

ผลของสารปนเปื้อนในแก๊สเอทิลีนที่มีต่อความว่องไวของตัวเร่งปฏิกิริยาซีเกลอร์-นัตตา
และสมบัติของพอลิเอทิลีน

นางสาวอักษรากค์ ฐริวัฒนา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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ปีการศึกษา 2555
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ที่ส่งผ่านทางบัณฑิตวิทยาลัย

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EFFECT OF IMPURITIES IN ETHYLENE GAS ON THE CATALYTIC
ACTIVITY OF ZIEGLER-NATTA CATALYST AND POLYETHYLENE
PROPERTIES

Ms. Auksarapuk Puriwathana

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

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2012

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อักษรศักดิ์ ภูริวัฒนา : ผลของสารปนเปื้อนในแก๊สเอทิลีนที่มีต่อความว่องไวของตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาและสมบัติของพอลิเอทิลีน. (EFFECT OF IMPURITIES IN ETHYLENE GAS ON THE CATALYTIC ACTIVITY OF ZIEGLER-NATTA CATALYST AND POLYETHYLENE PROPERTIES) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ศ.ดร. ปิยะสาร ประเสริฐธรรม, 95 หน้า.

ในวิทยานิพนธ์เล่มนี้ สารปนเปื้อนหลากหลายชนิดที่มักพบในแก๊สเอทิลีนได้นำมาใช้เพื่อศึกษาผลของสารปนเปื้อนที่มีต่อความว่องไวของตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาเชิงการค้าและสมบัติของพอลิเอทิลีน สารปนเปื้อนปริมาณที่ต้องการได้ฉีดเข้าไประหว่างกระบวนการเอทิลีนพอลิเมอร์ไรเซชันทั้งในระบบที่มีและไม่มีไฮโดรเจน ในระบบที่ไม่มีไฮโดรเจน CO , CO_2 และ CH_4 เป็นพิษต่อตัวเร่งปฏิกิริยาเป็นผลทำให้ความว่องไวของตัวเร่งปฏิกิริยาลดลง ในขณะที่ C_3H_6 และ C_2H_2 เพิ่มความว่องไวของตัวเร่งปฏิกิริยาเนื่องจากการโคพอลิเมอร์ไรเซชันกับเอทิลีน ในกรณีที่มีไฮโดรเจนไฮโดรเจนส่งผลต่อสารปนเปื้อนแตกต่างกัน โดยไฮโดรเจนส่งผลดีในกรณีของ CO ในขณะที่สารตัวอื่นให้ผลในทิศทางตรงกันข้าม ส่วนผลกระทบของ H_2O และ CH_3OH ขึ้นอยู่กับปริมาณของสารปนเปื้อนและภาวะที่ใช้ โดยไฮโดรเจนส่งผลดีต่อความว่องไวของตัวเร่งปฏิกิริยาดูด้วยเช่นเดียวกัน ผลของสารปนเปื้อนที่มีต่ออัตราในการใช้เอทิลีนและอัตราในการเสื่อมสภาพของตัวเร่งปฏิกิริยาก็ได้ทำการศึกษาในงานวิจัยนี้ด้วย นอกจากนี้ ผลการทดลองยังพบว่าสารปนเปื้อนลดน้ำหนักโมเลกุลและทำให้การกระจายตัวของน้ำหนักโมเลกุลแคบลงแต่ไม่ส่งผลต่อคุณสมบัติทางความร้อนของพอลิเอทิลีน

ภาควิชา วิศวกรรมเคมีลายมือชื่อนิสิต.....
 สาขาวิชา วิศวกรรมเคมีลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก.....
 ปีการศึกษา 2555

5470460221 : MAJOR CHEMICAL ENGINEERING

KEYWORDS : ZIEGLER-NATTA/ IMPURITY/ CATALYTIC ACTIVITY/
POLYETHYLENE PROPERTIES

AUKSARAPUK PURIWATHANA : EFFECT OF IMPURITIES IN
ETHYLENE GAS ON THE CATALYTIC ACTIVITY OF ZIEGLER-NATTA
CATALYST AND POLYETHYLENE PROPERTIES. ADVISOR : PROF.
PIYASAN PRASERTHDAM, Dr.Ing., 95 pp.

In this current study, the various types of impurity, which were mostly found in ethylene gas, were used to investigate the influence of impurities on the catalytic activity of a commercial Ziegler-Natta catalyst and polyethylene properties. A desired amount of impurities was injected during ethylene polymerization both in the absence and presence of hydrogen. In the absence of hydrogen, CO, CO₂ and CH₄ poisoned to the catalyst resulting in a decrease in the activity, while C₃H₆ and C₂H₂ enhanced the activity causing from the copolymerization with ethylene. In the presence of hydrogen, hydrogen was differently affected on impurities. It had a beneficial effect in the case of CO. While other compounds exhibited the results in the opposite side. The effects of H₂O and CH₃OH were varied relying on their quantities and operating condition. Hydrogen also gave a beneficial effect on the activity as well. The effects of impurities on ethylene consumption and catalyst decay rate between in the absence and presence of hydrogen were also investigated in this study. Moreover, our studies have been found that impurities reduced Mw and narrow MWD, but they did not affect on the thermal behavior of polyethylene.

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

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

Academic Year : 2012.....

ACKNOWLEDGEMENTS

First, I would like to express my sincere appreciation to my thesis advisor, Professor Dr. Piyasan Prasertdam, who is more than a teacher in my mind. I am profoundly thank for inestimable recommendations, valuable discussions and support as I received from him during I studied in the Ziegler-Natta and Metallocene group. Second, I would like to thank Associate Professor Dr. Bunjerd Jongsomjit for his encouragement and support throughout my study.

I sincerely thank Assistant Professor Dr. Anongnat Somwangthanaroj, Dr. Sirachaya Kunjara Na Ayudhya and Associate Professor Dr. Bunjerd Jongsomjit for their kindly guidance and serving as the committee members.

The financial support, instrument and chemical supports and nice suggestions of this work are gratefully acknowledge from Thai Polyethylene Co., Ltd.

Many thanks to all former and current friends in Ziegler-Natta and Metallocene group, Center of Excellent on Catalysis and Catalytic Reaction Engineering for our impress relationship, assistance and inspiration to eliminate my obstacles. Special thanks to Mr. Janewit Phromprasit for the chemical gases support in this work.

Finally, I would like to devote my prosperity to my parents and my family, who give the pure love, take care and always be beside me along of my life.

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CHAPTER I

INTRODUCTION

Since the biggest accomplishment of polyethylene production was discovered by Ziegler and his co-workers in 1953, the polyolefin development has been continuously expanded both in academic and industry. The major attention concentrated on the catalytic performance and properties of polymer [1-2]. High-density polyethylene (HDPE), the major commodity of plastic market, was produced via the catalytic reaction between metal catalyst and organometallic compound at low pressure and moderate temperature.

Ziegler-Natta catalysts are inactive when traces of oxygen and moisture introduced into the polymerization system. In contradiction to metallocene catalysts, small amounts of water and oxygen can enhance the activity due to highly active alkyl alumoxane was formed. Therefore, the purification of feedstocks such as monomer, solvent and other raw materials also is required for polyethylene processing [4]. Polar impurities, which contaminate in ethylene gas as being used for the monomer, may affect on the catalyst efficiency through catalyst poisoning. This phenomenon was the crucial effect in industrial section. Impurities reduced the catalytic productivity and polymer quality [5-7]. However, the influence of impurities is rather complex. They can either increase or decrease the capability of catalyst depending upon the adsorption strength and their chemical nature [6-7]. Dauphin et al. [8] found that most of impurities in ethylene inhibited the rate of polymerization, whereas ammonia exhibited the result in the opposite side.

A commercial Ziegler-Natta catalyst, $MgCl_2$ supported $TiCl_4$ ($TiCl_4/MgCl_2$), prepared by adduct method is appreciable in high-density polyethylene synthesis. It produces the highly active catalyst and provides the excellent activity. Thus, to employ the beneficial ability of commercial catalyst, the various types of impurity commonly found in ethylene gas have been used in order to investigate their influences on the activity and polyethylene properties both in the absence and

presence of hydrogen. Single and multiple bond compounds consisted of carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), propylene (C₃H₆), acetylene (C₂H₂), water (H₂O) and methanol (CH₃OH) were selected as impurities in this study. According to less attention on the effect of impurities in catalysis field, this research is also the first direct evident to compare their effect which has not been reported before.

This thesis can be divided into five chapters. Chapter I is the motivation and general details. Chapter II is the brief background and theory of Ziegler-Natta catalysts. The experimental methodology including the instrument and techniques used for characterizing the resulting polymers are also demonstrated in Chapter III. In Chapter IV, the effects of each impurity on the activity and polymer properties are also reported. Finally, conclusions of this research and some recommendations for further study are summarized in Chapter V.

1.1 Objective

The objective of this research is to investigate the influence of impurities commonly found in ethylene gas on the catalytic activity and polyethylene properties. The polymerization is performed with a commercial Ziegler-Natta catalyst (TiCl₄/MgCl₂) both in the absence and presence of hydrogen.

1.2 Research scopes

The scopes of this research are to utilize the impurities applying with a commercial catalyst by focusing on their effect on the catalytic activity and properties of polymer. The scopes are summarized in the below details :

- 1) The impurities in ethylene gas used in this study are only composed of CO, CO₂, CH₄, C₃H₆, C₂H₂, H₂O and CH₃OH.

2) The influence of impurities is performed during ethylene polymerization both in the absence and presence of hydrogen.

3) The reaction is polymerized with Al/Ti molar ratio of 140 in 100 ml stainless steel reactor.

4) Compared the effect of impurities on the commercial catalyst activity and polyethylene properties, the polymers are mainly characterized via DSC and GPC measurement.

5) Gas impurities, CO, CO₂, CH₄, C₃H₆ and C₂H₂, are varied in the range of impurity content (the molar ratio of impurity and titanium) between 0 to 1.6.

6) Liquid impurities, H₂O and CH₃OH, are tested in the range of impurity content (the molar ratio of impurity and titanium) between 0 to each ultimate value of that impurity which will not subject to made the complete catalyst deactivation.

1.3 Benefits

1) To understand how each type of impurities affects on the catalytic activity and polyethylene properties.

2) To observe the influence of each impurity, this information may help to emphasize the impurity effects. The purification of raw materials before use is very important factor to determine the activity and polymer properties.

3) Some impurities may be not a poison, but may act as a promoter to enhance the activity, produces new way to improve catalyst behavior.

4) Hydrogen can modify the influence of impurities both in positive and negative ways.

5) The results of this thesis can be used as the reference data for industrial process.

1.4 Research Methodology

The research methodology is shown in flow diagram as Figure 1.1

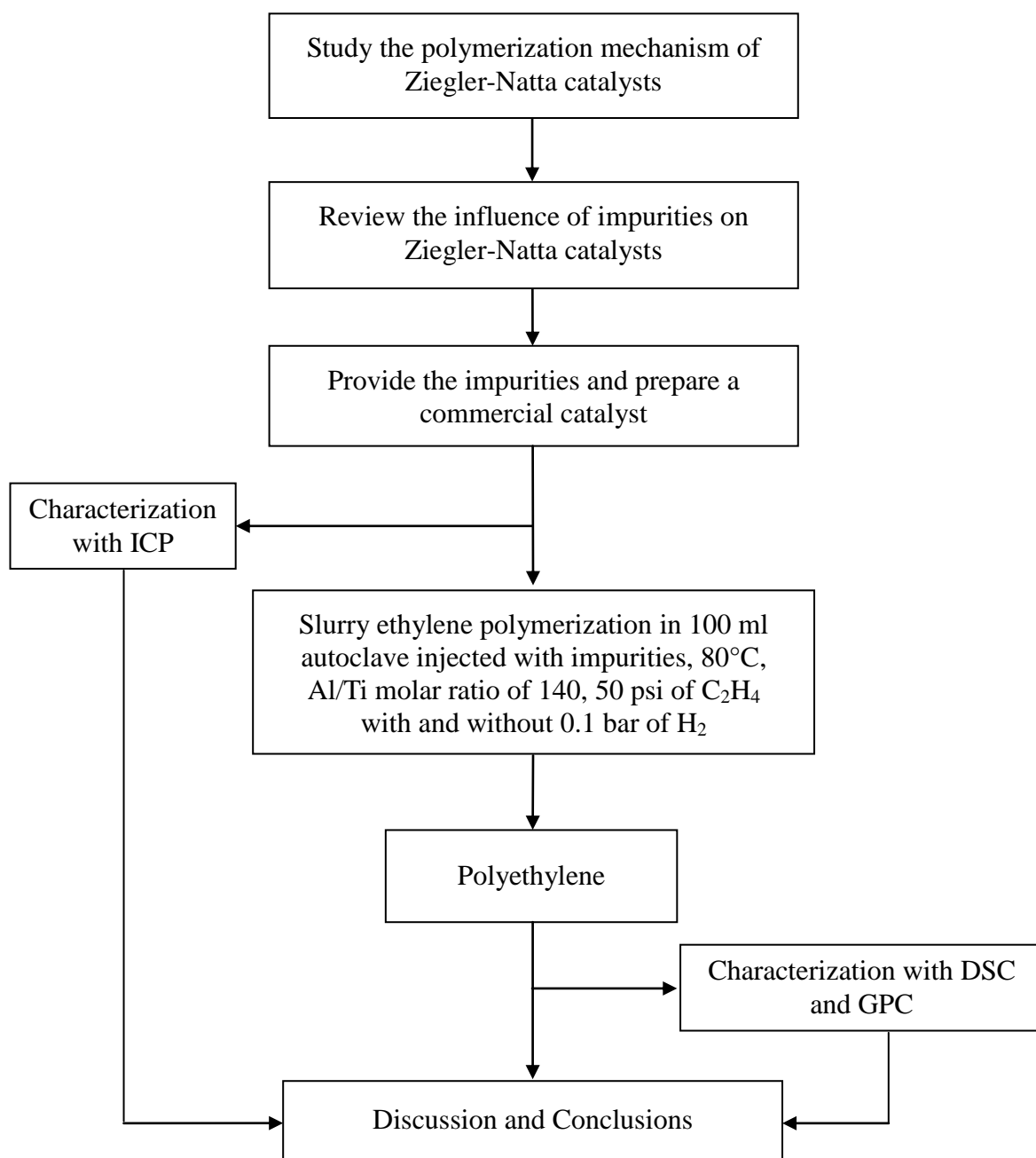


Figure 1.1 Flow diagram research methodology

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 The history of Ziegler-Natta catalysts [4]

The background of Ziegler-Natta catalysts began from aufban growth reaction, which was discovered by Ziegler in 1940. In this reaction, triethylaluminum reacted with ethylene in the absence of transition metal compounds to produce low molecular weight polyethylene. Under proper conditions, α -olefins could form by β -elimination. Ziegler required to enlarge the knowledge of aufban reaction until he unexpectedly discovered the beneficial effect of transition metal catalyst with alkylaluminum on the ethylene polymerization in 1953. Finally, he found that the combination of titanium tetrachloride and triethylaluminum produced the highly active catalyst. Then, Natta succeeded in the polymerization of propylene by studying the Ziegler's achievement.

2.2 Ziegler-Natta catalysts for ethylene polymerization

In ethylene polymerization, Ziegler-Natta catalysts are preferably used in the production of polyethylene both in commercial and industry based on TiCl_4 . It is important to note that the polymerization will be take place after catalyst is activated by reacting with alkylaluminum compound.

The performance of catalysts mainly depended on the catalyst preparation method. Thus, the support selection was also important. Generally, MgCl_2 and SiO_2 are commonly chose as support for Ziegler-Natta catalysts. They dispersed titanium metals give rise to increase the number of active centers. Because MgCl_2 provided the good catalyst morphology and excellent catalytic activity [4]. It became clear that MgCl_2 is also widely used to support TiCl_4 .

Silica has been used as a carrier or support in ethylene polymerization, it significantly gives the spherical morphology on catalyst and polymer particles. The activity strongly dependent upon the interaction of TiCl_4 with hydroxyl groups on silica surface. Therefore, the calcination temperature was an important parameter to determine the catalyst productivity and properties of polymers [9-10].

2.3 Ziegler-Natta catalyst polymerization mechanism [1,4,12]

The polymerization mechanism of Ziegler-Natta catalysts was typically included the initiation, chain propagation and chain termination steps.

In order to understand the mechanism of these complex catalysts, it is very important to know how the active centers are formed and how is their structure. According to the report of Cossee and Arlman, they have proposed the model to explain the polymerization of α -olefins at the active centers : inside the interior of each TiCl_3 crystal was composed of the coordination of six chlorine anions with titanium cation as octahedral geometry. While at the surface of crystal, titanium cation was only coordinated with five chlorine anions, other one was a vacant site which easily coordinated to other components. The structures of TiCl_3 at interior and exterior of crystal were shown in Figure 2.1 and Figure 2.2, respectively.

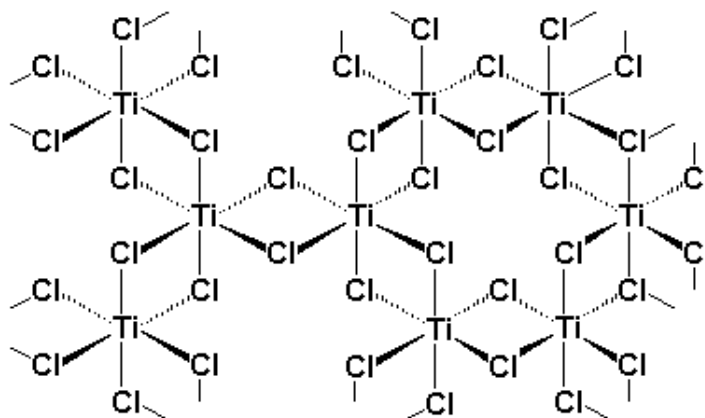


Figure 2.1 The interior structure of TiCl_3 crystal [12]

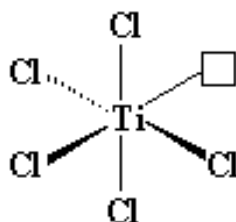


Figure 2.2 The structure of TiCl_3 at the surface of crystal [12]

At the surface of crystal, active centers were formed by the alkylation reaction resulting in generation of the titanium-alkyl ($\text{Ti-C}_2\text{H}_5$) bond which believed to represent the active centers in olefin polymerization. One chlorine ion was displaced from titanium complex and substituted by alkyl group of cocatalyst. The initiation step was exposed in Figure 2.3.

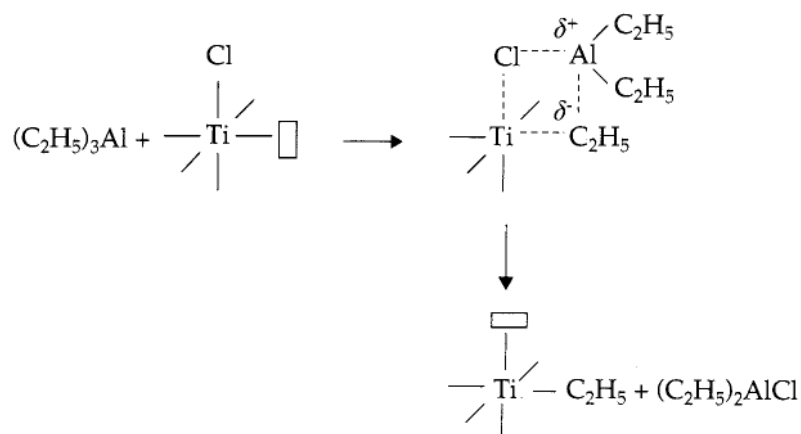


Figure 2.3 The active centers formation by the reaction of alkyl aluminum compound at the titanium centers [4]

After $\text{Ti-C}_2\text{H}_5$ bond was formed, ethylene will coordinate at the vacant site of active centers by π -complex and insert into Ti-C bond. Then, the vacant site opened again and ready coordinated with next ethylene molecule, is so called "chain propagation" step. The polyethylene chain is growing at the surface of catalyst as seen in Figure 2.4.

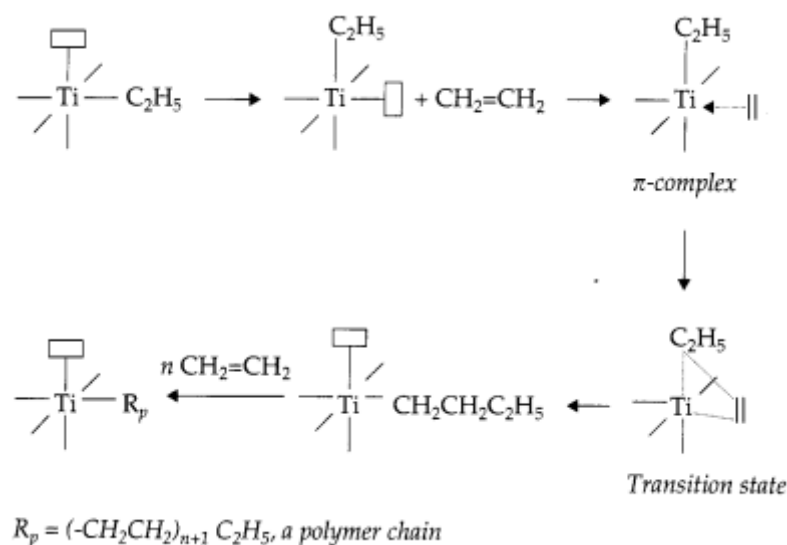


Figure 2.4 Propagation step of ethylene to produce long chain polyethylene at the surface of catalyst [4]

Due to $\text{Ti}-\text{C}_2\text{H}_5$ σ -bonds quite unstable, another mechanism as "bimetallic model" has been proposed. This model has explained the polymerization mechanism of monomer similar to the Cossee-Arlman model : the monomer can also insert into $\text{Ti}-\text{C}_2\text{H}_5$ bond whereas difference on the participation of aluminum-alkyl to titanium-alkyl, revealed in Figure 2.5. The coordination of aluminum-alkyl is believed to stabilize the $\text{Ti}-\text{C}_2\text{H}_5$ active centers.

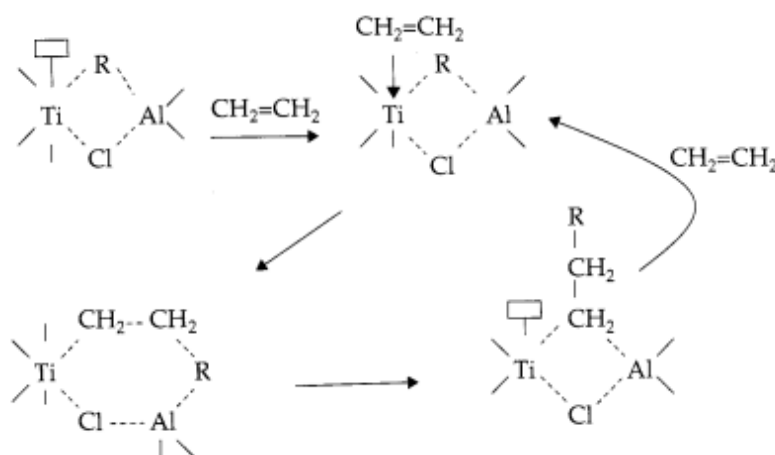


Figure 2.5 The bimetallic model for ethylene polymerization [4]

In the termination step, it can divide into two causes : termination by hydrogen and β -elimination mechanisms. In the former case, hydrogen produced the titanium-hydride and removed the polymer chain from active centers. The activity is also decreased. However, in the latter case, hydrogen from β -position of polymer chain is transferred to titanium or monomer.

Both of termination and chain transfer reaction by the effect of hydrogen and monomer sequentially, titanium center is still be active, next ethylene molecule can insert into the titanium centers and further proceed the chain propagation again. The mechanism of hydrogen and β -elimination at the active centers were exhibited in Figure 2.6 and Figure 2.7, accordingly.

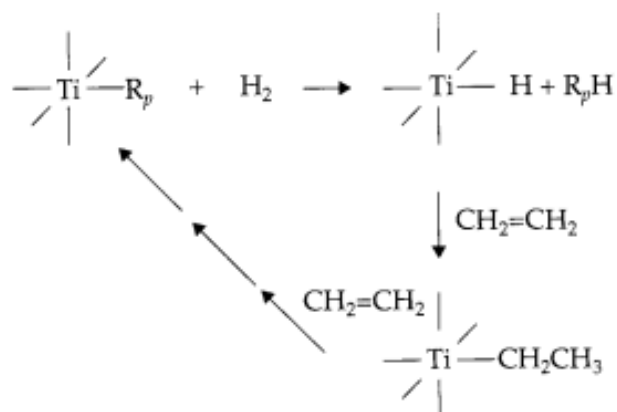


Figure 2.6 Chain termination mechanism by hydrogen [4]

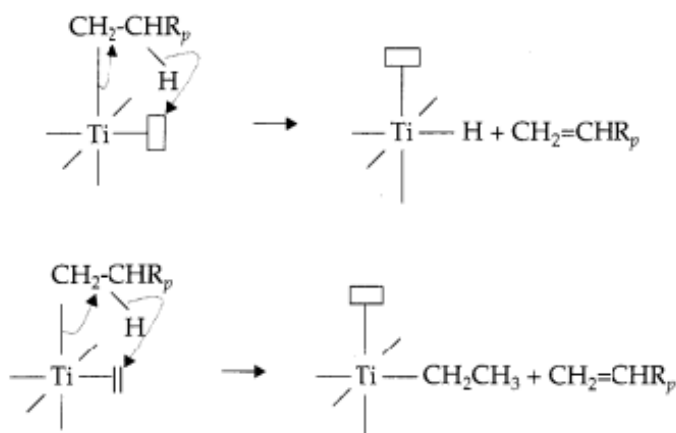


Figure 2.7 Chain termination by β -elimination [4]

2.4 General behavior of MgCl₂-titanium-based Ziegler-Natta catalysts for ethylene polymerization [10]

The general features of Ziegler-Natta catalysts polyethylene polymerization in homo and copolymerization can be summarized in the following details :

- Although the advantage of hydrogen is commonly known to adjust the molecular weight of polymer but it can reduce the catalytic activity in ethylene polymerization.
- The more amounts of hydrogen, the more amounts of ethane gas.
- The activity is enhanced when α -olefin presented in the system. Moreover, it also affected on density and molecular weight of polymers.
- The role of cocatalyst is not only activated Ziegler-Natta catalysts. It has the deactivation effect when high concentration of cocatalyst is used.
- The molecular weight decreased with increasing amounts of alkyl aluminum cocatalyst.
- In homo polymerization, the polymerization process is quite stable. In contrast with copolymerization, the deactivation is obviously observed.

The copolymerization of ethylene and α -olefins such as propylene, 1-butene, 1-hexene etc. produced linear low density polyethylene (LLDPE). The function of comonomer is to modify the properties of polymer particles. It incorporated into the polymer chain resulting in lower densities and melting points of polymers.

2.5 Impurities in ethylene gas

Ethylene gas is generally composed the major impurities such as methane and ethane. However, a trace amount of other compounds, for example, propane, propylene, acetylene, water, carbon dioxide and methanol also found in ethylene as

well [8,13-14]. Impurities in ethylene destroyed the catalysts, led to reduce the quality of products, process downtime and catalyst productivity [5,13-14].

2.6 Poisoning deactivation of active centers

Ziegler-Natta catalysts are highly sensitive to polar organic and inorganic compounds, probably contaminated in diluent, solvent, monomer, or other raw materials [4,15]. This phenomenon is the crucial effect in polyolefin polymerization due to upon materials can be considered as the poisoning materials, possibly reduced the catalyst efficiency and number of active centers through catalyst poisoning.

Poisoning is the strong chemisorption of reactants, products or impurities on the active sites. Usually, poisons retarded the polymerization process by physically blocking of an active site or changing the adsorption ability of nearest metal atoms depending on chemical nature and their adsorption strength. Besides, poisons can also modify the nature of active sites and generate new species on the catalyst surface resulted into the catalytic performance is obviously changed [6-7].

Poisons can be classified into two groups as coordinative and destructive poisons. Coordinative poison is the chemical compounds which coordinate at metal atoms of the active centers during growing the polymer chains. If poisons are removed, the polymerization will continue but without an effect on titanium centers ; for instance, CS_2 , propadiene and PR_3 . For another group, destructive poison is the chemical compounds which strongly interacted with the metal-carbon bond at active centers and destroyed them. They usually included O-H, S-H and N-H bonds [10].

In other words, poisons can be divided according to chemical makeup as selective and nonselective poisoning. In the former case, poisons are preferably adsorbed only the active sites resulting in rapidly of the catalytic activity with low amounts of poison whereas nonselective poisoning, poisons are uniform chemisorption onto the catalyst surface. Hence, the activity is also decreased with the linear function of poison chemisorbed [6-7].

The best prevention from the poisoning effect is to select the proper operating condition and purify the reactant feed streams before using. Because they can modify the catalytic resistance and sensitivity from the influence of poisoning compounds [6-7].

2.7 Literature reviews

Kim et al., 1990 [16] studied the determination of active centers via CO inhibition method during propylene polymerization. They found that after injected carbon monoxide by gas-syringe, carbon monoxide was instantaneously dissolved in solvent and chemisorbed on the active centers. The polymerization rate was also suddenly dropped. The number of active centers can extrapolate on an assumption that one CO molecule only adsorbed on each active site. However, the authors have mentioned that this method gave the lowest possible concentration of active centers because of the side reaction of CO was occurred.

Grigoryan, 1984 [17] reviewed the effect of methane on Ziegler-Natta catalysts. The result was indicated that the interaction between methane and catalysts can contribute to generate the methyl derivative at the metal centers and alkane molecules as shown in Figure 2.8.

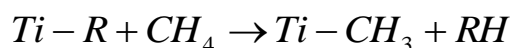


Figure 2.8 The reaction of methane with Ziegler-Natta catalysts [17]

Additionally, the activity decreased by the formation of methyl derivative which was less active than Ti-R centers. Ethylene molecules can insert into Ti-CH₃ bond and further propagated the polymer chains once. This mechanism was demonstrated in Figure 2.9.

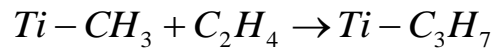


Figure 2.9 Propyl derivative formation by the reaction of Ti - CH₃ center with ethylene [17]

Lesna et al., 1977 [18] interested in the effect of retarders as CO₂ and CO in propylene polymerization. The kinetic equation was derived based on Langmuir isotherm. The mechanism concentrated on the adsorption of retarders onto polymerization sites which formed from organometallic cocatalyst according to equation (2-1).

$$\frac{1}{\theta_A} = \frac{k_0}{k} = 1 + K_R [R] \quad (2-1)$$

- Where,
- θ_A = fractions of polymerization site, occupied by organometallic compound
 - k_0/k = ratio of rate constant in the absence and presence of the retarder, subsequently (l/mol.s)
 - K_R = adsorption constant of retarder on the polymerization active sites (l/mol)
 - $[R]$ = retarder concentration (mol/l)

From the equation (2-1), the adsorption constant (K_R) of retarders can be obtained from the slope of graph between k_0/k versus $[R]$. The adsorption constant of CO was approximately about 4.9×10^4 l/mol, higher than CO₂ which had an adsorption constant around 3.5×10^2 l/mol. These results can be concluded that CO had a retardation effect stronger than CO₂.

Dauphin et al., 1967 [8] investigated the effect of impurities and additives found in ethylene. Impurities were composed of oxygen, water, carbon dioxide, propylene and acetylene while hydrogen, methanol, saturated hydrocarbon and

ammonia were represented to the additives. In their study, oxygen was the strongest inhibitor. Additives such as hydrogen, methanol and alkane had little effect on catalyst but the reduction in polymer molecular weight was obtained. In contradiction to ammonia, it enhanced the polymerization rate during propylene polymerization.

Kissin et al., 1999 [19] studied the kinetic mechanism of ethylene polymerization with Ziegler-Natta catalysts. The experimental results revealed that the presence of 0.009% of acetylene poisoned to the reaction and reduced the reaction rate by 60%. Due to the fact that acetylene can copolymerize with ethylene, the reaction rate was also gradual recovery, which temporarily affected on the catalyst.

Zohuri et al., 2001 [20] researched on the copolymerization of ethylene and propylene with Ziegler-Natta catalysts. In their study, the ratio of propylene to ethylene was varied in the range of 1.5 to 2.5. The results described that the ratio of propylene to ethylene at 2 : 1 gave the maximum productivity. The higher amounts of propylene the lower productivity could be taken.

Wook Ha et al., 1997 [21] investigated the catalytic behavior of ethylene homo and copolymerization both of Ziegler-Natta and metallocene catalysts with different comonomer types (propylene, 1-butene, 1-hexene and 1-octene). The result demonstrated that both of catalysts showed a similar tendency. The presence of comonomer gave a catalytic activity higher than ethylene homo polymerization, the highest activity was observed in the case of propylene. However, comonomer could affect on the thermal properties of polymer relying on the types of them.

Dennis, 2010 [4] reviewed some reactions of contaminants with triethylaluminum compound. For illustration, oxygen and water also reacted with cocatalyst and converted them to alkyl derivative products which were less damage to the catalyst as shown in Figure 2.10.

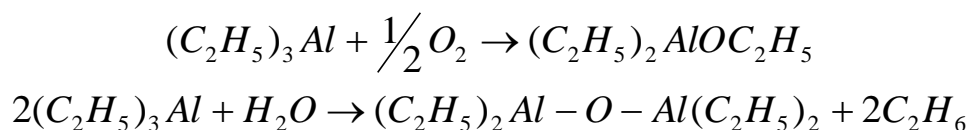


Figure 2.10 Scavenger of some poisons by cocatalyst [4]

The amount of cocatalyst may have a favorable effect on the poisoning ability of impurities. The ratios of Al to metal catalysts is commonly used around 30 in an industry. An excess amount of cocatalyst might be completely scavenged poisons.

Zakharov et al., 1983 [22] reviewed the effect of selective quenching agents of CO and CO₂. When CO was introduced into the polymerization system, it could suddenly adsorb on the active centers. The coordination of CO with Ti metal inducing the insertion of CO molecules into Ti-C bond as exhibited in Figure 2.11. Nevertheless, coordinated CO at active centers could copolymerize with olefins. More CO molecules were also presented in the polymer chains. If CO was eliminated from the reaction, the polymerization will recover again while inserted CO molecules were not lost. The coordination of CO₂ at the active centers was similar to CO as demonstrated in Figure 2.12. However, CO₂ can react with organometallic compound, this case was not observed in the case of CO.

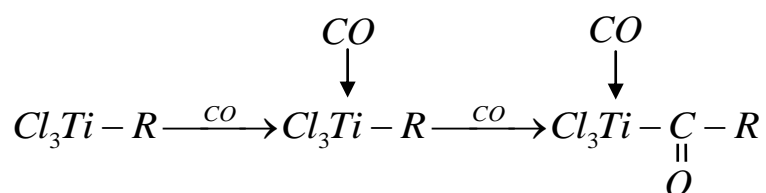


Figure 2.11 The coordination of CO at active centers [22]

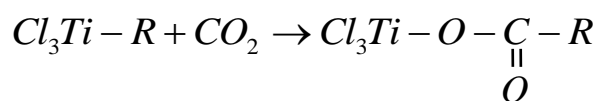


Figure 2.12 The reaction of CO₂ with Ti-R centers [22]

John et al., 1988 and 1991 [23-24] found that the displacement of chemisorbed CO on Ni(100) and Pt (111) metals could be take place when hydrogen was introduced into the system. These effects were confirmed by temperature programmed displacement (TPD) and *temperature-programmed sulfidation* (TPS) instruments. After hydrogen presented in the reaction, CO molecules was removed from the metals. They have been proposed that hydrogen will coadsorb with CO and form the crowding island leading to displace CO molecules from catalyst surface. This phenomenon was the thermal activation, the higher temperature the higher CO removal.

Garoff et al., 2002 [25] studied the deactivation effect of hydrogen in ethylene polymerization with different types of Ziegler-Natta catalyst. The aim of their research was to investigate the effect of hydrogen compared with Kissin's theory. According to this theory, hydrogen formed Ti-H bond and generated β -agostic interaction at active centers around 90% as revealed in Figure 2.13. Only 10% of Ti centers could continue the polymerization. The activity was also decreased. This effect was observed when smalls of hydrogen was used in their study.

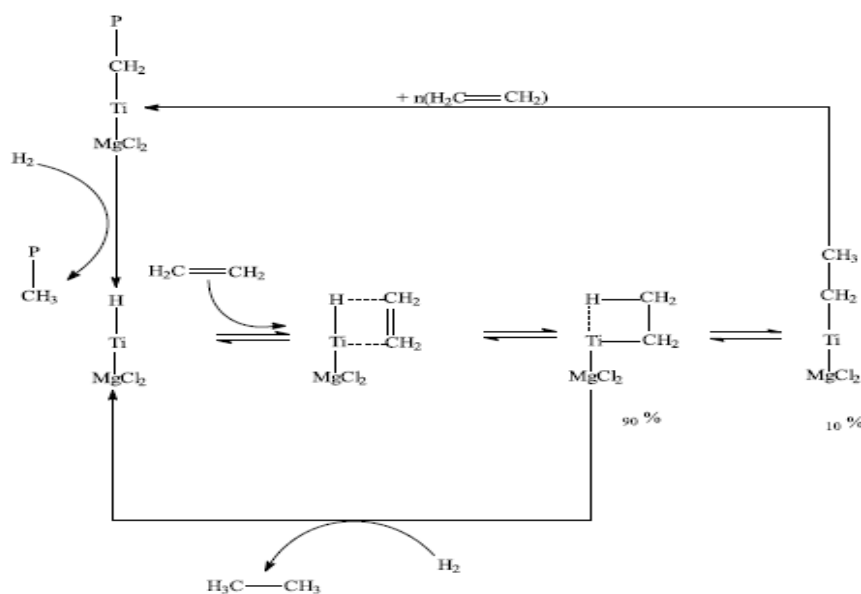


Figure 2.13 Deactivation effect by hydrogen in ethylene polymerization [25]

Nuyken et al., 2006 [26] reviewed the influence of water by using Ziegler-Natta catalyst based on Nd metal during butadiene polymerization. From their results, with increasing amounts of water the conversion of butadiene enhanced to the maximum value whereas molecular weight and molecular weight distribution depressed. In addition, they have been claimed that Al/H₂O at 2:1 was the optimal mol ratio. The reaction of water and alkylaluminum compound formed the highly active alumoxane which contribute the overall activity.

Edward et al., 1969 [27] intended to modified the properties of polyethylene products by employing water into Ziegler-polymerization. The results found that water improved melt index properties and narrow molecular weight distribution of polymers. They mentioned that water inhibited the reduction of Ti⁴⁺ to Ti³⁺ to Ti²⁺, it is widely accepted that Ti³⁺ and Ti²⁺ are actived for ethylene polymerization especially Ti²⁺. Hence, the initial number of polymerization sites was also minimized.

Wang et al., 2006 [28] investigated the variation effects of cocatalyst in propylene polymerization. Different oligomeric degree of EAOs can synthesize from the different ratio of TEA and water. For this investigation, the ratio of Al/H₂O at 2: 1 exhibited the maximum activity, higher than TEA and other Al/H₂O ratios, especially when the polymerization temperature was performed over than 90 °C.

Andrew et al., 2005 [29] have been studied the determination of active centers by using tritiated ethanol (CH₃CH₂OH) as a quenching agent. The polymerization was carried out with fourth and fifth generation of Ziegler Natta catalysts during propylene polymerization. The result demonstrated that alcohol will react with propagation centers and form alkoxide species as exposed in Figure 2.13.

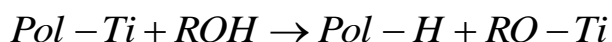


Figure 2.14 The reaction of alcohol at polymer propagation centers [29]

Besides, they claimed that if CO was chosen as quenching agent in the reaction instead of alcohol, lower active centers concentration was obtained. Although CO could suddenly stop the polymerization but it had the side reaction by copolymerization with monomer resulted into multiple CO insertion into the polymer chain.

Tangjituabun et al., 2008 [30] studied the effect of methanol on the activity and stereospecificity of synthetic catalyst during propylene polymerization. The results were demonstrated that methanol was the poisoning material which reduced the activity of catalyst due to the reaction of its with TiCl_4 resulting in generation of inactive species as titanium alkoxide. Furthermore, an activation power of cocatalyst decreased causing from its reaction with HCl. It was more interesting that the kinetic parameter could be obtained by stopped flow method. Methanol reduced the number of active centers whereas the stereospecificity of polypropylene was not changed.

John, 2003 [31] studied and characterized the industrial catalyst decay. In his research, he has been shown the kinetic of catalyst decay based on the power-law expressions. Moreover, he also found that the decay of catalysts mainly depended upon operating condition and catalyst design. The decay rate of catalysts was slow when isothermal or adiabatic reactor was preferably selected. Indeed, the position of reactants injection and preparation of guard bed also helped to reduce the catalyst decay in industrial operation as well.

Hideharu et al., 1999 [32] interested in the hydrogen effect on propylene polymerization. Their effect was focused on the activity, molecular weight, molecular weight distribution, kinetic behavior and stereospecificity. The kinetic behavior of each catalyst was shown in rate-time profile. The average decay rate of each sample could be determined from the slope of profile in the decay period.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

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

1. Chemically pure grade of ethylene (C_2H_4) was used as received from Thai Industrial Gas Co., Ltd.
2. High purity carbon dioxide (99.5%) was purchased from Thai Industrial Gas Co., Ltd. and used without further purification.
3. High purity carbon monoxide (99.5%), purchased from Thai Industrial Gas Co., Ltd. and used without further purification.
4. Ultra high purity methane (99.99%) was used without purification from Air Gas Co., Ltd.
5. Ultra high purity acetylene (99.99%) was used as received from Praxair Co., Ltd.
6. Propylene (99.35%) was donated from Thai Polyethylene Co., Ltd. and used as received.
7. Ultra high purity of argon (99.999%) was purchased from Thai Industrial Gas Co., Ltd. and used without further purification.
8. Commercial grade of n-hexane was supplied from Thai Polyethylene Co., Ltd.
9. Triethylaluminum (TEA) diluted in hexane solution 209 mmol/l, supplied from Thai Polyethylene Co., Ltd.
10. A commercial Ziegler-Natta catalyst ($TiCl_4/MgCl_2$) was supplied from Thai Polyethylene Co., Ltd.
11. Hydrochloric acid (Fuming 36.7%), was purchased from SR lab and used as received.
12. Commercial grade of methanol, was purchased from SR lab and used as received.

13. Anhydrous methanol was purchased from CT chemical and used without further purification.
14. Ultra high purity hydrogen (99.99%) was purchased from Thai Industrial Gas Co., Ltd. and used without further purification

n-Hexane, TEA and a commercial catalyst were denoted as solvent, cocatalyst and catalyst, respectively. They were kept and operated under an argon atmosphere via glove box and glove bag.

3.2 Ethylene polymerization

Ethylene polymerization was carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer and connected with ethylene and hydrogen feed line. To avoid the side effect of moisture and oxygen, reactor and all feed lines required to purify by evacuation and purging many times before used.

For gas impurities : CO, CO₂, CH₄, C₃H₆ and C₂H₂

In the glove box, a desired amount of n-hexane (25ml), triethylaluminum (5ml) and solid catalyst (the molar ratio of Al/Ti = 140) were prior added into the reactor. Then, the reaction was frozen in liquid nitrogen to stop the reaction of catalyst and cocatalyst. The reactor was evacuated to remove the remaining argon. After ethylene saturated in solvent, a required amount of impurity was injected into the reactor by gas syringe at 30 °C and atmospheric pressure. The polymerization was performed at 80 °C. Polymerization was started by feed ethylene at constant pressure of 50 psi. After ethylene was consumed at 18 mmol (or 30 cm³ which observed from mass flow meter), the reaction was terminated by venting the reactor and adding acidic methanol. The polymer obtained was filtered and dried.

For liquid impurities : H₂O and CH₃OH

The polymerization method for liquid impurities was identical with polymerization method of gas impurities, but different in the step of impurity addition. After termination of the activation reaction in liquid nitrogen, we also injected the liquid phase compound followed by removing the remain argon in reactor. So, in this method we had not fed ethylene to saturate in hexane as same as gas impurities method.

A difference in the polymerization step between gas and liquid impurity can be explained by following details: due to the polymerization cannot operate if argon remained in the reactor. So, the injection of gas impurity before argon evacuation was not a suitable procedure because both of impurity and argon will be removed from the reactor. However, to ensure that some molecules of moisture and oxygen cannot enter into the system during impurity addition through the vacuum state inside of the reactor. Feeding of ethylene to saturate in the reactor after the argon evacuation followed by an addition of gas impurity was a suitable solution in our studied.

A required amount of hydrogen (0.1 bar) was fed into the reactor after the impurity injection both in gas and liquid impurity systems (the reported value of hydrogen pressure was converted from 1 bar of hydrogen which was observed from pressure gauge at the polymerization line). The polymerization steps of gas and liquid impurity were shown in Figures 3.1 and 3.2, respectively.

Ethylene consumption profile during the polymerization was monitored by mass flow meter (Kofloc model) to obtain the direct kinetic data from the experimental [15]. The data was plotted in the coordinates of "ethylene consumption rate (cm³/sec) vs polymerization time (sec)". Due to the experiment was fixed the ethylene consumption at 18 mmol, the polymerization time was also an important parameter to define the activity of catalyst. Finally, the abbreviations of each sample in this study were reported in Table 3.1.

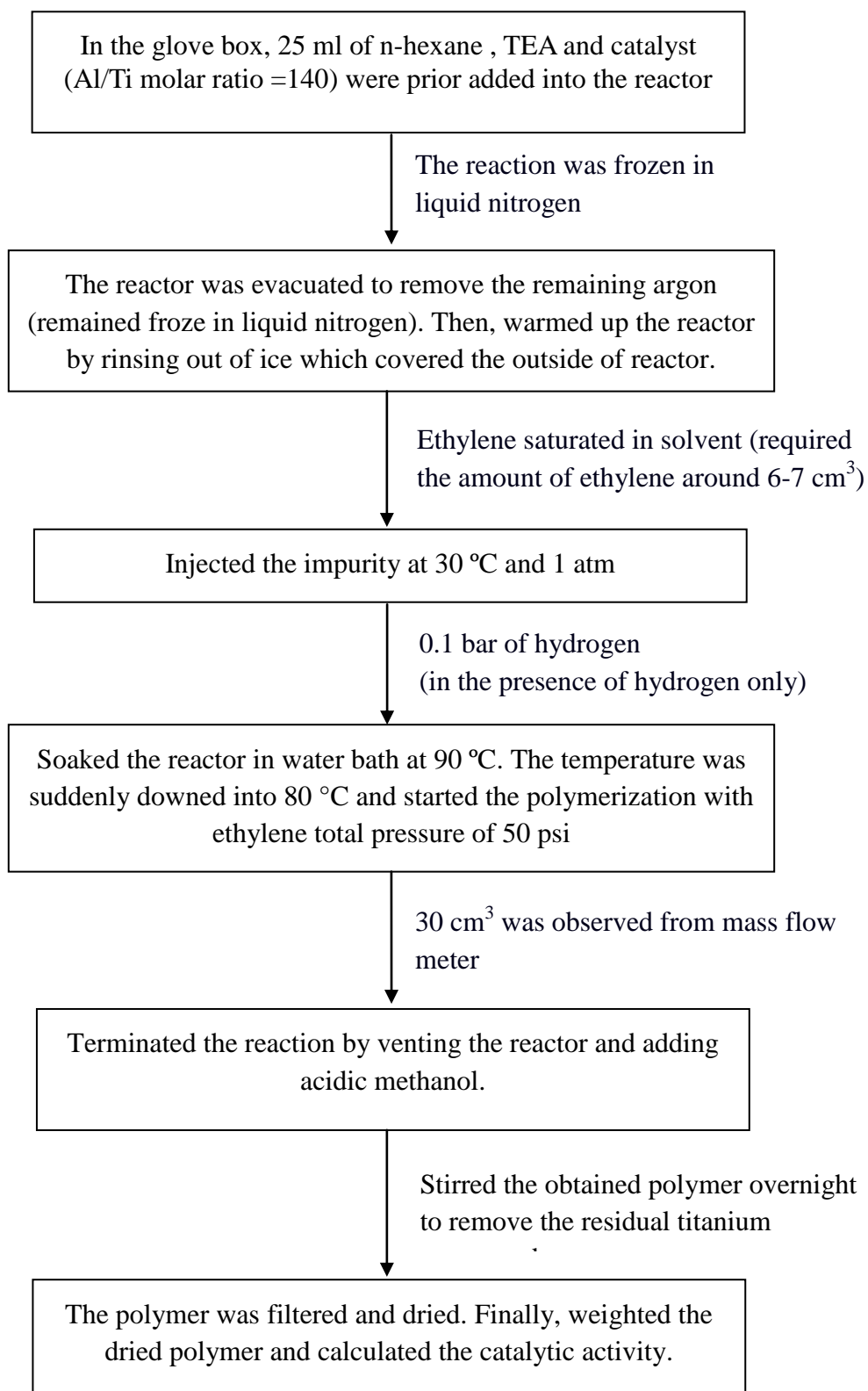


Figure 3.1 Polymerization steps for gas impurity system

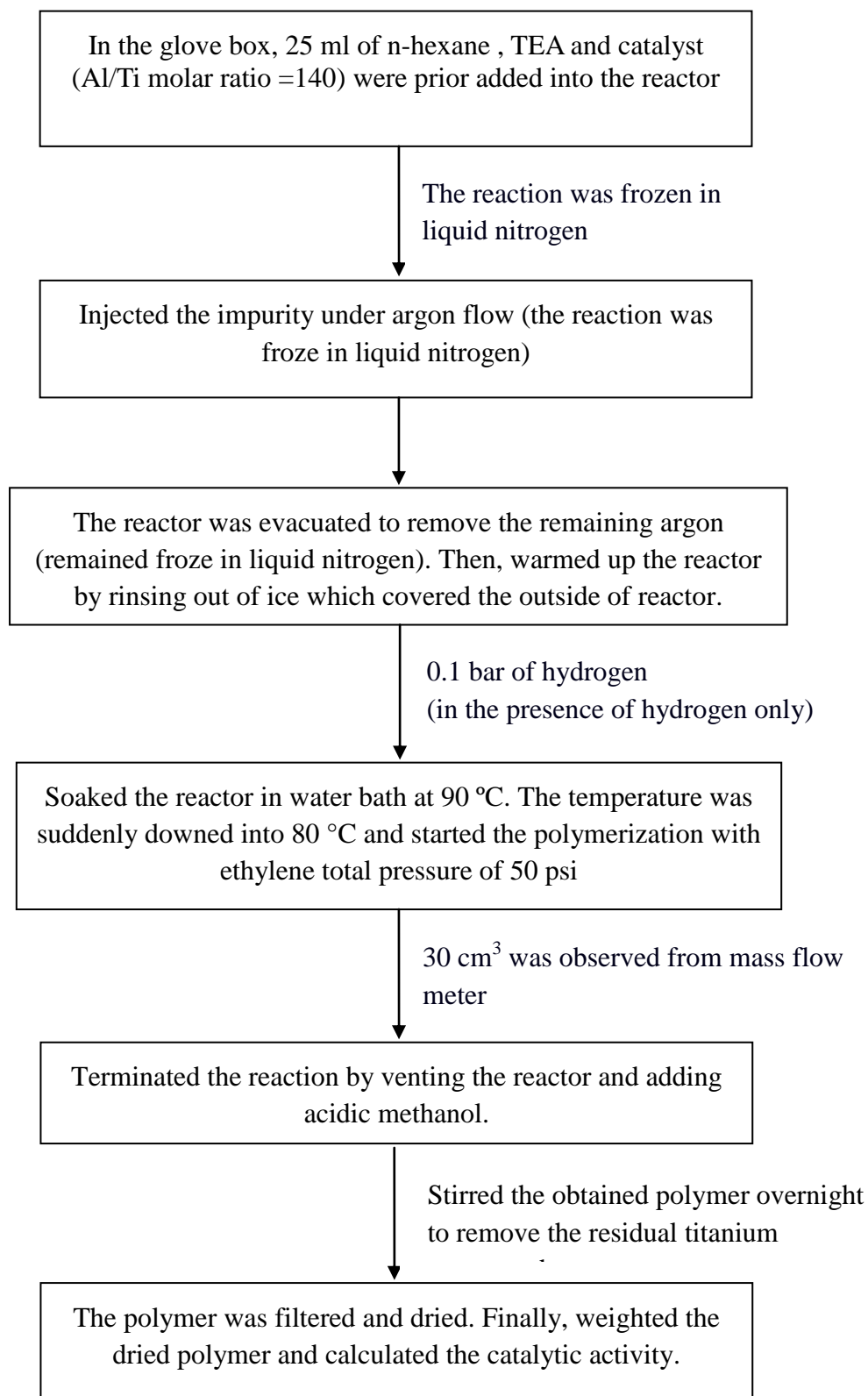


Figure 3.2 Polymerization steps for liquid impurity system

Table 3.1 The abbreviation symbols of all samples

Abbreviation	Detail
ZN/pure	Blank sample for gas impurity system
ZN/CO	CO addition with ZN catalyst
ZN/CO ₂	CO ₂ addition with ZN catalyst
ZN/CH ₄	CH ₄ addition with ZN catalyst
ZN/C ₃ H ₆	C ₃ H ₆ addition with ZN catalyst
ZN/C ₂ H ₂	C ₂ H ₂ addition with ZN catalyst
ZN/pure liq	Blank sample for liquid impurity system
ZN/H ₂ O	H ₂ O addition with ZN catalyst
ZN/CH ₃ OH	CH ₃ OH addition with ZN catalyst

3.3 Characterization

3.3.1 Inductive Couple Plasma (ICP)

Inductively coupled plasma atomic emission spectroscopy equipment (ICP-OES optima 2100 DV from PerkinElmer) was used to find the total amount of titanium in bulk. The catalyst was digested with hydrofluoric acid (HF) and the mixtures were stirred overnight. After catalyst was completely dissolved, the solution sample was diluted with DI water.

3.3.2 Differential scanning calorimetry (DSC)

The melting temperature (T_m) and crystallinity (X_c) of polyethylene were determined by Perkin-Elmer diamond DSC as revealed in Figure 3.3. The characterizations were performed at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ in the temperature

range of 50–200 °C. The samples were heated and cooled to room temperature in the first scan. Then, heated the sample again at the same rate. Due to avoidance of any impurities in samples of first scan. So that the result of the second scan was only reported. The crystallinity of polymers was calculated by the heat of fusion parameter as shown in the equation (3-1) ;

$$X_c = \frac{H_m}{H_p} \times 100 \quad (3-1)$$

Where, H_m is the enthalpy of tested samples

H_p is the enthalpy of a totally crystalline polyethylene, was assumed to be 293 J/g [33,34]

X_c is the percent crystallinity of the samples



Figure 3.3 Perkin-Elmer diamond DSC machine

3.3.3 Gel permeation chromatography (GPC)

Molecular weight and molecular weight distributions of polymers were determined by using a high temperature GPC (Waters 150-C) equipped with a viscometric detector. The characterization was performed at 140°C and used 1, 2, 4-trichlorobenzene as a solvent

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effects of impurities on ethylene polymerization

4.1.1 Impurities affecting the catalytic activity

In this study, we intended to investigate the influence of impurities found in ethylene, which were injected during ethylene polymerization, on the commercial catalyst activity. Impurities can be classified into the following groups: gas and liquid impurities. The former group was composed of CO, CO₂, CH₄, C₃H₆ and C₂H₂, while H₂O and CH₃OH were categorized in latter group. They have a high potential for poisoning to Ziegler-Natta catalyst by the coordination of lone pair electron at the vacant sites of active centers. This phenomenon reduced the catalyst efficiency leading to catalyst deactivation. Thus, we were also interested in impurity effect based on the fact that each type of impurity differently affected on the activity. The molecular structures of all impurities were shown in Figure 4.1 and Figure 4.2, respectively.

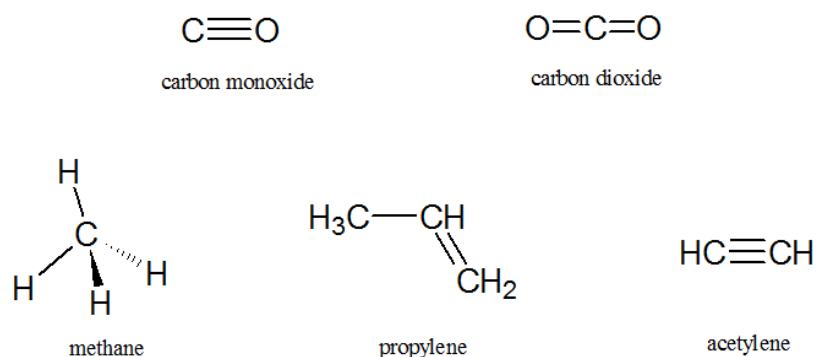


Figure 4.1 Molecular structures of different types of gas impurities

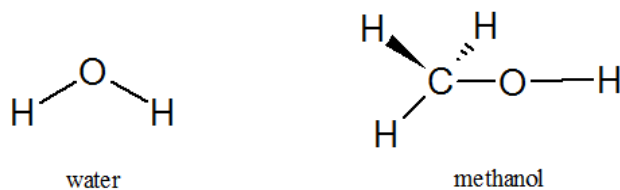


Figure 4.2 Molecular structures of different types of liquid impurities

(1) Effects of gas impurities on the catalytic activity both in the absence and presence of hydrogen

The ethylene polymerization was performed in 100 ml semi-batch reactor with impurity gas additions. A small amount of impurities with impurity/Ti molar ratio of 0.54 was prior selected. In the presence of hydrogen, a desired amount of hydrogen (0.1 bar) was fed into the reactor according to the reported method in Chapter III. The results were demonstrated in Table 4.1.

In the absence of hydrogen, CO exhibited the strongest retardation and maximized activity loss. It could deprive the activity by 39%. It was typically accepted that CO was strongly chemisorbed on the vacant sites of active centers. Adsorbed CO molecules blocked the coordination of ethylene and interrupted the polymer propagation caused in highly reduced the activity [16,18,22]. Its behavior seems to be a selective poisoning [18,22].

In the case of CO₂, although it was also selectively adsorbed on the active centers similarly to CO, but the side reaction between CO₂ and triethylaluminum was formed the ethyl derivative, which reduced the power of CO₂ poisoning [4,22]. Therefore, CO₂ had a less effect on the activity than CO. This result was consistent with Lesna et al. [18]

The effect of CH₄ in the presence of Ziegler-Natta catalyst was considered to be analogous with the reaction of hydrogen at active centers, so called methylation reaction [17]. The interaction of CH₄ with complex catalyst generated the methyl derivative (Ti-CH₃) at titanium centers, which interrupted the polymer propagation. The activity was also found to have only little effect [8].

While the influence of C₃H₆ and C₂H₂ was opposed to CO, CO₂ and CH₄, it can be rationalized by the fact that the injection of C₃H₆ and C₂H₂ at the beginning of polymerization can enhance the activity by 10 and 31%, respectively [10,15,19-21]. This effect can be elucidated by the copolymerization of its with ethylene, which was saturated in the mixture before the polymerization started. As a result of lower steric effect of C₂H₂, it also inserted into the polymer chain faster than C₃H₆. The next ethylene molecules could easily diffuse through the less crystalline polyethylene layer, which covered on the catalyst surface resulted in more ethylene concentration around the active centers [21]. However, the effect of C₂H₂ in this study was unusual for available literature reports. In contrast to the copolymerization of ethylene and C₃H₆, this was in good agreement with the observation of many literatures [15,21].

It was observed that the activity decreased substantially in the order of: ZN/C₂H₂ > ZN/C₃H₆ > ZN/pure > ZN/CH₄ = ZN/CO₂ > ZN/CO. It can also be said that CO, CO₂ and CH₄ retarded the ethylene polymerization, while C₃H₆ and C₂H₂ enhanced the activity in the absence of hydrogen.

Table 4.1 Catalytic activity of all gas impurities on two systems, absence and presence of hydrogen, at low impurity content^a

Sample	Absence of hydrogen (kgPE/molTi.h)	Presence of hydrogen ^b (kgPE/molTi.h)	Activity ratio ^c
ZN/pure	1253	1180	0.94
ZN/CO	762	1120	1.47
ZN/CO ₂	1108/970 ^d	975/783 ^d	0.81
ZN/CH ₄ (alkane)	1122	1077	0.96
ZN/C ₃ H ₆ (alkene)	1382	1156	0.84
ZN/C ₂ H ₂ (alkyne)	1643	987	0.60

^aAddition of impurities to impurity/Ti molar ratio = 0.54

Slurry ethylene polymerization was carried with Al/Ti molar ratio = 140, polymerization temperature : 80 °C and ethylene pressure : 50 psi

^bAddition of hydrogen at 0.1 bar

^cCalculated by the ratio of activity between presence and absence of hydrogen

^dNew experiment data which used to compare the result between presence and absence of hydrogen

A decrease in activity of ZN/pure in the presence of hydrogen can be explained by Kissin's theory as shown in Figure 4.3 [25]. This model described the formation of β -agostic coordination at Ti metal which reduced the number of polymerization sites in ethylene polymerization. After Ti-C₂H₅ active center was formed, short chains polyethylene were generated at the surface of catalyst by the reaction of catalyst and ethylene molecules that saturated in hexane. When hydrogen was fed into the reaction system, hydrogen could interact at Ti-center and form Ti-H bond. The first ethylene molecule that fed to start the polymerization also changed Ti-H bond into two structures: Ti in the complex of β -agostic coordination and Ti in open form. No polymerization can be take place from β -agostic inactive sites whereas the latter compound was capable of inserting of ethylene molecules.

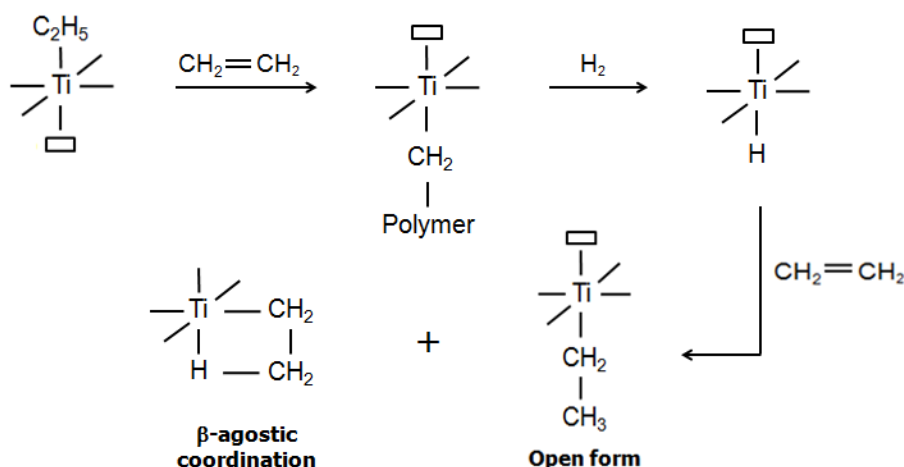


Figure 4.3 A decrease in catalytic activity of ZN catalysts caused by hydrogen [15,25]

From Table 4.1, we found that impurities were affected on the hydrogen influences which can be classified into three groups; activity has increased, decreased and unaffected. The discovery of β -agostic coordination contributed to explanation of the role of hydrogen on impurity effects as follows:

In the first group, it was observed that the activity increased in the case of CO. It was also interesting that why the strongest poisoning compound like CO did not have twice the effect when hydrogen also presented in the polymerization system. This ambiguity can be explained by John and coworkers's studies [23-24]. When CO was introduced into the system, CO could suddenly coordinate at the active centers through the triple bond. However, CO molecules were displaced from Ti metal when hydrogen introduced into the reaction leading to regenerate the fresh active sites as shown in Figure 4.4. Several hydrogen atoms required in the displacement of each CO molecules [24].

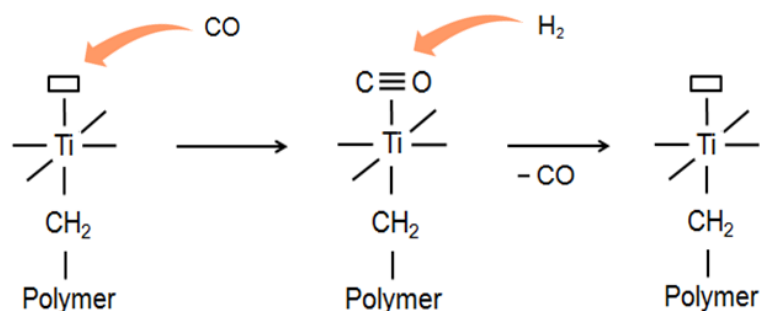


Figure 4.4 A plausible model of the displacement of CO by hydrogen

In the second group, the activity was highly decreased in the presence of hydrogen causing from the effects of hydrogen and impurity. The list of this group consisted of CO_2 , C_3H_6 and C_2H_2 . According to hydrogen interrupted the copolymerization of C_3H_6 and C_2H_2 by generating the β -agostic coordination at Ti centers that reduced the insertion rate of C_3H_6 and C_2H_2 into the polyethylene chains [25]. The activity also decreased when comparing with the data in the absence of hydrogen. For a selective poisoning of CO_2 , the presence of hydrogen led to maximum loss in the activity because twice the effect from β -agostic coordination combined with CO_2 poisoning. CO_2 molecules could adsorb onto the vacant of active centers in Ti open form. A decrease in the activity of CO_2 , C_3H_6 and C_2H_2 was shown in Figures 4.5 and 4.6, respectively.

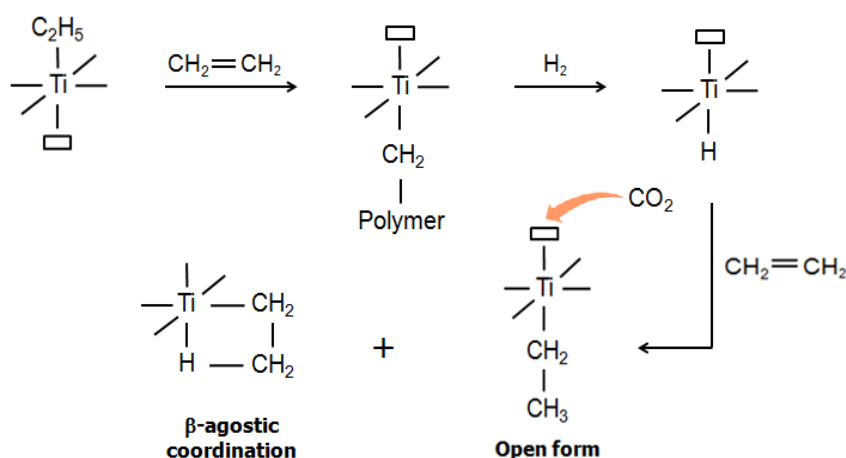


Figure 4.5 A plausible model of CO_2 poisoning and β -agostic coordination

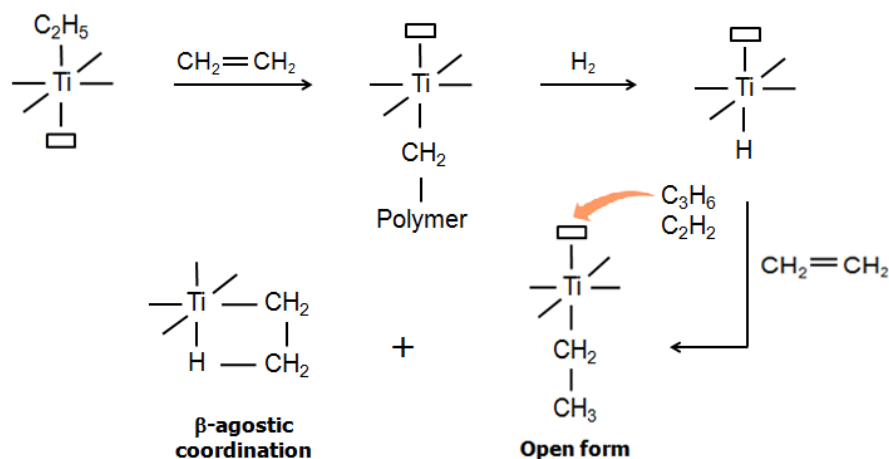


Figure 4.6 A plausible model of copolymerization of C_3H_6 and C_2H_2 in the section of Ti open form

At last, it is widely known that hydrogen manifested the highest reactivity [17]. Thus, an addition of CH_4 and hydrogen into the reaction, hydrogen could coordinate at the active centers and form Ti-H bond faster than CH_4 . However, hydrogen may be replaced by CH_4 in the hydrogenation of ethylene [17]. Methyl-derivative (Ti- CH_3 bond) was generated as the product of this reaction as same as in the absence of hydrogen. The activity was unaffected by hydrogen together with CH_4 . A plausible model to describe this effect is shown in Figure 4.7.

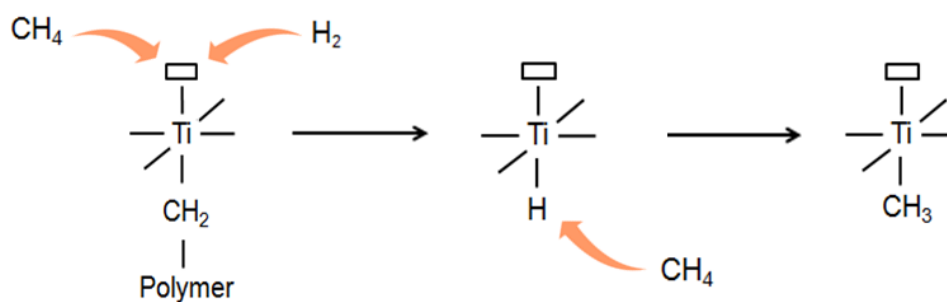


Figure 4.7 A plausible model of replacement of hydrogen by CH_4

In order to clarify the effect of impurities on hydrogen at high impurity content. Gas impurity/Ti molar ratio at 1.07 was selected. The results between in the absence and presence of hydrogen are shown in Table 4.2.

Table 4.2 Catalytic activity of all gas impurities on two systems, absence and presence of hydrogen, at high impurity content^a

Sample	Absence of hydrogen (kgPE/molTi.h)	Presence of hydrogen ^b (kgPE/molTi.h)	Activity ratio ^c
ZN/pure	1253	1180	0.94
ZN/CO	653	820	1.26
ZN/CO ₂	1083/998 ^d	1034/785 ^d	0.79
ZN/CH ₄ (alkane)	1099	999	0.91
ZN/C ₃ H ₆ (alkene)	1318	1119	0.85
ZN/C ₂ H ₂ (alkyne)	1327	891	0.67

^aAddition of impurities to impurity/Ti molar ratio = 1.07

Slurry ethylene polymerization was carried with Al/Ti molar ratio = 140, polymerization temperature : 80 °C and ethylene pressure : 50 psi

^bAddition of hydrogen at 0.1 bar

^cCalculated by the ratio of activity between presence and absence of hydrogen

^dNew experiment data which used to compared the result between presence and absence of hydrogen

As seen in Table 4.2, hydrogen increased the activity in the case of CO. This effect can be interpreted in the term of the CO displacement by hydrogen similar to the impurity content at 0.54. Contrary with other compounds, the activity decreased in the presence of hydrogen. A decrease in the activity was mainly related to the formation of β -agostic coordination which reduced the insertion rate of C₃H₆ and C₂H₂ into PE chains or combined with CO₂ poisoning in the case of CO₂. While in the case of CH₄, the higher the CH₄ content the higher the Ti-CH₃ bonds. The activity

was decreased due to high amounts of Ti-CH₃. This center had a lower reactivity in the polymer chain growth and generated by the replacement of hydrogen by CH₄ [17].

A comparison in the activity of hydrocarbon compounds was also investigated in this study. CH₄, C₃H₆ and C₂H₂ were used to represent a compound in the group of alkane, alkene and alkyne, respectively. It was found that alkyne relatively highest affected on catalytic activity, followed by alkene and alkane. This trend was observed both in the absence and presence of hydrogen.

(2) Effects of liquid impurities on the catalytic activity both in the absence and presence of hydrogen

In order to study the effect of liquid impurities on the activity of a commercial catalyst. The polymerization was also performed in 100 ml reactor. A desire amount of liquid impurities consisted of H₂O or CH₃OH was injected during ethylene polymerization. Hydrogen (0.1 bar) was fed into the reactor in the presence of hydrogen. The amounts of impurity with the molar ratio of impurity/Ti of 16.43 were prior chosen. The results are shown in Table 4.3.

As seen from Table 4.3, the activity of all samples is similar to the absence of hydrogen. This phenomenon was considered to be due to the complete reaction between impurities and triethylaluminum [9]. Hence, we can said that the activity was not affected by CH₃OH and H₂O at impurity content of 16.43 in the absence of hydrogen.

In the presence of hydrogen, low activity in the presence of hydrogen of ZN/pure liq was observed. This effect can be elucidated by the formation of β -agostic coordination at Ti-center which reduced the number of polymerization sites as we mentioned previously [25].

Table 4.3 Catalytic activity of all liquid impurities on two systems, absence and presence of hydrogen, at low impurity content^a

Sample	Absence of hydrogen (kgPE/molTi.h)	Presence of hydrogen ^b (kgPE/molTi.h)	Activity ratio ^c
ZN/pure liq	1661	1018	0.61
ZN/H ₂ O	1571	1175	0.75
ZN/CH ₃ OH	1747	1345	0.77

^aAddition of impurities to impurity/Ti molar ratio = 16.43

Slurry ethylene polymerization was carried with Al/Ti molar ratio = 140, polymerization temperature : 80 °C and ethylene pressure : 50 psi

^bAddition of hydrogen at 0.1 bar

^cCalculated by the ratio of activity between presence and absence of hydrogen

It was found that the activity increased obviously in the order of: ZN/CH₃OH > ZN/H₂O > ZN/pure liq. It can be noticed that H₂O and CH₃OH enhanced the activity by 15% and 32%, respectively. Even though both of them can increase the activity, but the activity was still lower than the absence of hydrogen because the reduction in the polymerization sites from β -agostic coordination. The enhancement in the activity may be possibly due to the fact that the reaction of H₂O or CH₃OH with triethylaluminum could obstruct some parts of β -agostic coordination.

At high impurity content, the ratio of H₂O/Ti at 59.10 and CH₃OH/Ti at 26.29 were chosen in order to clarify the effect of impurity on the activity both in the absence and presence of hydrogen. The results are shown in Table 4.4.

In the absence of hydrogen, it was clear that an addition of H₂O to impurity content at 59.10 could contribute to beneficial effect of activity. It may be plausibly described that the reaction between H₂O and triethylaluminum formed the highly active ethylaluminumoxane (EAO) which boosted the activity up by 19% [4,26,28]. This phenomenon should be occurred when the ratio of cocatalyst and H₂O was closed to 2:1 [4,26,28]. In the case of CH₃OH, the reduction of activity was observed. It was

reported that CH₃OH destroyed the titanium active centers by reacting with TiCl₄ and produced the inactive specie as Ti-alkoxide to inhibit the ethylene polymerization [22,29,30]. In addition, it also generated HCl which reduced an activation ability of TEA [30]. The activity was highly deprived.

Table 4.4 Catalytic activity of all liquid impurities on two systems, absence and presence of hydrogen, at high impurity content^a

Sample	Absence of hydrogen (kgPE/molTi.h)	Presence of hydrogen ^b (kgPE/molTi.h)	Activity ratio ^c
ZN/pure liq	1661	1018	0.61
ZN/H ₂ O [59.10]	2038	1411	0.69
ZN/CH ₃ OH [26.29]	1458	1026	0.70

^aRatio of impurity was exposed as a number in square brackets

Slurry ethylene polymerization was carried with Al/Ti molar ratio = 140, polymerization temperature : 80 °C and ethylene pressure : 50 psi

^bAddition of hydrogen at 0.1 bar

^cCalculated by the ratio of activity between presence and absence of hydrogen

In the presence of hydrogen, it was cleared that the injection of H₂O or CH₃OH was affected on the activity similar to the absence of hydrogen. Low activity was also observed in the presence of hydrogen due to the formation of β -agostic coordination. However, hydrogen had a beneficial effect on the activity in the case of H₂O and CH₃OH. These effects may be described by the reaction of impurities with TEA that could obstruct some parts of β -agostic coordination.

4.1.2 Impurities affecting the ethylene consumption rate

In order to get the better understanding of the influence of impurities. The kinetic behavior can be interpreted in terms of ethylene consumption rate profile. Consumption rate profile of CO, CO₂, CH₄, C₃H₆ and C₂H₂ with impurity content of 0.54 in the absence of hydrogen is shown in Figure 4.8. It can be stated that all

samples had a similar profile shape, but different in decay and active center formation rate (at the initial of profile). This indicated that impurities only affected on the activity without putting an effect on the shape of ethylene consumption rate profile [6-7].

For ZN/pure sample used as a reference, the active center formation rate was rapidly formed and followed by a drastic decay. When CO was introduced into the reaction system, the active centers were formed much more slowly due to the fact that CO could suddenly chemisorb on the active centers [16,18,22]. This effect reduced the available number of polymerization sites and decreased the activity. In the part of experiment, ethylene consumption was fixed at 18 mmol. Therefore, the longest polymerization time was also observed in the case of CO. While for CO₂ and CH₄, the polymerization time was found to be a little different from reference sample. The activity was also dropped slightly.

The presence of C₃H₆ at the beginning of polymerization can accelerate the rate of active center formation more than reference sample giving rises to enhance the activity [15]. However, C₂H₂ formed the active center slower than reference, but the lowest polymerization time led to obtain the highest activity.

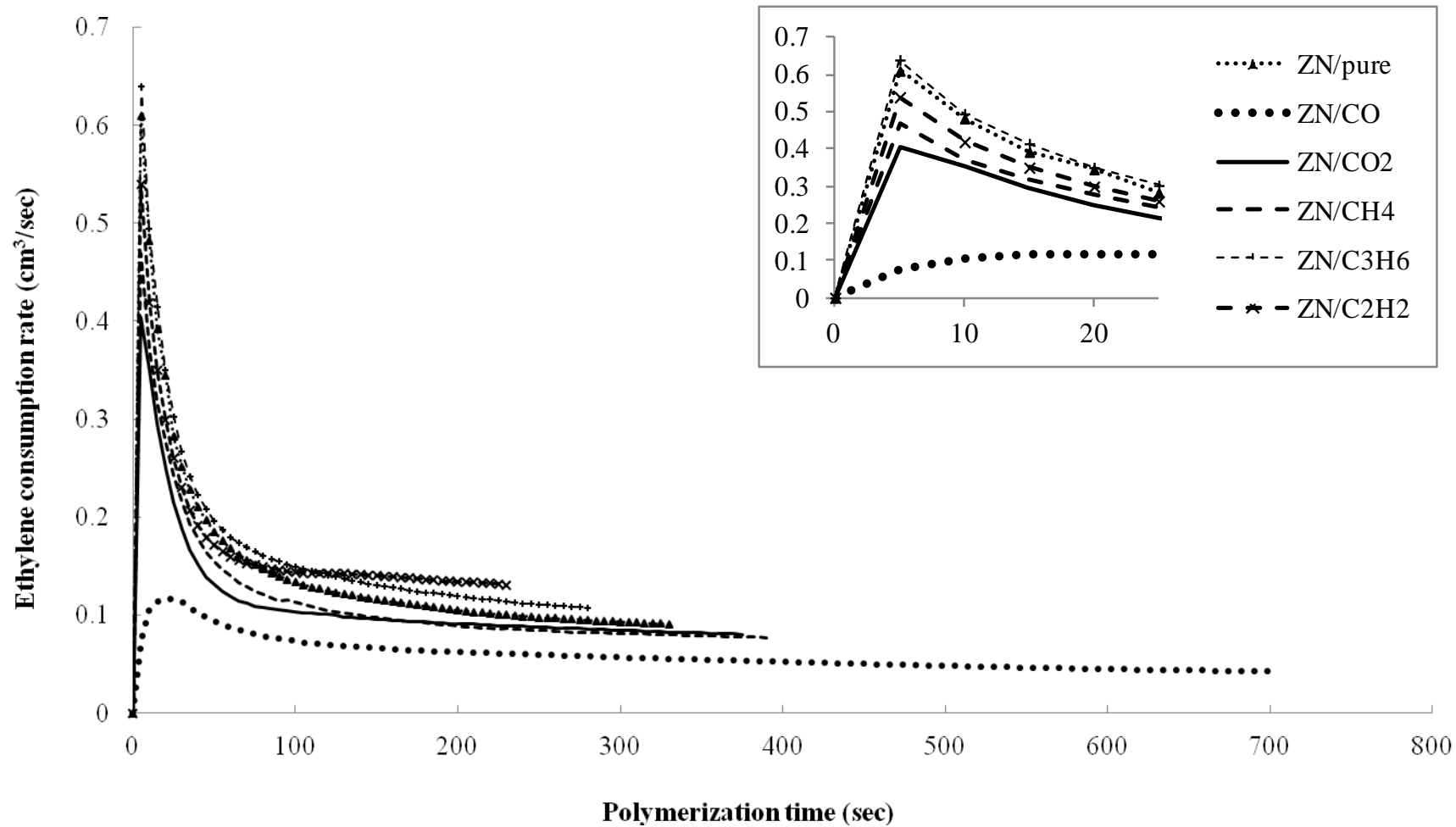


Figure 4.8 Ethylene consumption rate profile of gas impurities compared with reference sample (absence of hydrogen)

A comparison of ethylene consumption rate profile between the absence and presence of hydrogen of ZN/pure and ZN/pure liq are shown in Figures 4.9 and 4.10, respectively. We found that hydrogen affected on the active center formation rate. Decreasing in the maximum rate value in the presence of hydrogen was observed in both samples. This behavior was widely seen when using Ti-based catalysts in ethylene polymerization [15].

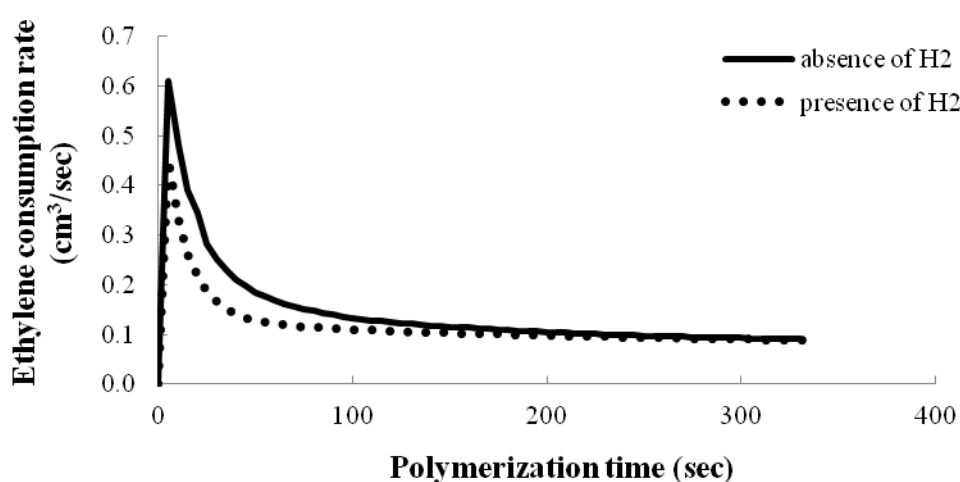


Figure 4.9 Ethylene consumption rate profile of ZN/pure in the absence and presence of hydrogen

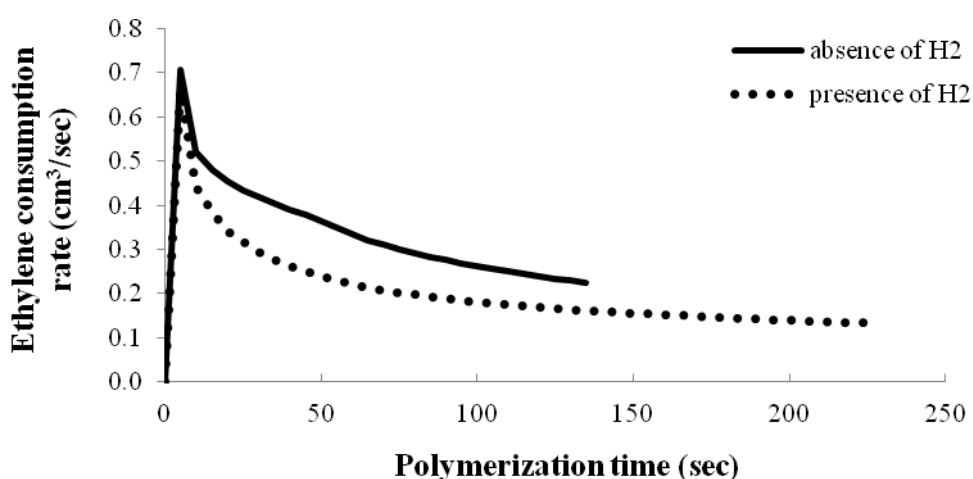


Figure 4.10 Ethylene consumption rate profile of ZN/pure liq in the absence and presence of hydrogen

A comparison of ethylene consumption rate profiles of gas impurities with impurity content of 0.54 between the absence and presence of hydrogen are shown in Figure 4.11. It was demonstrated that the active center formation rate in the presence of hydrogen was higher than in the absence of hydrogen only in the case of CO. The explanation has been suggested with respect to the displacement of CO by hydrogen that increased the number of active centers leading to obtain the a high formation rate.

In the case of CO₂, the active center formation rate was not changed much, but long polymerization time in the presence of hydrogen led to obtain low activity. Contrary with CH₄, the active center formation rate in the presence of hydrogen was higher in the absence of hydrogen. A possible explanation was that the replacement of hydrogen by CH₄ was fast in the initial of reaction. However, the same polymerization time of two systems give rise to unchanged in the activity.

While for C₃H₆ and C₂H₂, the active center formation rate in the presence of hydrogen was lower than the absence of hydrogen. It might be rationalized by the fact that hydrogen and ethylene molecule could generate the β -agostic coordination that was inert in the polymerization process. This compound reduced the insertion rate of C₃H₆ and C₂H₂ into the PE chains resulting in produced a low ethylene consumption rate as seen at the initial of profile.

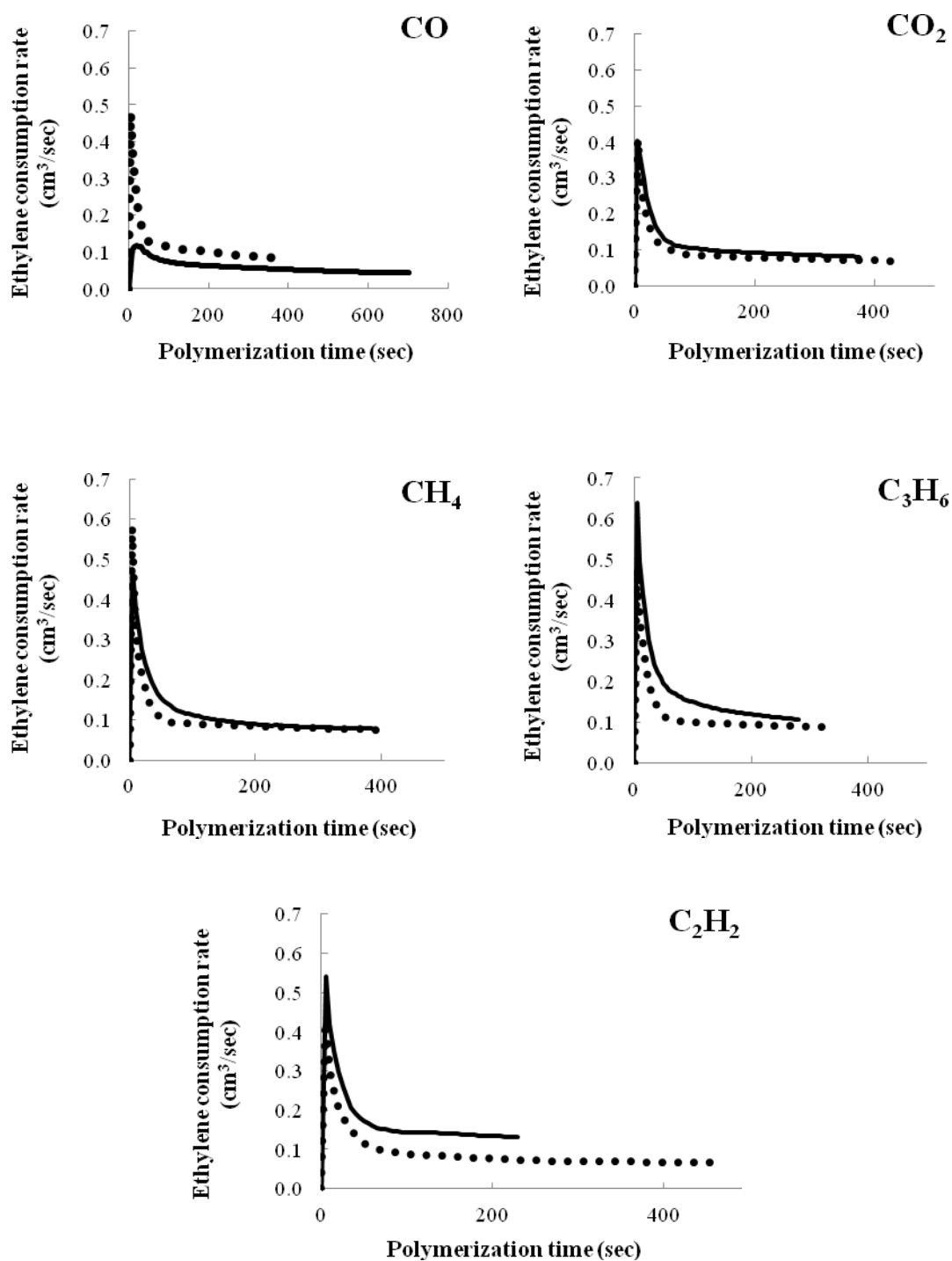


Figure 4.11 Ethylene consumption rate profile between the absence and presence of hydrogen at low impurity content of gas impurities (The solid and dotted line indicated the results in the absence and presence of hydrogen, respectively)

Ethylene consumption rate between alkane, alkene and alkyne was also compared and reported in Table 4.5. In the absence of hydrogen, the results were indicated that alkene produced the maximum rate of ethylene consumption, followed by alkyne and alkane, respectively. While in the presence of hydrogen, alkane produced the maximum ethylene consumption rate, followed by alkene and alkyne, sequentially.

Table 4.5 A comparison in ethylene consumption rate between alkane, alkene and alkyne

Sample	Absence of hydrogen	Presence of hydrogen
ZN/CH ₄ (alkane)	minimum	maximum
ZN/C ₃ H ₆ (alkene)	maximum	middle
ZN/C ₂ H ₂ (alkyne)	middle	minimum

Ethylene consumption rate profile of liquid impurities with impurity content of 16.43 in the absence of hydrogen is shown in Figure 4.12. It was cleared that the profile shape in this system was quite similar to the system of gas impurities. The active center was suddenly formed and followed by the decay period because this system had not required the saturation of ethylene into the reactor before injected the impurities. The maximum consumption rate of liquid impurities was higher than gas impurities. It can be seen that H₂O and CH₃OH did not affect the active center formation rate, but a slight difference in the polymerization time causing in no significantly changed in the activity was observed.

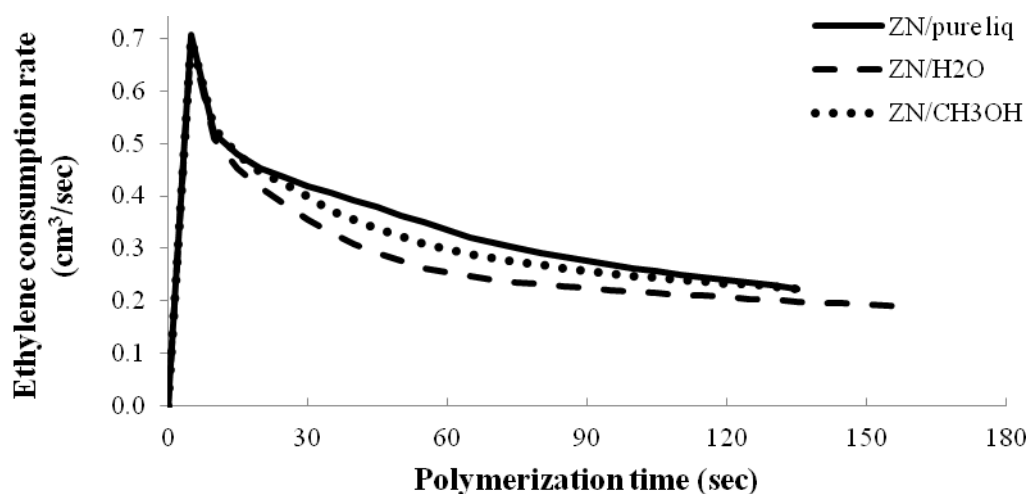


Figure 4.12 Ethylene consumption rate profile of liquid impurities compared with reference sample (absence of hydrogen)

A different in ethylene consumption rate profile of liquid impurities with impurity content of 16.43 between the absence and presence of hydrogen are shown in Figure 4.13. It was observed that the active center formation rate in the presence of hydrogen was lower than the absence of hydrogen both in H₂O and CH₃OH. It seems reasonable to suppose that the formation of β -agostic coordination, which formed by the addition of hydrogen and first ethylene molecule, was the main cause to explain this effect. Low activity in the presence of hydrogen was also observed.

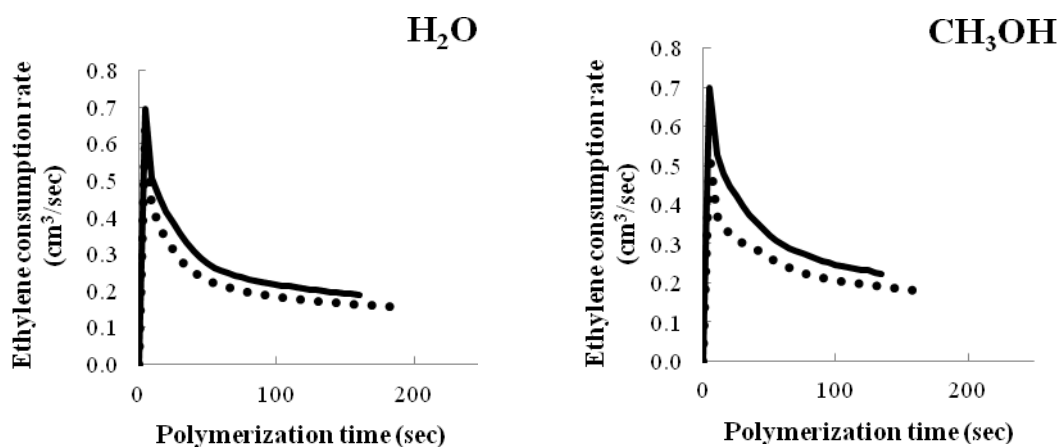


Figure 4.13 Ethylene consumption rate profile between the absence and presence of hydrogen at low impurity content of liquid impurities (The solid and dotted line indicated the results in the absence and presence of hydrogen, respectively)

4.1.3 Impurities affecting the deactivation rate

It is well known from literature that the decay rate of catalyst was mainly related to operating condition and the design of catalysts [31]. Thus, it was also interested that impurities could affect the catalyst decay or not. In order to obtain more details concerning the impurity effects the average decay rate of a commercial catalyst in the presence of each impurity was evaluated based on the method of Hideharu et al. [32]. For gas impurities, the average decay rate was estimated from slope of ethylene consumption rate profile in the decay period. The result values are reported in Table 4.6, while the values of liquid impurities are summarized in Table 4.8. The obtained data used the same calculation method to gas impurities.

It can be seen that impurities changed the decay rate of catalyst both in positive and negative ways. For gas impurities (at impurity content of 0.54) and in the absence of hydrogen, the catalyst decayed substantially in the following order: $\text{ZN}/\text{C}_3\text{H}_6 > \text{ZN}/\text{C}_2\text{H}_2 > \text{ZN}/\text{pure} > \text{ZN}/\text{CH}_4 > \text{ZN}/\text{CO}_2 > \text{ZN}/\text{CO}$. The results in the presence of hydrogen contrasted from upon trend and became: $\text{ZN}/\text{CH}_4 > \text{ZN}/\text{C}_3\text{H}_6 >$

ZN/CO > ZN/pure > ZN/C₂H₂ > ZN/CO₂. For liquid impurities (at impurity content of 16.43), the decay rate decreased in the order of: ZN/pure liq > ZN/CH₃OH > ZN/H₂O in the absence of hydrogen, while the trend was changed into ZN/H₂O > ZN/pure liq > ZN/CH₃OH in the presence of hydrogen. Besides, it can be observed that the average decay rate of catalyst in the presence of hydrogen was lower than in the absence of hydrogen except ZN/CO and ZN/CH₄. One may say that in the case of CO an without hydrogen, the centers formation rate was slow due to the initial of polymerization process. Thus, the decay rate of ZN/CO was less than the presence of hydrogen. The situation of CO displacement by hydrogen led to higher in the centers formation rate and catalyst decay [23-24].

Table 4.6 Results of catalyst decay rate during ethylene polymerization with gas impurities addition^a

^aThe average decay rate was evaluated from slope of rate profile in decay period (impurity content = 0.54)

^bThe origin

Sample	Average decay rate x 10 ⁻³ (cm ³ /sec ²)	
	Absence of hydrogen ^b	Presence of hydrogen ^b
ZN/pure	1.60	1.09
ZN/CO	0.11	1.11
ZN/CO ₂	0.88	0.79
ZN/CH ₄ (alkane)	1.02	1.29
ZN/C ₃ H ₆ (alkene)	1.94	1.15
ZN/C ₂ H ₂ (alkyne)	1.82	0.81

data was taken from Figures 4.9 and 4.11 in the case of ZN/pure and gas impurities, respectively

When comparing the change in catalyst decay rate between alkane, alkene and alkyne. It can be also stated that alkene exhibited the maximum decay rate, followed by alkyne and alkane, respectively. While in the presence of hydrogen, alkane exhibited the maximum decay rate, followed by alkene and alkyne as seen in Table 4.7.

Table 4.7 A comparison in the catalyst decay rate between alkane, alkene and alkyne

Sample	Absence of hydrogen	Presence of hydrogen
ZN/CH ₄ (alkane)	minimum	maximum
ZN/C ₃ H ₆ (alkene)	maximum	middle
ZN/C ₂ H ₂ (alkyne)	middle	minimum

Table 4.8 Results of catalyst decay rate during ethylene polymerization with liquid impurities addition^a

Sample	Average decay rate x 10⁻³ (cm³/sec²)	
	Absence of hydrogen^b	Presence of hydrogen^b
ZN/pure liq	3.73	2.41
ZN/H ₂ O	3.27	2.58
ZN/CH ₃ OH	3.69	2.12

^aThe average decay rate was evaluated from slope of rate profile in decay period (impurity content = 16.43)

^bThe origin data was taken from Figures 4.10 and 4.13 in the case of ZN/pure liq and liquid impurities, respectively

4.2 Effects of impurities on the properties of polyethylene

It was interesting that impurities only affected on the activity and catalyst decay or not. In this section, we also appreciated in analyzing of impurity effect on the properties of polyethylene. The characterization included the thermal behavior and molecular weight of produced polymer measured by the DSC and GPC method is summarized in Table 4.9.

It can be noticed from Table 4.9 that the melting temperature of polymers, which was analyzed by DSC, was around 133-137 °C. It was found that melting temperature and percent crystallinity of polyethylene were not affected by the influence of impurities, while molecular weight and molecular weight distribution were apparently affected. We can said that impurities may reduce the variation in active centers types resulting in lower molecular weight and narrow molecular weight distribution.

A difference in Mw and MWD between ZN/pure and ZN/pure liq can be elucidated by the different polymerization methods, due to hydrogen can dissolve in solvent of ZN/pure liq easier than ZN/pure which had the saturation of ethylene in the reactor. Therefore, the capability of chain transfer agent by hydrogen was better than ZN/pure sample leading to depression at twice in Mw and MWD of ZN/pure liq.

At low impurity content (impurity/Ti molar ratio of 0.54), the selective poisoning of CO and CO₂ onto the active centers of catalyst could contribute to apparently reduced in the molecular weight and molecular weight distribution of polyethylene. On the contrary, with CH₄ the reduction in the activity and molecular weight was revealed, but without effecting on MWD. At last, β -agostic coordination that inerts in ethylene polymerization would interrupt the insertion of C₃H₆ and C₂H₂ into the polymer chain resulting in depression in the Mw and MWD. In the case of liquid impurities, the destructive poison of H₂O and CH₃OH could destroy the polymerization sites in irreversible [9]. So that the molecular weight and molecular weight distribution also slightly diminished [8].

Molecular weight and molecular weight distribution of polymer at high impurity/Ti molar ratio are also shown in Table 4.9. The number in square brackets indicated the impurity content of each sample. The molecular weight and molecular weight distribution in the case of CO were not changed when comparing with low impurity content. In contrast with CO₂, a little effect on Mw, but the lowest MWD was observed. With higher amounts of CH₄, C₃H₆, C₂H₂ and CH₃OH, the decrease in Mw and MWD were also observed.

Table 4.9 Properties of polyethylene with impurity addition^a

Sample	T _m ^b (°C)	%X _c ^b	Mw ^c (g/mol)	Mn ^c (g/mol)	MWD ^c	Mw ratio	MWD ratio
ZN/pure	137	56	145794	3472	41.99	1.00	1.00
ZN/CO [0.54]	136	50	118968	3748	31.74	0.82	0.76
ZN/CO [1.07]	-	-	118506	3731	31.76	0.81	0.76
ZN/CO ₂ [0.54]	135	55	108238	3412	31.72	0.74	0.76
ZN/CO ₂ [1.61]	-	-	129742	4984	26.03	0.89	0.62
ZN/CH ₄ [0.54]	134	53	116715	2698	43.27	0.80	1.03
ZN/CH ₄ [1.61]	-	-	131314	3886	33.80	0.90	0.80
ZN/C ₃ H ₆ [0.54]	135	56	121543	3566	34.08	0.83	0.81
ZN/C ₃ H ₆ [1.61]	-	-	106757	3439	31.05	0.73	0.74
ZN/C ₂ H ₂ [0.54]	135	57	125172	4024	31.11	0.86	0.74
ZN/C ₂ H ₂ [1.61]	-	-	128321	3563	36.01	0.88	0.86
ZN/pure liq	135	59	61818	2922	21.16	1.00	1.00
ZN/H ₂ O [16.43]	133	48	49918	2565	19.46	0.81	0.92
ZN/H ₂ O [59.10]	-	-	53092	2879	18.44	0.86	0.87
ZN/CH ₃ OH [16.43]	136	54	57414	2918	19.68	0.93	0.93
ZN/CH ₃ OH [26.29]	-	-	53756	2850	18.86	0.87	0.89

^aThe impurity content used in each sample was shown in the square brackets.

^bDetermined by DSC, the crystallinity was calculated from heat of crystalline formation based on HDPE.

^cDetermined by GPC.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1 Conclusions

This research aims to investigate the influence of several impurities, both in gas and liquid compounds, which were commonly found in ethylene with a commercial catalyst. Our results focused their effects on the catalytic activity and properties of polyethylene produced. We found that impurities affected on the activity both in positive and negative ways.

In the absence of hydrogen, CO poisoned to the catalyst resulting in a decrease in the activity. This phenomenon was opposed to the activity in the presence of hydrogen. Hydrogen could displace CO molecules from the active centers. The activity was also found to increase when comparing with the result in the absence of hydrogen. Ethylene consumption rate profile between the absence and presence of hydrogen in the case of CO was indicated that the active center formation rate in the absence of hydrogen was lower than in the presence of hydrogen. Whereas the decay rate value exhibited the result in the opposite side.

A decrease in the activity by CO₂ was interpreted in the term of selective poisoning. With the combination of hydrogen, the activity was highly decreased. One reason was the effect from CO₂ poisoning and another one was the β -agostic coordination. The latter compound was generated by the addition of hydrogen and ethylene molecule into the active centers. The active center formation rate between absence and presence of hydrogen was not changed much, but long polymerization time in the presence of hydrogen led to obtain low activity. A little decrease in the average decay rate between the absence and presence of hydrogen was observed.

The methylation reaction at Ti-centers was formed by CH₄ in the absence of hydrogen. The activity was decreased slightly. In the presence of hydrogen, the replacement of hydrogen by CH₄ was demonstrated. Ti-CH₃ bond that inactive in the chain growth process was generated as the product of this reaction. The activity tend to decrease when using the higher amounts of CH₄. Moreover, it was found that the active center formation and decay rate in the presence of hydrogen were higher than in the absence of hydrogen.

C₃H₆ and C₂H₂ enhanced the activity in the absence of hydrogen causing from the copolymerization with ethylene. Contrary with the result in the presence of hydrogen. The activity was highly reduced because of β -agostic coordination that inerts for ethylene polymerization was generated. This structure was reduced the insertion rate of C₃H₆ and C₂H₂ into PE chains. The formation of β -agostic coordination led to obtain the low active center formation rate in the presence of hydrogen. Consequently, the low decay rate in the presence of hydrogen was also observed.

The effect of CH₄ (alkane), C₃H₆ (alkene) and C₂H₂ (alkyne) on the activity was also considered. Alkyne relatively highest affected on catalytic activity, followed by alkene and alkane. This trend was observed both in the absence and presence of hydrogen. However, the trends of ethylene consumption and decay rate were uncertain.

In the case of H₂O and CH₃OH, the effects of impurities on the activity were depended on their amounts. While in the presence of hydrogen, hydrogen had a beneficial effect on the activity both in low and high impurity content. When considering the change in ethylene consumption rate profile between absence and presence of hydrogen. Hydrogen was affected on the maximum rate value when introducing hydrogen into the system. The presence of hydrogen led to obtain the low average decay rate.

Moreover, all impurities tend to reduce the molecular weight and variation in active centers types leading to narrow molecular weight distribution. Finally, thermal behavior and percent crystallinity of polyethylene were not affected by the influence of impurities

5.2 Recommendations

1) The effects of impurities in this study were discussed only their influence on the catalytic activity, ethylene consumption rate profile and polyethylene properties, while other factors such as an oxidation state of Ti species and the coordination of impurities at active centers should be characterized to support our data as we reported in Chapter IV.

2) It is ambiguity that why molecular weight and molecular weight distribution obtained from 100 ml reactor in the system of gas and liquid impurities were greatly different. This occurrence is still open discussion and should be considered in the further study.

3) Proving the mechanism of impurities on catalyst surface in deep details is interesting especially in the presence of hydrogen combined with impurities. Some of our explanation needed the characterization data for more reliability. For instance, the displacement of CO molecules by hydrogen and the replacement of hydrogen by CH₄ should be confirmed by TPD instrument.

4) In order to obtain the correct decay rate value, the kinetic expression as deactivation equation should be considered more than using the estimation method.

5) The reaction of TEA with H₂O or CH₃OH which used to explain the enhancement in the activity in the presence of hydrogen is still open discussion and should be considered in the further study.

6) The copolymerization of acetylene with ethylene should be analyzed by IR or NMR instrument to ensure their effect as we mentioned in Chapter IV.

7) Some content of CO₂ which increased the activity in the presence of hydrogen should be found an another reason to describe.

8) The explanation of impurities on ethylene consumption rate in the presence of hydrogen should be considered in the further study.

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APPENDICES

APPENDIX A
EFFECTS OF IMPURITIES ON ACTIVITY
BOTH IN THE ABSENCE AND PRESENCE OF HYDROGEN

The influence of impurities in the absence of hydrogen was summarized in Table A.1-7. The polymerization was carried out in 100 ml stainless steel reactor with Al/Ti molar ratio of 140, 80 °C and 50 psi of ethylene pressure. The number in square brackets was shown the impurity content (the molar ratio of impurity/Ti) of each sample.

Table A.1 The influence of CO on the catalytic activity (absence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	329	0.88	1253
ZN/CO[0.27]	530	1.00	902
ZN/CO[0.54]	588	0.95	762
ZN/CO[0.80]	790	1.20	720
ZN/CO[1.07]	947	1.28	653

Table A.2 The influence of CO₂ on the catalytic activity (absence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	329	0.88	1253
ZN/CO ₂ [0.54]	321	0.77	1108/970
ZN/CO ₂ [1.07]	394	0.90	1083/998
ZN/CO ₂ [1.61]	482	0.98	943

Note: The value after "/" was the new experimental result (used this value when comparing the effect of CO₂ between in the absence and presence of hydrogen only)

Table A.3 The influence of CH₄ on the catalytic activity (absence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	329	0.88	1253
ZN/CH ₄ [0.54]	382	0.91	1122
ZN/CH ₄ [1.07]	410	0.96	1099
ZN/CH ₄ [1.61]	501	1.02	956

Table A.4 The influence of C₃H₆ on the catalytic activity (absence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	329	0.88	1253
ZN/C ₃ H ₆ [0.54]	278	0.82	1382
ZN/C ₃ H ₆ [1.07]	327	0.92	1318
ZN/C ₃ H ₆ [1.61]	300	0.82	1277

Table A.5 The influence of C₂H₂ on the catalytic activity (absence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	329	0.88	1253
ZN/C ₂ H ₂ [0.54]	227	0.79	1643
ZN/C ₂ H ₂ [1.07]	284	0.81	1327
ZN/C ₂ H ₂ [1.61]	321	0.89	1294

Table A.6 The influence of H₂O on the catalytic activity (absence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure liq	131	0.46	1661
ZN/H ₂ O[16.43]	153	0.53	1571
ZN/H ₂ O[59.1]	109	0.47	2038
ZN/H ₂ O[147.75]	140	0.44	1458
ZN/H ₂ O[295.51]	138	0.42	1414

Table A.7 The influence of CH₃OH on the catalytic activity (absence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure liq	131	0.46	1661
ZN/CH ₃ OH[16.43]	133	0.53	1747
ZN/CH ₃ OH [26.29]	190	0.59	1458

The influence of all impurities in the presence of hydrogen was demonstrated in Table A.8-15. The polymerization condition was used similar to the absence of hydrogen. All samples were preferably performed with hydrogen pressure of 0.1 bar. The number in square brackets was shown the impurity content (the molar ratio of impurity/Ti) of each sample.

Table A.8 The influence of gas impurities in the presence of hydrogen^a

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	339	0.86	1180
ZN/CO	345	0.83	1120
ZN/CO ₂	435	0.91	975/785
ZN/CH ₄	372	0.86	1077
ZN/C ₃ H ₆	348	0.86	1156
ZN/C ₂ H ₂	451	0.94	987

Note: The value after "/" was the new experimental result (used this value when comparing the effect of CO₂ between in the absence and presence of hydrogen only)

^aAddition of impurities to impurity/Ti molar ratio = 0.54

Table A.9 The influence of CO on the catalytic activity (presence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	339	0.86	1180
ZN/CO[0.54]	348	0.83	1120
ZN/CO[0.80]	386	0.91	1106
ZN/CO[1.07]	513	0.91	820

Table A.10 The influence of CO₂ on the catalytic activity (presence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	339	0.86	1180
ZN/CO ₂ [0.54]	435	0.91	975/783
ZN/CO ₂ [1.07]	390	0.87	1034/785
ZN/CO ₂ [1.61]	387	0.89	1090
ZN/CO ₂ [2.67]	350	0.87	1152
ZN/CO ₂ [3.74]	526	0.98	869

Note: The value after "/" was the new experimental result (used this value when comparing the effect of CO₂ between in the absence and presence of hydrogen only)

Table A.11 The influence of CH₄ on the catalytic activity (presence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	339	0.86	1180
ZN/CH ₄ [0.54]	372	0.86	1077
ZN/CH ₄ [1.07]	498	1.06	999
ZN/CH ₄ [1.61]	560	1.01	839

Table A.12 The influence of C₃H₆ on the catalytic activity (presence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	339	0.86	1180
ZN/C ₃ H ₆ [0.54]	348	0.86	1156
ZN/C ₃ H ₆ [1.07]	390	0.93	1119
ZN/C ₃ H ₆ [1.61]	387	0.87	1049

Table A.13 The influence of C₂H₂ in on the catalytic activity (presence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure	339	0.86	1180
ZN/C ₂ H ₂ [0.54]	451	0.94	987
ZN/C ₂ H ₂ [1.07]	533	1.02	891
ZN/C ₂ H ₂ [1.61]	489	0.97	934

Table A.14 The influence of H₂O on the catalytic activity (presence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure liq	224	0.49	1018
ZN/H ₂ O[16.43]	192	0.49	1175
ZN/H ₂ O[59.1]	109	0.47	1411

Table A.15 The influence of CH₃OH on the catalytic activity (presence of hydrogen)

Sample	Polymerization time (sec)	Polymer yield (g)	Activity (kgPE/molTi.h)
ZN/pure liq	224	0.49	1018
ZN/CH ₃ OH[16.43]	169	0.48	1345
ZN/CH ₃ OH [26.29]	257	0.56	1026

APPENDIX B
THERMAL BEHAVIOR OF POLYETHYLENE
(DSC CURVE)

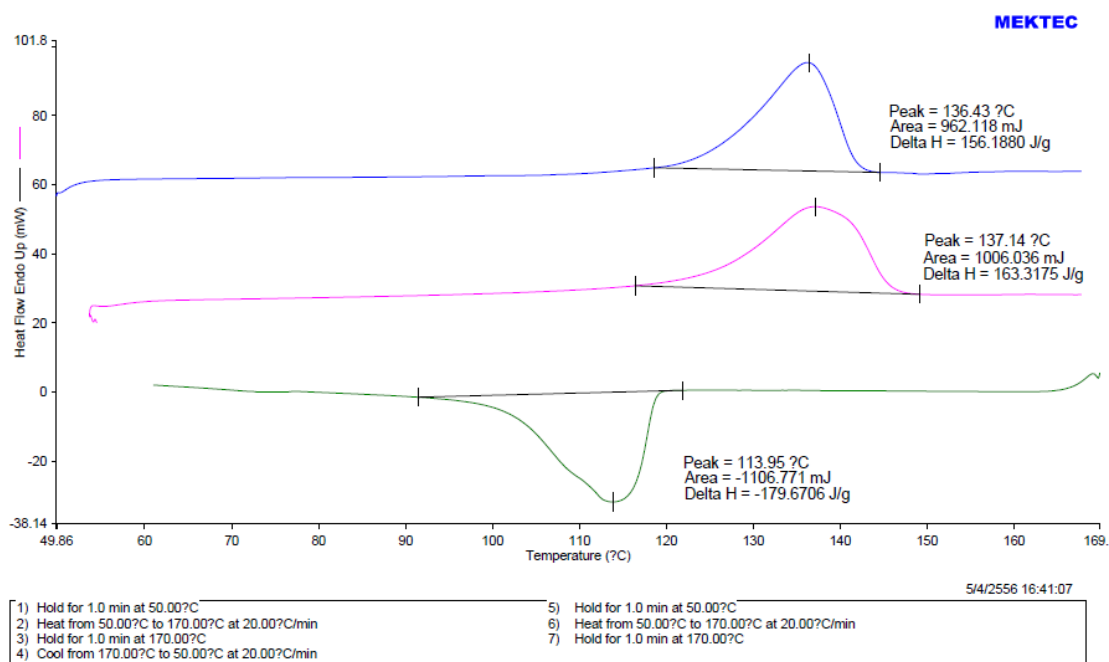


Figure B.1 The thermal behavior of polyethylene produced from blank sample (ZN/pure sample)

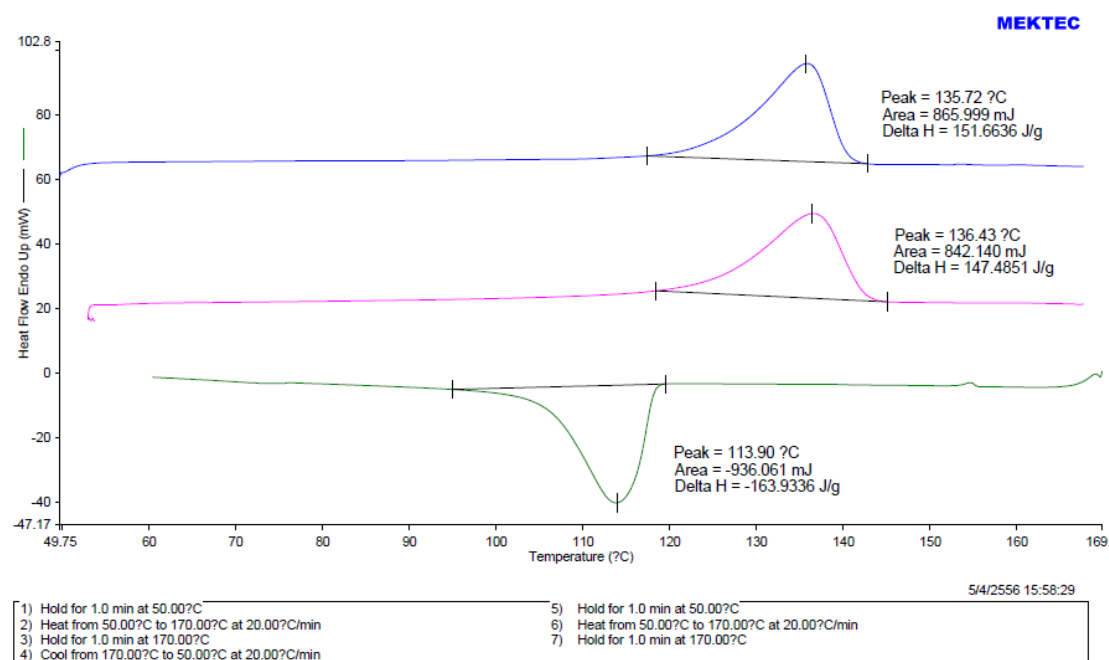


Figure B.2 The thermal behavior of polyethylene produced from catalyst injected with CO (ZN/CO sample)

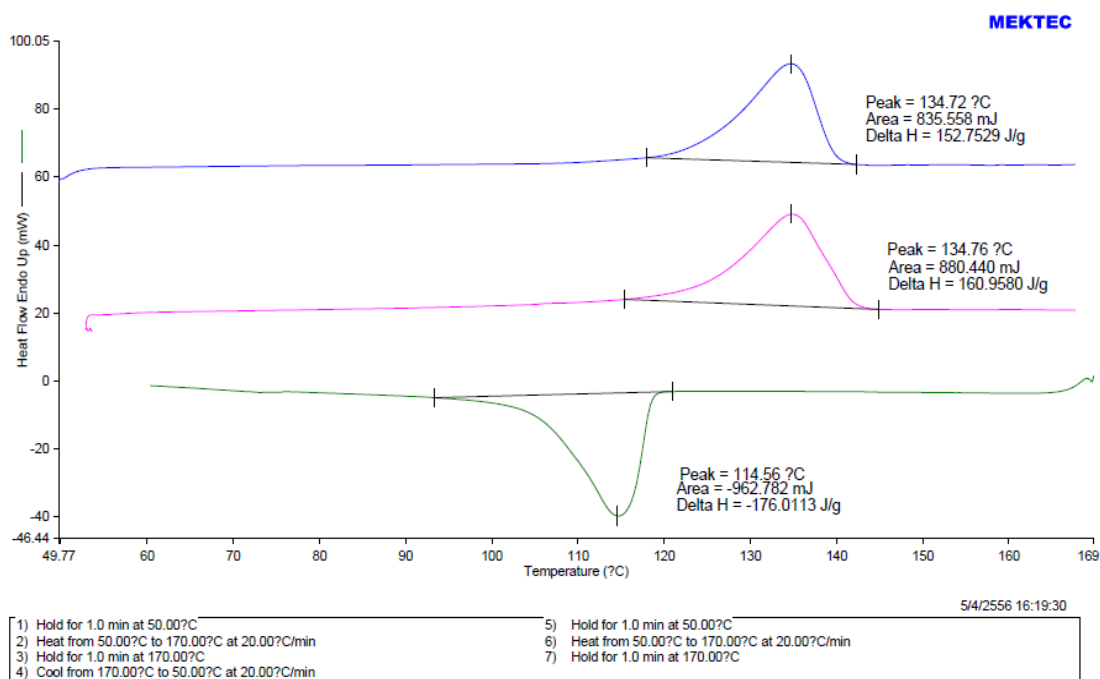


Figure B.3 The thermal behavior of polyethylene produced from catalyst injected with CO₂ (ZN/CO₂ sample)

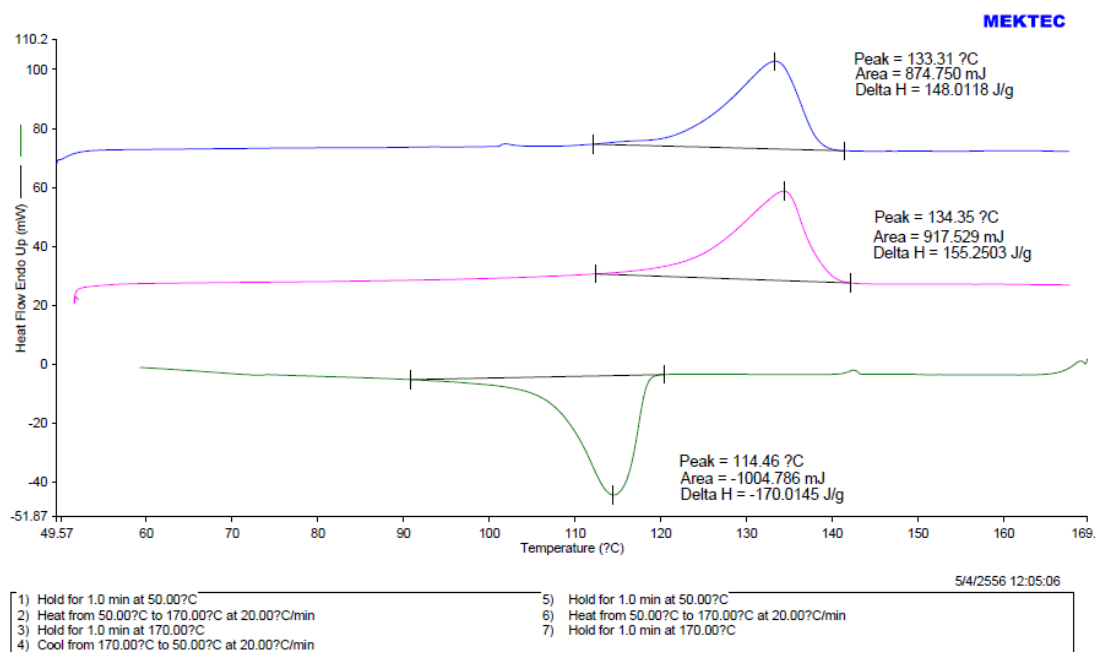


Figure B.4 The thermal behavior of polyethylene produced from catalyst injected with CH₄ (ZN/CH₄ sample)

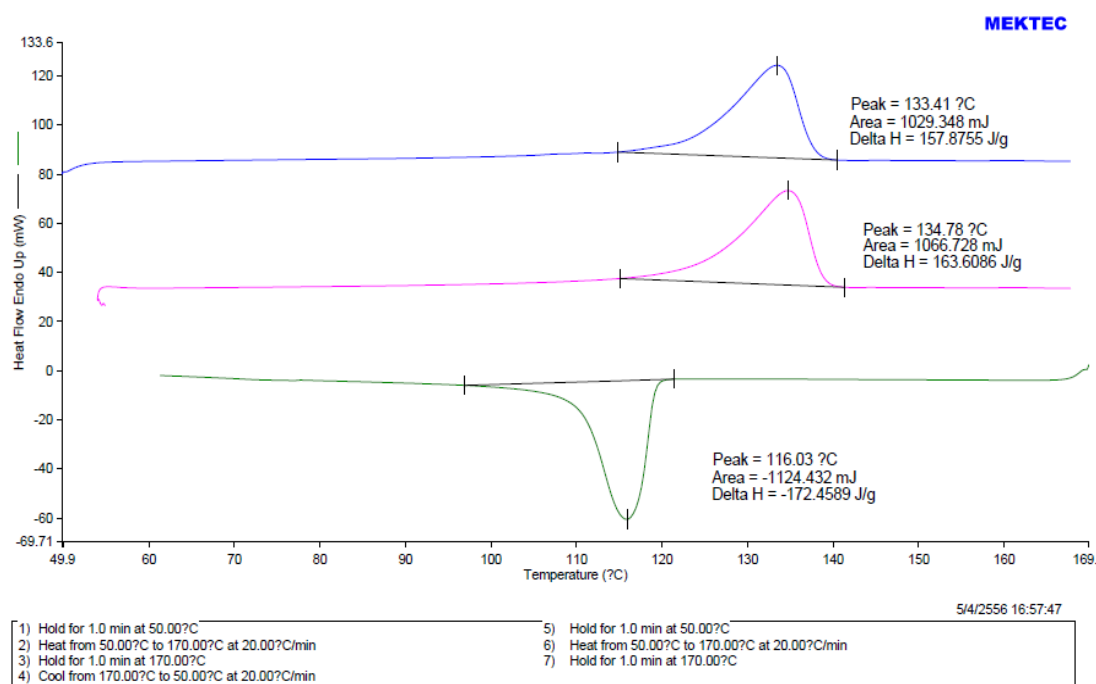


Figure B.5 The thermal behavior of polyethylene produced from catalyst injected with C_3H_6 (ZN/ C_3H_6 sample)

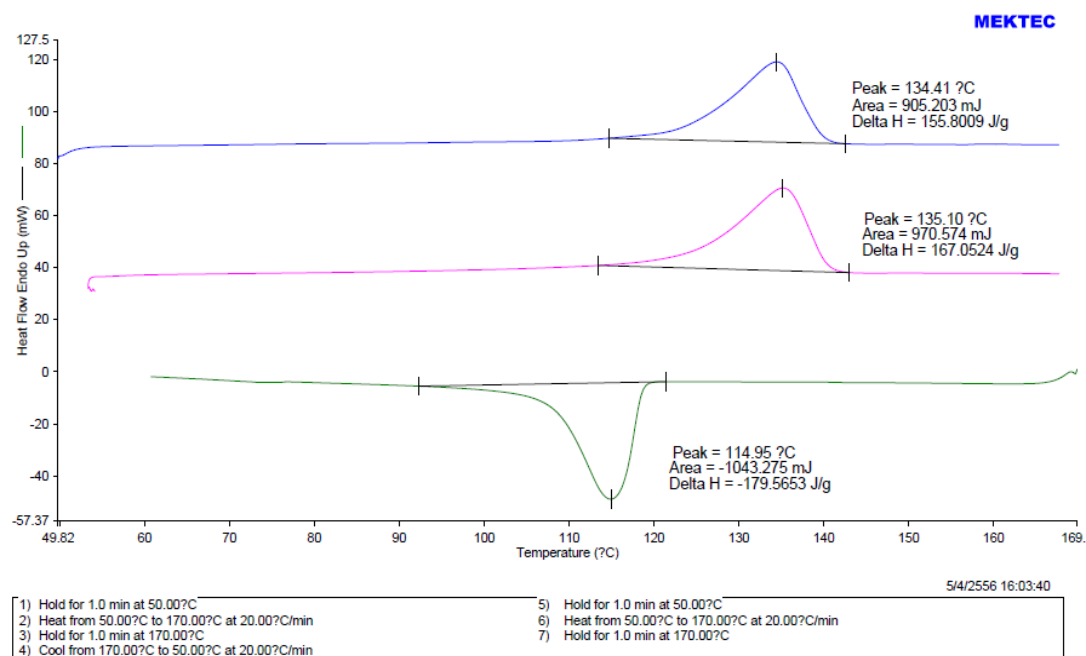


Figure B.6 The thermal behavior of polyethylene produced from catalyst injected with C_2H_2 (ZN/ C_2H_2 sample)

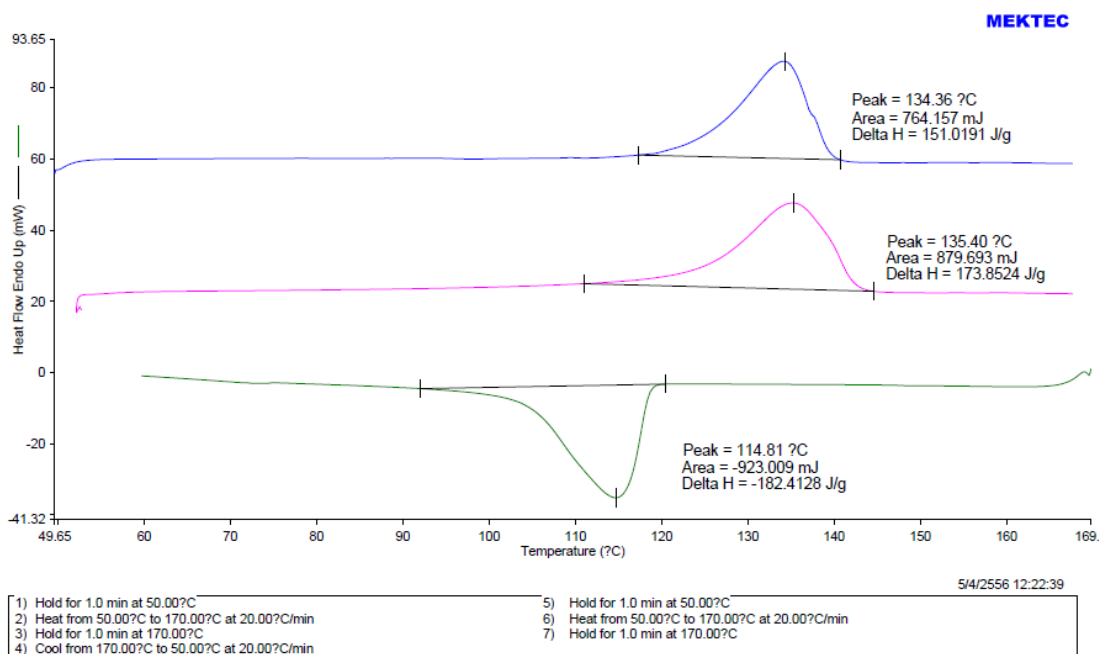


Figure B.7 The thermal behavior of polyethylene produced from blank sample (ZN/pure liq sample)

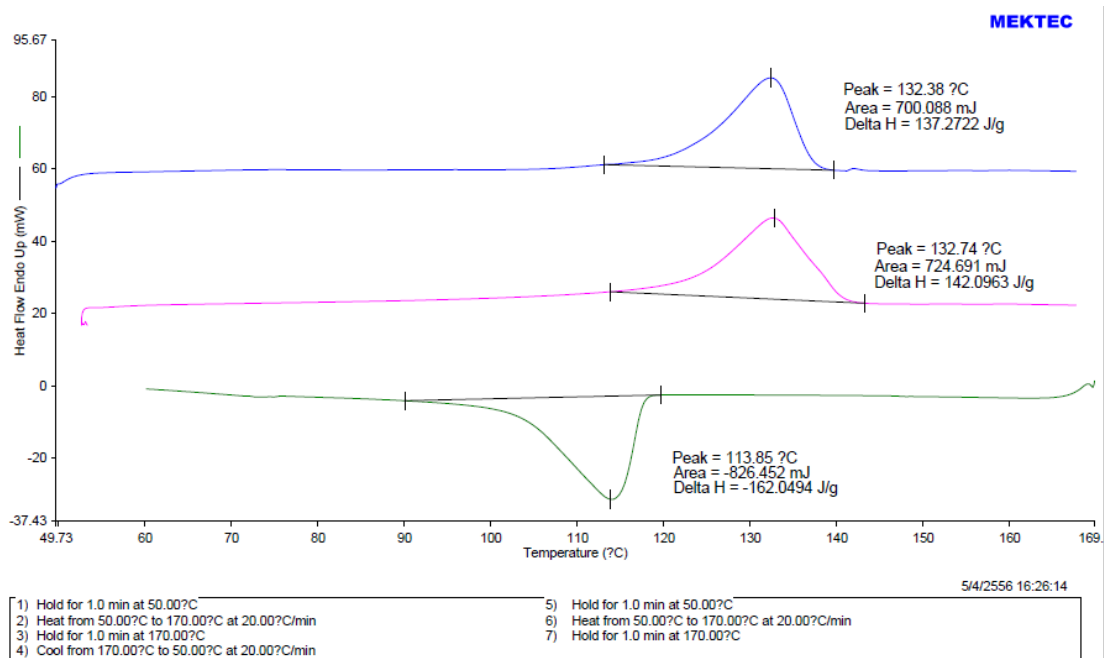


Figure B.8 The thermal behavior of polyethylene produced from catalyst injected with H₂O (ZN/H₂O sample)

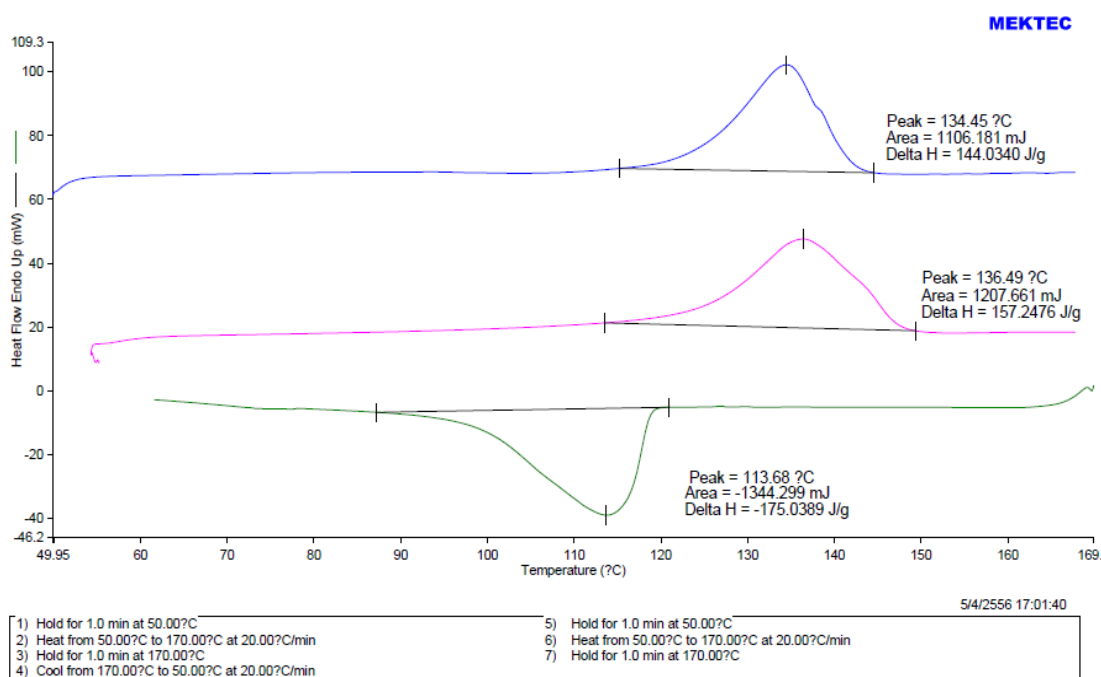


Figure B.8 The thermal behavior of polyethylene produced from catalyst injected with CH₃OH (ZN/CH₃OH sample)

APPENDIX C
DETERMINATION OF POLYETHYLENE CRYSTALLNITY

The crystallinity of polymer was calculated by the heat of fusion parameter as shown in the equation (C-1) ;

$$X_c = \frac{H_m}{H_p} \times 100 \quad (\text{C-1})$$

Where, H_m is the enthalpy of tested sample

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

X_c is the percent crystallinity of the sample

APPENDIX D
DETERMINATION OF ETHYLENE CONSUMPTION RATE DATA
AND AVERAGE DECAY RATE

Ethylene consumption rate data in this study was acquired from each accumulated ethylene consumption at 5 sec interval, which observed from mass flow meter, divided by polymerization time. Thus, an example of ethylene consumption rate calculation of ZN/pure sample in the absence of hydrogen was shown as follows :

Table D.1 Ethylene consumption rate calculation of ZN/pure sample

Polymerization time (sec)	Accumulated ethylene consumption (cm ³)	Ethylene consumption rate (cm ³ /sec)
0	0.000	0.000
5	3.050	3.050/5 = 0.610
10	4.818	4.818/10 = 0.482
15	5.877	5.877/15 = 0.392

All of ethylene consumption rate data were used to plot the ethylene consumption rate profile in the coordinates of "ethylene consumption rate (cm³/sec) vs polymerization time (sec)" as demonstrated in Chapter IV.

The estimation method used for determination of the average decay rate referred to Hideharu et. al. as exposed in Figure D.1. The average decay rate value can be obtained from the slope of the decay period in ethylene consumption rate profile of each sample. An example of the calculation of ZN/pure sample in the absence of hydrogen was shown as follows :

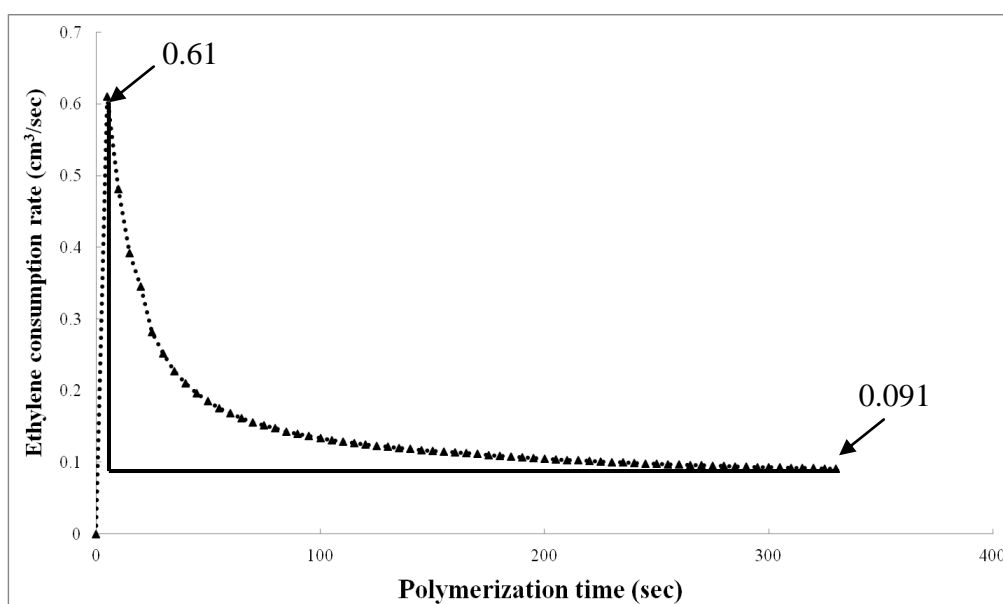


Figure D.1 Estimation method for calculation of average catalyst decay rate

$$\text{Hence, average decay rate} = \frac{(0.61 - 0.091) \text{ cm}^3/\text{sec}}{(330-5) \text{ sec}} = 1.6 \times 10^{-3} \text{ cm}^3/\text{sec}^2$$

APPENDIX E
ERROR BAR

To obtain the precise discussion in this study, percent error in the polymerization step should be declared.

Error in the experimental in the absence of hydrogen = 5.05%

Error in the experimental in the presence of hydrogen = 5.82%

APPENDIX F
LIST OF PUBLICATION

Auksarapuk Puriwathana and Piyasan Prasertdam. "Influence of contaminants commonly found in ethylene gas on the catalytic activity of Ziegler-Natta catalyst". (The proceeding of The 2nd TIChE International Conference (TIChE 2012), Nakornratchasima, Thailand)

VITA

Auksarapuk Puriwathana was born on June 09,1988 in Nakhon Pathom, Thailand. She graduated on the major of Chemical Engineer, Faculty of Engineering from Thammasat University with GPA 3.08 in Feb 2010. She decided to work in UTAC Thai Limited company for one year to obtain some experience before continued her education in Master's degree at Chulalongkorn University. She began her studied at the Catalysis and Catalytic Reaction Engineering group, Department of Chemical Engineering in June 2011.