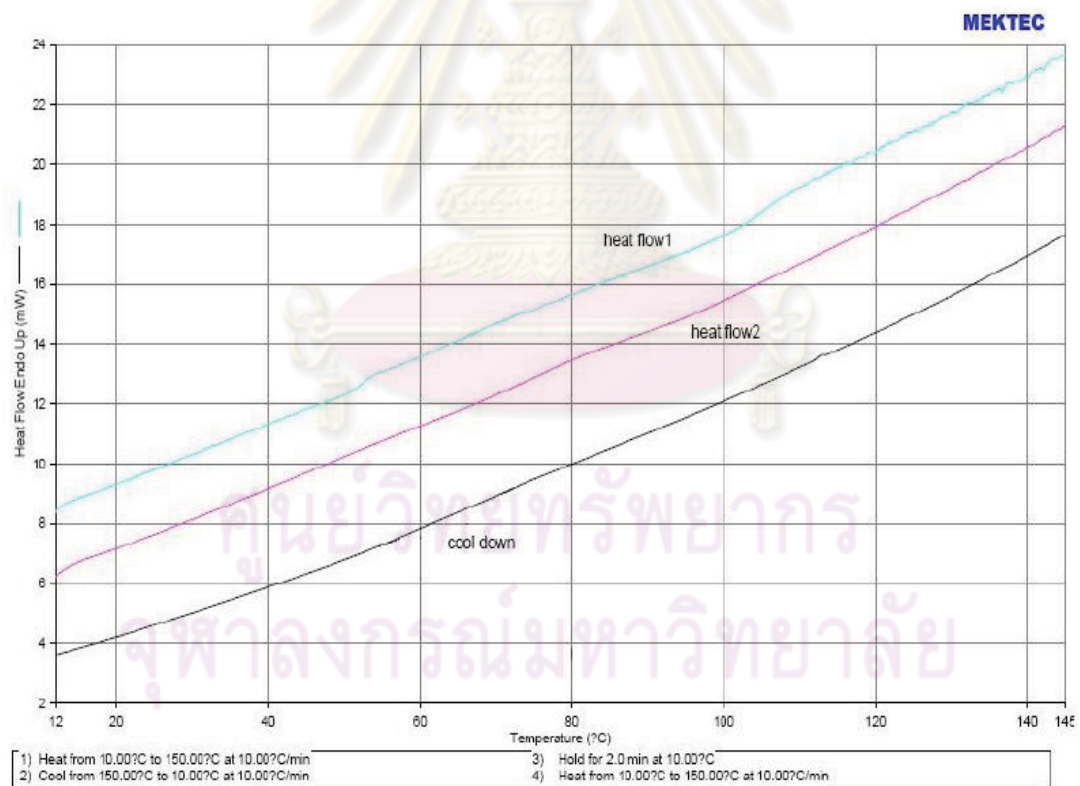


Figure C-1 DSC curve of ethylene/1-octene copolymer produce with homogenous via ex situ impregnation

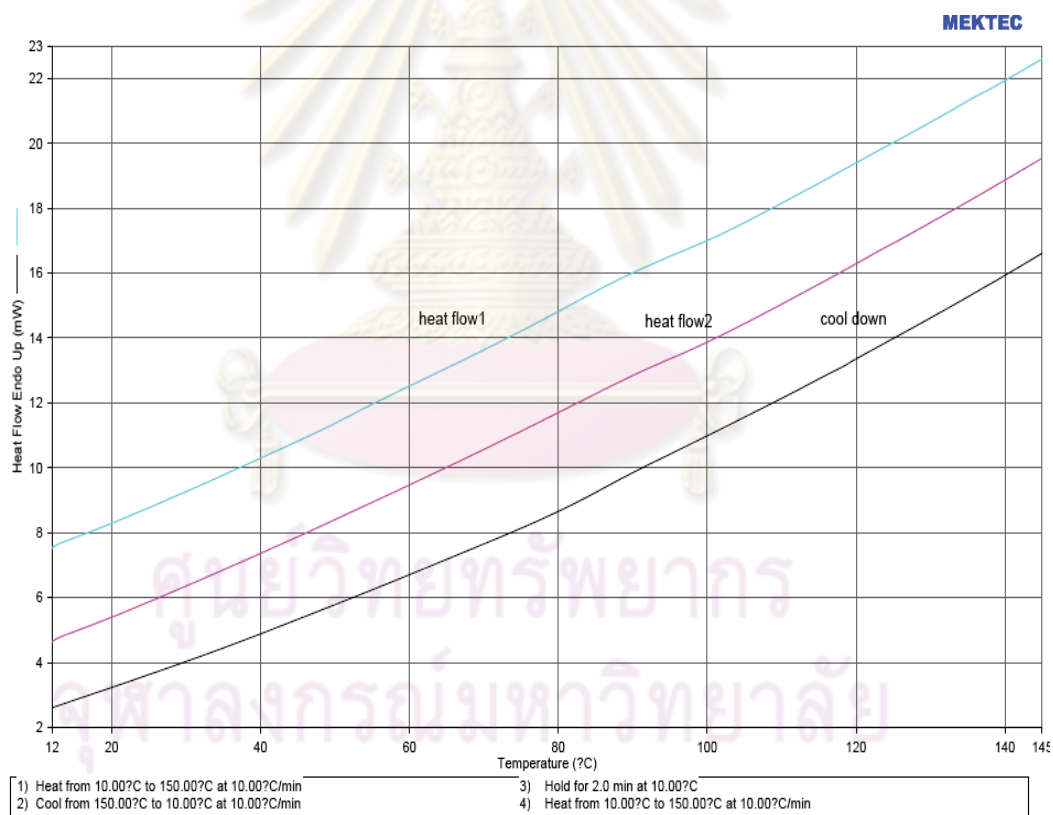


Figure C-2 DSC curve of ethylene/1-octene copolymer produce with SiO₂ (LP)
via ex situ impregnation

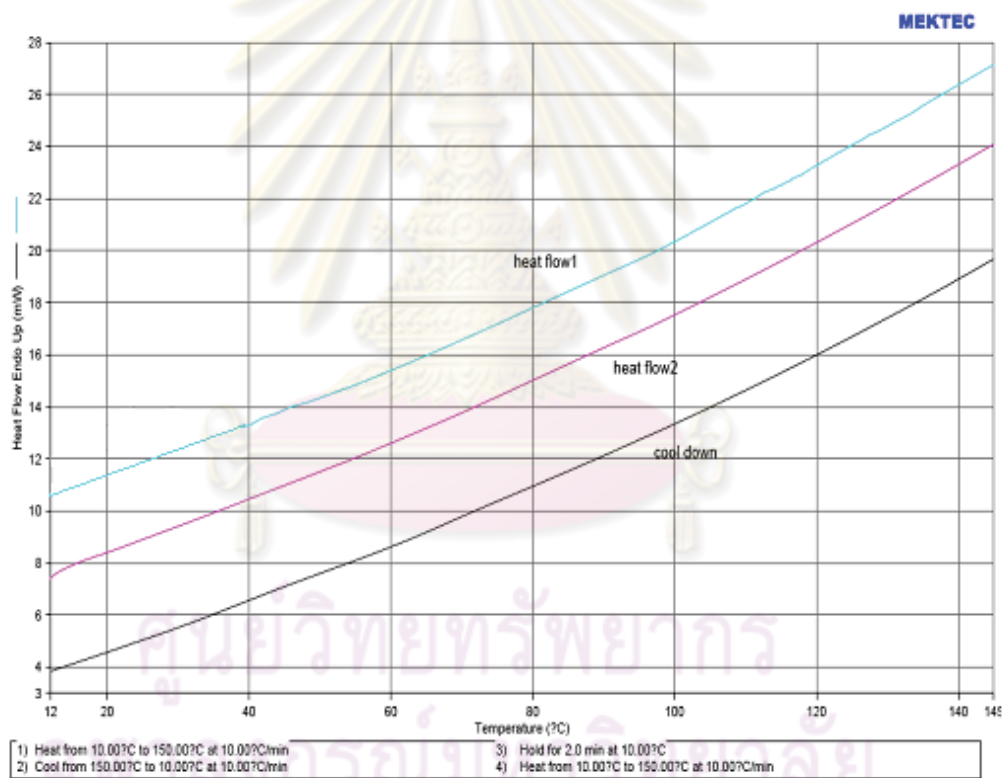


Figure C-3 DSC curve of ethylene/1-octene copolymer produce with SiO₂(LP)-0.2% via ex situ impregnation

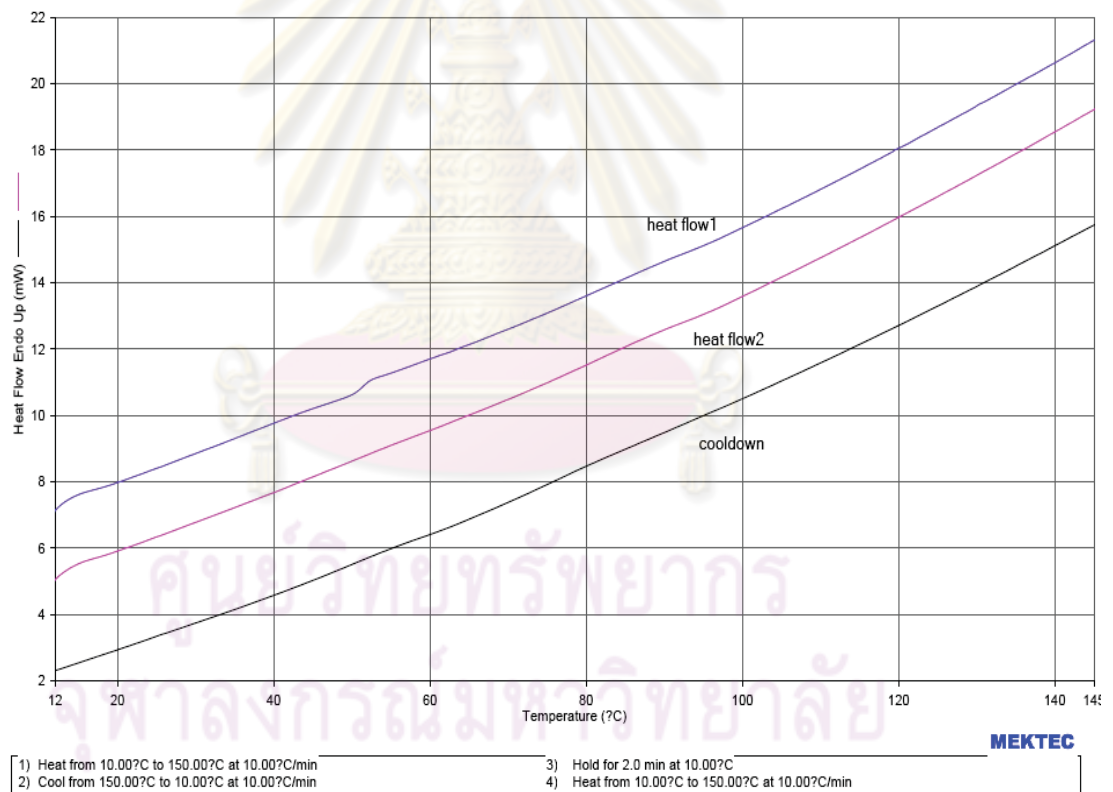


Figure C-4 DSC curve of ethylene/1-octene copolymer produce with SiO₂ (LP)-1%
via ex situ impregnation

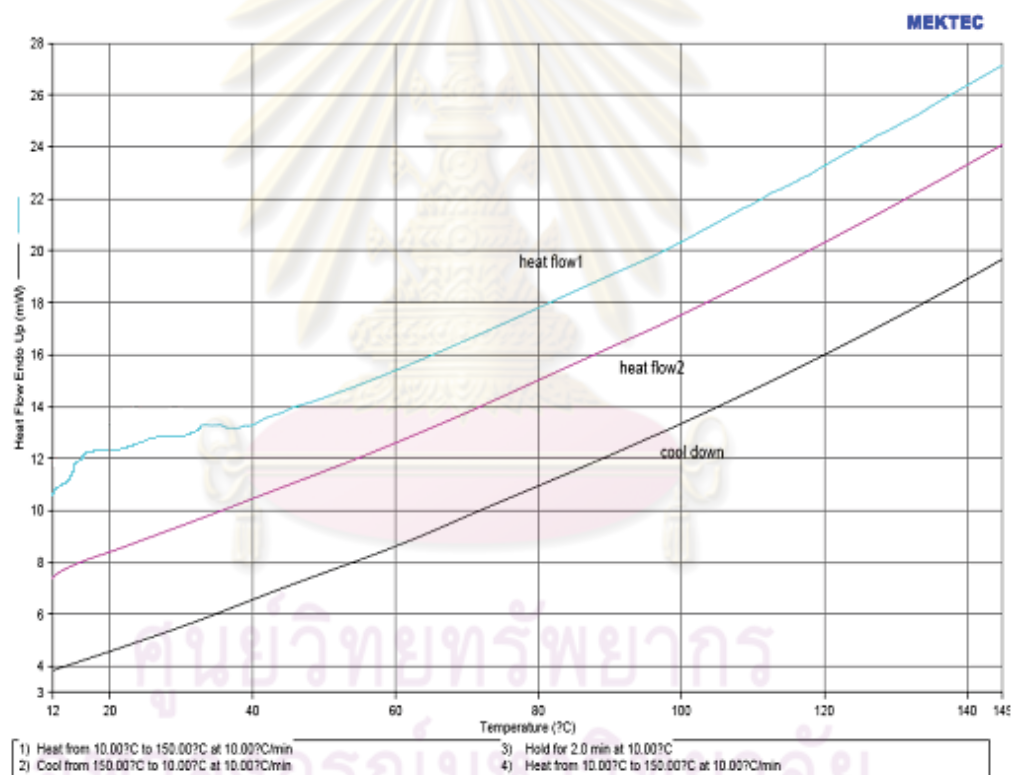


Figure C-5 DSC curve of ethylene/1-octene copolymer produce with homogenous via in situ impregnation

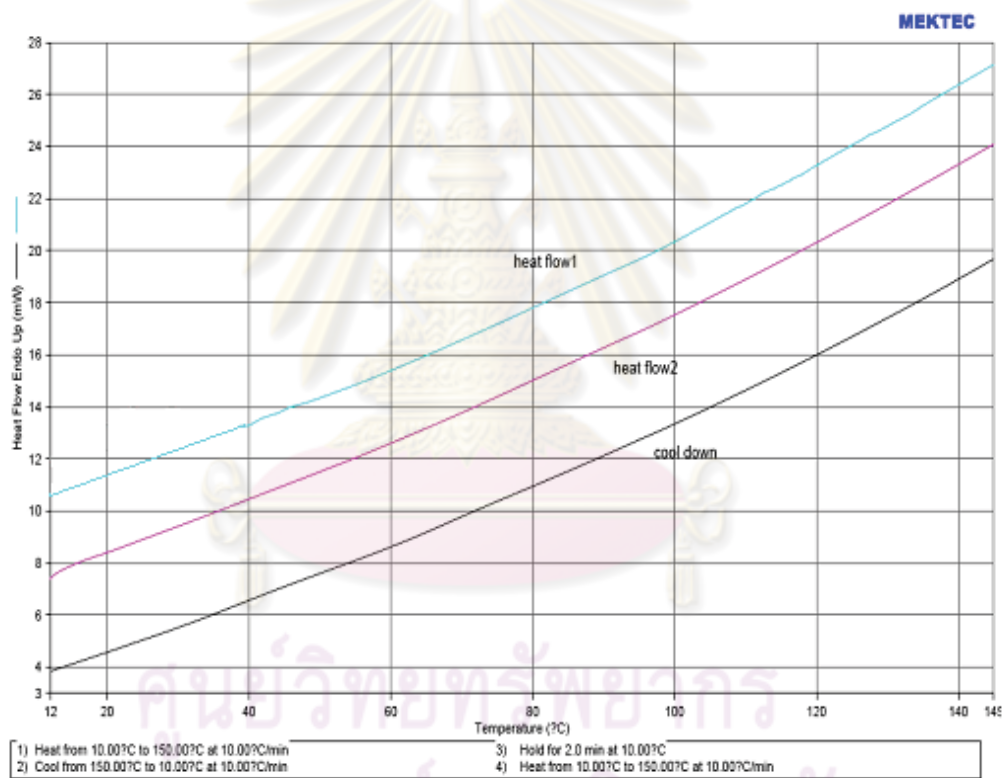


Figure C-6 DSC curve of ethylene/1-octene copolymer produce with SiO₂ (LP) via in situ impregnation

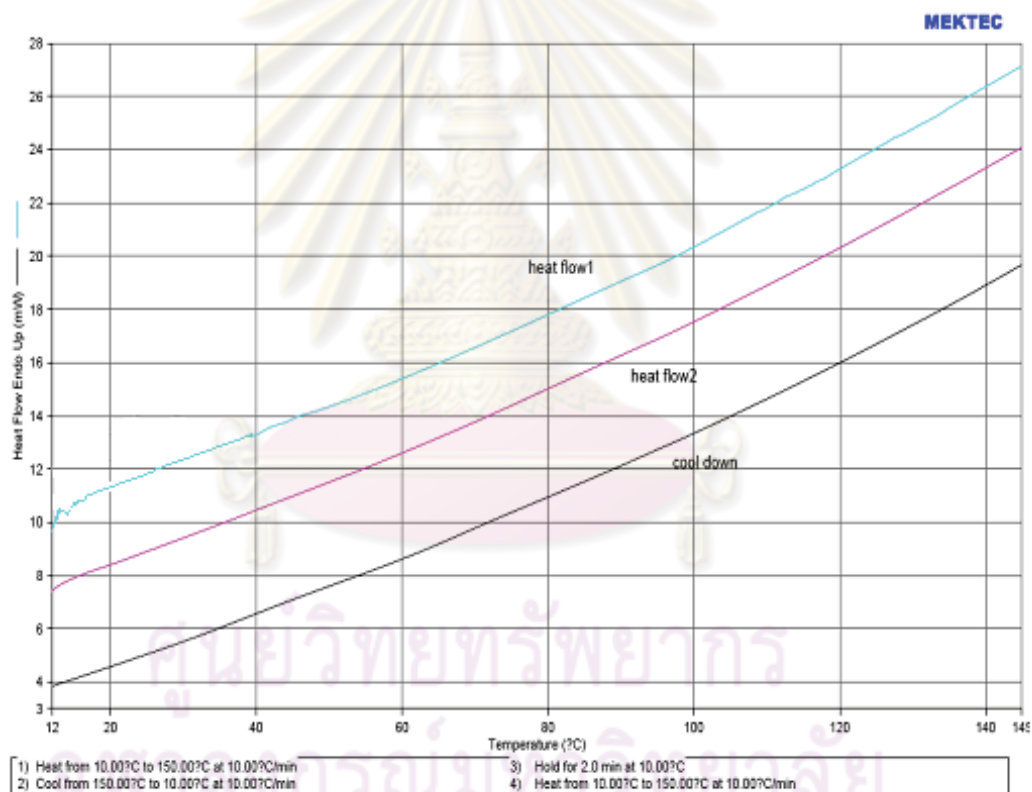


Figure C-7 DSC curve of ethylene/1-octene copolymer produce with SiO₂(LP)-0.2% via ex situ impregnation

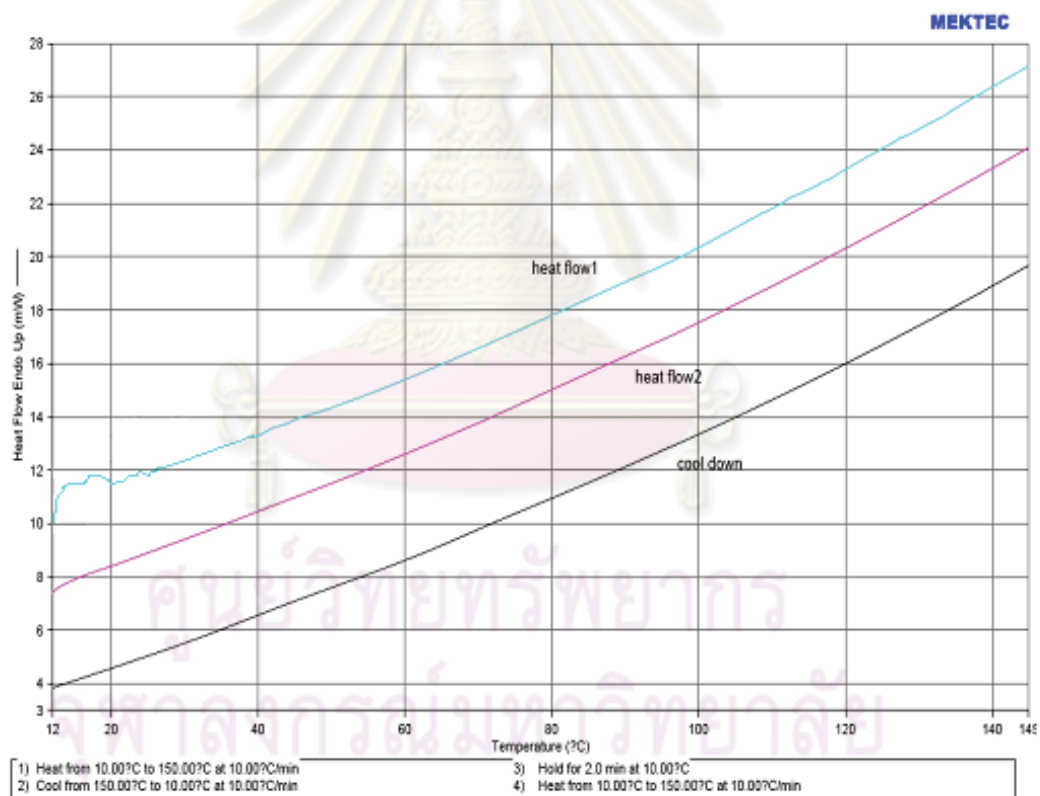


Figure C-8 DSC curve of ethylene/1-octene copolymer produce with SiO₂ (LP)-1% via in situ impregnation

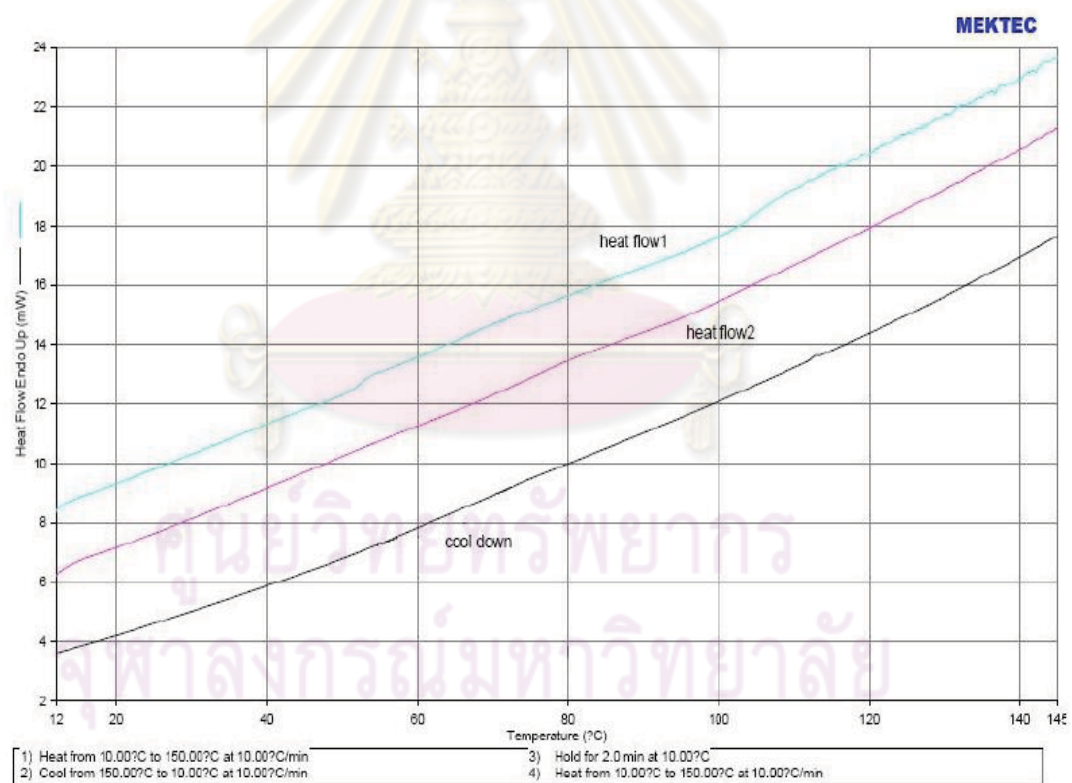


Figure C-9 DSC curve of ethylene/1-octene copolymer produce with SiO₂ (SP) via in situ impregnation

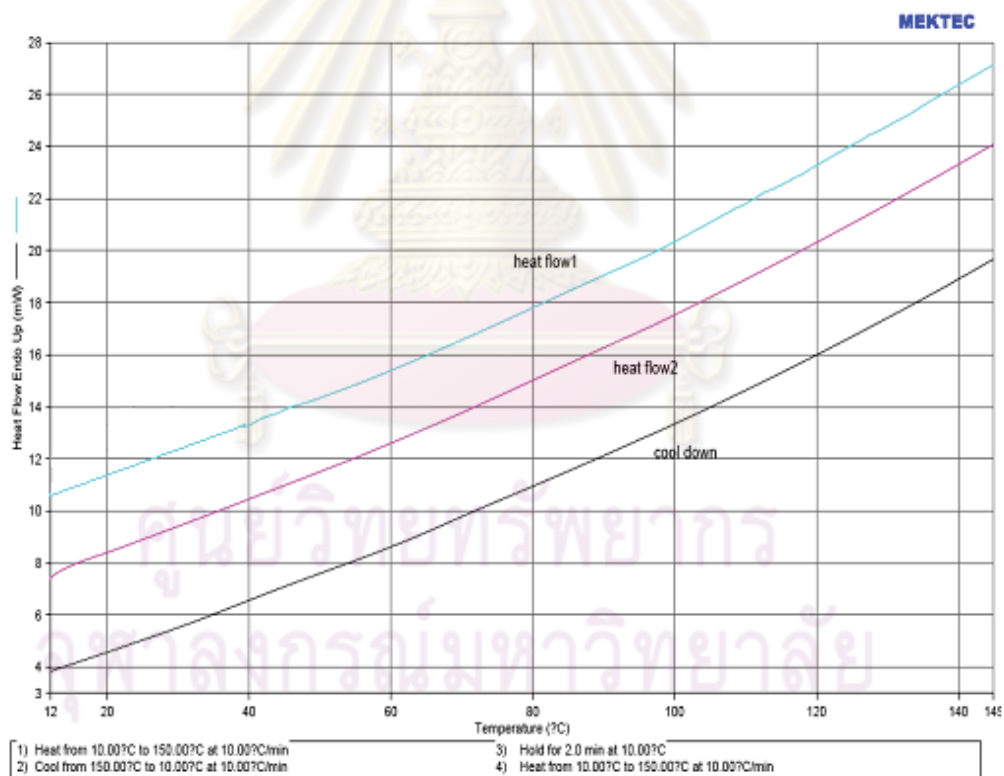


Figure C-10 DSC curve of ethylene/1-octene copolymer produce with SiO₂(SP)-0.2% via in situ impregnation

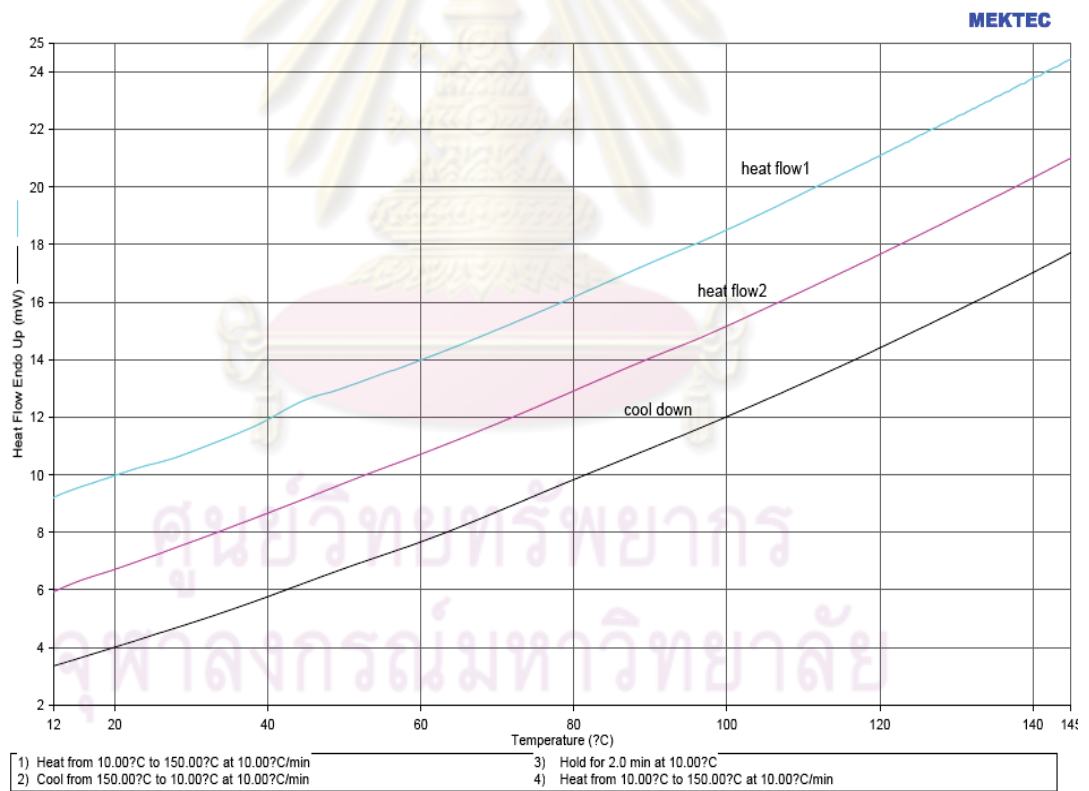


Figure C-11 DSC curve of ethylene/1-octene copolymer produce with SiO₂ (SP)-1% via in situ impregnation



APPENDIX D
(CALCULATION OF POLYMER PROPERTIES)

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D-1 Calculation of polymer microstructure

Polymer microstructure and also triad distribution of monomer can be calculated according to the Galland *et al.* [1996] in the list of reference. The detail of calculation for ethylene/ α -olefin copolymer was interpreted as follow.

1-Octene

The integral area of ^{13}C -NMR spectrum in the specify range are listed.

T_A	=	39.5 - 42	ppm
T_B	=	38.1	ppm
T_C	=	36.4	ppm
T_D	=	33 - 36	ppm
T_E	=	32.2	ppm
T_F	=	28.5 - 31	ppm
T_G	=	25.5 - 27.5	ppm
T_H	=	24 - 25	ppm
T_I	=	22 - 23	ppm
T_J	=	14 - 15	ppm

Triad distribution was calculated as the followed formula.

$k[\text{OOO}]$	=	$T_A - 0.5T_C$
$k[\text{EOO}]$	=	T_C
$k[\text{EOE}]$	=	T_B
$k[\text{EEE}]$	=	$0.5T_F - 0.25T_E - 0.25T_G$
$k[\text{OEO}]$	=	T_H
$k[\text{OEE}]$	=	$T_G - T_E$

Table D-1.1 Reactivity ratios of ethylene and 1-octene monomers (part1)

system	method	comonomer	r_{EFC}
Homogeneous	EI	1-octene	0.90
	II		0.92
SiO ₂	EI	1-octene	0.92
	II		2.58
SiO ₂ -Ga-0.2%	EI	1-octene	1.20
	II		1.87
SiO ₂ -Ga-1%	EI	1-octene	1.06
	II		2.51

Table D-1.2 Reactivity ratios of ethylene and 1-octene monomers via in situ impregnation method (part2)

Samples	comonomer	r_{EFC}
Homogeneous	1-octene	0.92
SiO ₂ (LP)	1-octene	2.58
SiO ₂ (LP) -Ga-0.2%	1-octene	1.87
SiO ₂ (LP) -Ga- 1.0%	1-octene	2.51
SiO ₂ (SP)	1-octene	2.26
SiO ₂ (SP) -Ga- 0.2%	1-octene	2.65
SiO ₂ (SP) -Ga- 1.0%	1-octene	1.92

All copolymer was calculated for the relative comonomer reactivity (r_E for ethylene and r_C for the comonomer) and monomer insertion by using the general formula below.

$$r_E = 2[EE]/([EC]X)$$

$$r_C = 2[CC]X/[EC]$$

- where r_E = ethylene reactivity ratio
 r_C = comonomer (α -olefin) reactivity ratio
 $[EE]$ = $[EEE] + 0.5[CCE]$
 $[EC]$ = $[CEC] + 0.5[CCE] + [ECE] + 0.5[ECC]$
 $[CC]$ = $[CCC] + 0.5[ECC]$
 X = $[E]/[C]$ in the feed = concentration of ethylene (mol/L) /
 concentration of comonomer (mol/L) in the feed.
 $\%E$ = $[EEE] + [EEC] + [CEC]$
 $\%C$ = $[CCC] + [CCE] + [ECE]$

D.2 Calculation of crystallinity for ethylene/ α -olefin copolymer

The crystallinities of copolymers were determined by differential scanning calorimeter. %crystallinity of copolymers is calculated from equation [Liu *et al.*, 1997].

$$\chi (\%) = \frac{\Delta H_m}{\Delta H_{m_0}} \times 100$$

Where $\chi (\%)$ = %crystallinity

ΔH_m = the heat of fusion of sample (J/g)

ΔH_{m_0} = the heat of fusion of perfectly crystalline polyethylene

(286 J/g) [90]



APPENDIX E
(LIST OF PUBLICATION)

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Wannaborworn, M.; Jongsomjit, B. “Effect of gallium-modified silica-supported metallocene catalyst on LLDPE synthesis” (The Proceeding of 18th Thailand Chemical Engineering and Applied Chemistry Conference, TIChe 2008, Pattaya)



ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

VITA

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