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Design of novel homogeneous chromium-based catalyst system using silsequioxane support and high-efficiency activator for ethylene polymerization

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by

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Preface

The present dissertation is the result of the studies under the direction of Professor Dr. Minoru Terano during 2012-2015. The purpose of this dissertation is to shed new light for precise control of polyethylene structure with designed Phillips-type catalysts. The first chapter is a general introduction according to the object of this research. Chapter 2 describes the design of novel homogeneous Phillips catalyst using the model of trivalent chromium site and support. Chapter 3 describes the design of novel homogeneous Phillips catalyst using the model of hexavalent chromium site and support. Chapter 4 describes the effects of catalyst surface modifications on ethylene polymerization properties. The last chapter summarizes the conclusive items of this dissertation.

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Chapter 1

General Introduction

1.1 Backgrounds of industrial polyethylene (PE)

In world market of polymer materials, commercial polyethylene (PE) plays the most important role due to its specific properties, such as high mechanical resistance, easy processibility and low specific gravity. Up to now, PE still has the highest production volumes, whose current global production reaches 100 million tons annually and is growing continuously.[1] PE is very successful in competition with other materials, since it holds the clear merits, like an excellent chemical resistance, a high impact strength, and stiffness even at low temperature. Not only industrial processes are at low cost, but also PE is environmental friendly material. When PE has lost its performance, it can be recycled for energy production.

PE with a structure formula of $(-CH_2-)_n$ is seemingly the most simplest polymer. However, nowadays hundreds of specialized PE grades are tailored by various catalysts and different polymerization processing produced by hundreds of suppliers for dozens of special application. These grades vary in molecular weight (MW), molecular weight distribution (MWD), branching type and amount, and molecular architecture.

According to architecture, there are three basic commercial forms of PE as following: low density polyethylene (LDPE), high density polyethylene (HDPE) and

linear low density polyethylene (LLDPE). Different architectures contribute to a wide variety of physical properties and molding characteristics, especially the degree and type of branching.

PE with a mixture of interconnected crystalline and amorphous forms is a semi-crystalline material. Branches disrupt the crystalline leading to more amorphous from polymer chains.[1] This phenomenon can be most easily detected by the density, since the density of crystalline phase is higher than the one of amorphous phase. As a consequence, the measured density can reflect a degree of branching in polymer.

The first commercial polyolefin (LDPE), was produced in 1933, used high-pressure technique at 140 MPa in an attempt to condense ethylene and benzaldehyde at 200°C.[2] This discovery makes high-pressure techniques contributing much amount of PE production. However, this radical polymerization just can produce LDPE with more branching at high pressure due to high chain transfer reaction at a high temperature.

Subsequent turning points in PE synthesis have revolved around the development of several types of catalysts that promote ethylene polymerization at more mild temperatures and low pressures. The first of these was a chromium based catalyst discovered in 1951 by Hogan and Banks at Phillips Petroleum. In 1953, Ziegler developed a catalytic system based on titanium chlorides and organoaluminum compounds that worked at even milder conditions than the Phillips catalyst.[3, 4] By the end of the 1950s, both the Phillips and Ziegler type catalysts

were being used for industrial HDPE production.   Tremendous evolution has taken place, because these discoveries: the catalysts are nowadays responsible for the commercial production of more than half of all PE sold worldwide.

Recently, the commercial productions of single-site molecular catalyzed PE have been announced.   Especially, group 4 metallocene catalysts, reported in 1976 by Sinn and Kaminsky,[5, 6] and constrained-geometry catalysts (CGCs)[7-11] have been at the forefront of this development, producing a wide array of polymer with distinctive microstructures: e.g. LLDPE, elastomers and plastomers.   However, application of single-site catalysts for the commercial plants has been limited because of the high cost of the organometallic catalyst precursors.

1.2 Industrial ethylene polymerization catalysts

1.2.1   Ziegler-Natta catalyst

At first, this catalyst consisted of a combination of titanium chloride and an alkylaluminium chloride as a cocatalyst, polymerizes ethylene at low temperatures and pressures to give PE with an essentially linear structure, which was discovered at 1953 by Ziegler.[12, 13]   Following close on the heels of this discovery was the recognition, this type catalyst was capable of polymerizing α-olefins to yield stereoregular polymers by Natta.[14, 15]   The catalyst developed by Ziegler and Natta became known as Ziegler-Natta catalysts.

The number of compounds and combinations fit into the category of Ziegler-Natta catalysts.   Most commonly, the catalyst component consists of halides,

alkoxydes or oxyhalides of titanium, vanadium or zirconium. Activators are usually alkyl or aryls of metal such as aluminum, lithium or zinc. By far the most important and most thoroughly studied Ziegler-Natta systems are combinations of $MgCl_2$-supported titanium chlorides with alkylaluminum compounds.[16-19]

1.2.2 Phillips catalyst

Phillips catalysts (Cr/SiO_2) based on a chromium oxide and an amorphous material like silica, were discovered by Hogan and Banks at Phillips Petroleuum Co. in 1951. The Phillips HDPE product has many unique properties and applications due to the unique polymer chain conformation such as LCB (about one LCB per 10,000 of ethylene units) and broad MWD (typical polydispersity is between 10 and 30). The detail of Phillips catalyst was introduced in the followed sections. With the exception of LDPE, which is made by a high pressure radical process, the other types of PEs (HDPE and LLDPE) are produced by using either homogeneous or heterogeneous catalysts. Phillips catalyst [20] composed of chromium oxide supported on silica have long maintained their industrial importance after the discovery in 1950's in the polyolefin manufacture to produce nearly 10 million tons of a special grade of HDPE per year over the world. The specialty of the Phillips catalyst is an ability to produce HDPE with fine mechanical properties such as elasticity and impact resistance, and superior moldability due to its high melt viscosity. These properties come from both broad MWD and adequate amounts of SCBs and LCBs incorporated. Although finer controls of polymer micro structures with the

Phillips catalysts have been continuous demands for further multipurpose materials, significant efforts still deposit obscurities in the mechanistic origin of the unique catalytic features.

1.2.3 Metallocene catalyst

Metallocene catalyst shows high activity for ethylene/α-olefin copolymerization, and exhibits higher reactivity for α-olefins than conventional Ziegler–Natta catalyst. The produced copolymers are characterized by narrow MWD and chemical composition with a random distribution. The characteristic structure affects the properties of LLDPE prepared by metallocene catalyst. For example, the film which made of LLDPE shows superior mechanical properties and heat-sealing properties.

The polymerization activity of the non-metallocene catalyst, which has no cyclopentadienyl ligands, was generally lower than that of the metallocene catalyst. However, some non-metallocene catalysts with high activity for ethylene polymerization have been developed. For example, Fujita et al. developed zirconium and titanium complexes with bis (phenoxy-imine) ligand, called as FI catalysts, whose polymerization activity reached 6,552 kg-PE/mmol-cat·h.

For the productions of PE with LCBs, Dow and Exxon developed *ansa*-mono-cyclopentadienyl amido group 4 catalysts, such as Me$_2$Si(Me$_4$Cp)(N-*t*Bu)TiCl$_2$, called as CGCs.[21-25] The formation mechanism of LCBs in the PE chains can be explained by the formation of vinyl-terminated macromonomers via *β*-hydrogen elimination of growing polymer chains following

re-insertion into the growing polymer chains.　The CGCs incorporate LCBs (about 3 LCBs per 1000 carbons) in PE chains, and these LCBs affect some properties, in particular, processability and scalability, of the resulting PE.[26]

The Union Carbide catalyst which is composed of chromium and two cyclopentadienyl ligands supported on silica is most widely used for the production of LDPE, because this type of catalyst is high activity and removing of residue for process is unnecessary.

1.2.4　Comparison of three catalysts

Nowadays, polyethylenes are manufactured with three different catalyst systems: Phillips chromium oxide catalyst, Ziegler titanium chloride catalyst, and metallocene catalyst.　These three catalysts are different from one another, especially in the produced polymers.　For example, Phillips catalysts produce the broadest MWD. MWD in polymer made by Phillips catalyst can range from as little as 4.0 to more than 100.　On the contrary, metallocene which was called single site catalysts produce the narrowest MWD which is around 2.0.　This is the theoretical minimum that can be produced from a nonliving system.　In between, the Ziegler catalysts tend to produce polymers with MWD of about 4.　These differences in the breadth of the polymer MWD from one catalyst to another reflect the number of active-site types present in these catalysts.　The MWD which are typical of the three polymers are 2.0 (metallocene), 4.0 (Ziegler), and 8-65 (Phillips).

To a molten resins, various MWD give distinctive flow characteristic that

determine what molding processes can be used. Different melt viscosity of each of these three polymers imparts various shear rates. The polymer produced with the Phillips catalyst is considerably more shear thinning than the other two, owing to its broader MWD. It means that the polymer flows more easily under pressure. Thus, it is easily extruded at high shear rates. This second property is called "melt strength and combination of these two characteristics makes the resins produced with Phillips catalysts excellently suited for extrusion applications. For example, such polymers perform well in blow-molded bottles, drums, other containers, extruded pipe, sheet, and sheeting.

For the molded items, physical properties also benefit from the broad MWD. In a word, one can view the short chains as lubricating the flow of the longer chains during molding. At the same time, these longer chains dominate polymer properties in the finished article. Thus, a broad MW distribution excels in many commercial applications.

The degree of LCB also differs substantially in the polymers made with these catalysts. Ziegler resins typically have little or none, whereas the Phillips and metallocene polymers can have widely. These different characteristics mean that these three catalyst types do not usually compete with one another in the market; instead, each serves a different part of the market's diverse needs. Phillips and Ziegler resins together comprise most of the linear PE market, perhaps 95%, but metallocene catalysts are slowly gaining acceptance for some specialty application, especially low-density film.

1.3 Phillips processes of ethylene polymerization

The heart of the Phillips polymerization process is a supported chromium oxide catalyst stored under dry nitrogen until loaded in the polymerization reactor. The polymerization of ethylene can be done over a relatively broad range of temperatures; however, the commercial temperatures range between 65°C and 180°C.[27] The relative rate of termination of the polyethylene chain determines the average chain length i.e., MW of the polyethylene.

The ethylene pressure is also an important factor. In general, the higher the ethylene pressures in the polymerization reactor, the higher will be the MW of the polyethylene produced. Ethylene polymerization usually is carried out at ethylene pressures varying from 20 to 30 bars.

There are three different Phillips modes of operation for the polymerization processes: namely the slurry, solution and gas phase process.

1.3.1   Slurry phase process

The slurry phase process is known as the Phillips particle form process (licensed by Phillips Petroleum) and is carried out in a continuous stirred tank reactor (CSTR) or a loop reactors with a heterogeneous catalyst. In the slurry process a paraffinic (e.g., pentane, hexane) solvent is used and both the catalyst and the formed polymer are kept in suspension during polymerization. To achieve this, the polymerization

temperature can be chosen to a maximum of about 110°C. During polymerization the catalyst particles break up and after the reaction small catalyst fragments remain in the polymer particle. Generally, slurry reactors require catalysts with high activities so that catalyst removal is not required. Due to the high activity of Phillips catalyst residual amount can be neglected and is left in the polymer resin.[28]

1.3.2 Solution phase process

In the solution phase process a solvent (e.g., cyclohexane) is chosen that dissolves the polymer at reaction temperatures between 125 and 175°C while the catalyst is kept in suspension under continuous stirred tank reactor (CSTR). After the reaction the catalyst is removed by filtration and the polymer is obtained on evaporation of the solvent. The main advantage of solution phase polymerization is the short residence times. This process is very flexible for production of many grades of polymer. Solution phase polymerization is typically used for production of low-density polymers. The disadvantages are the large volume of solvent to vaporize and recycle, leading to high costs. High molecular weight polymers are difficult to obtain, since viscosity increases with molecular weight. Solution phase polymerization is typically used for production of low-density polymers.[29]

1.3.3 Gas phase process

The gas phase process is known as the Unipol process (licensed by Union Carbide)

and utilizes fluidized bed reactors or mechanically stirred reactors. The gas phase contains an inert carrier phase, as well as the monomers. The gas stream is responsible for cooling the reaction, as well as volatilizing the monomer. The reactor is generally operated at temperatures from 70-115°C and pressures from 20-30 bar. The catalysts are heterogeneous and usually require a pre-polymerization step.[28, 29] The main advantage to gas phase polymerization is that it eliminates the need for solvent removal from the final polymer. Most new polymerization plants are based on gas phase technology due to its flexibility and efficiency.

1.4 Phillips catalysts

1.4.1   Catalyst preparations

The Phillips catalysts are usually prepared by impregnation of wide pore SiO_2 (although other supports, such as alumina, silica-alumina, aluminophosphates, and silica-titania, are also used) with Cr compound, for example, CrO_3, $CrO_2(OR)_2$, or various Cr(III) salts such as $Cr(OAc)_3$.[30] The silica surface is treated with approximately 1 wt.% Cr. This impregnated material is subsequently heated in oxygen at high temperature (around 500-900ºC). CrO_3 begins to decompose above 200°C with releasing O_2 and generating Cr_2O_3, if there are no reactive hydroxyl groups on the surface. Cr(VI) surface compounds are stabilized by attachment to the SiO_2 surface, which are supposed to be the precursors of the polymerization active sites as scheme 1-4-1.
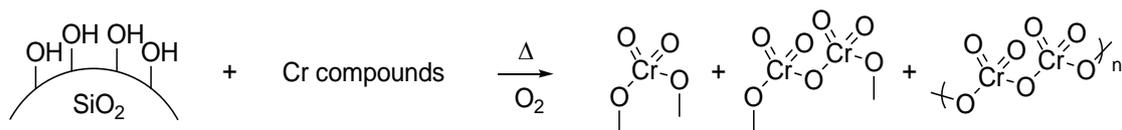
Scheme 1-4-1.

In early stage, hexavalent chromium compounds, such as chromic oxide (CrO_3), are often used as the source of chromium, because of their high solubility in water. Ammonium chromate or ammonium dichromate whose NH^{4+} ion is lost during calcination can also be used. However, because alkali metal ions on the catalyst can promote sintering, sodium or potassium chromates are not suitable. Other hexavalent chromium compounds which include chromyl chloride and even organic chromates such as bis (t-butyl) chromate have been used in nonaqueous environments. Early Phillips commercial catalysts used aqueous CrO_3 as the precursor.

However, Cr(VI) became identified as a suspected carcinogen. Therefore, trivalent chromium compounds were used replaced. Because Cr(III) oxidizes to Cr(VI) during calcination, many Cr(III) salts can take over CrO_3 and the anion is also burned away. Cr(III) nitrate, acetate, acetylacetonate, chloride, or sulfate can be used. Basic chromic(III) acetate is currently the most common commercial source of chromium used in catalyst manufacture.[22-24]

1.4.2 Chromium anchored process and calcination

When Phillips catalyst is synthesized, a carrier is impregnated with a chromuium compound followed by calcination in dry air or oxygen to activate the catalyst.[21] The calcination process is a crucial stage, because during this time the chromium

oxide is anchored onto surface stabilized a series of chromate species containing mono-, di-, and polychromate. In the calcination period, a highly dispersed chromate species can be achieved through thermal decomposition and stabilization of bulk CrO_3 on a carrier surface. During this procedure, chromium becomes oxidized to Cr(VI), which reacts with surface hydroxyl groups to become anchored and monodispersed. In general, the Phillips catalyst comprises hexavalent chromium supported on a high-surface-area, wide-pore oxide carrier which is composed of silica. Industrially, a loading of about 0.2-2.0 wt% chromium is used, most often around 1wt%.

At high temperatures, there is a reaction with hydroxyl group on silica surface which tends to fix the chromium and stabilize it. The bulk CrO_3 started to transform into supported chromate species at temperatures about 200ºC and partially decompose into O_2 and Cr_2O_3 due to an incomplete stabilization of bulky CrO_3 into chromate species, and could totally stabilize on silica surface as a chromate site at around 400ºC. At temperatures of 150-350ºC, anchoring of chromium compound occurs by esterification to surface chromate and perhaps also dichromate species, whereby each Cr atom is directly bonded onto the support. Although oxidation of Cr(III) and subsequent anchoring of the hexavalent form occurs at 150-350ºC, respectable polymerization activity does not develop until the catalyst is calcined at much higher temperature, such as 600-900ºC. As the temperature is raised, surface silanol groups condense to release water. At first, the paired silanol groups condense, but at temperatures above 600ºC only isolated silanol groups remain.[25, 30, 31] As the

temperature is raised further, surface annealing permits condensation of even some of these hydroxyl groups, but the silanol group population never reaches zero, even as sintering begins at temperatures around 900ºC.　Exposure to trace of moisture, especially at temperatures above about 600ºC, destabilizes the surface Cr(VI) by hydrolysis of the Si-O-Cr attachment, which results in the decomposition of Cr(VI) to Cr_2O_3.[27, 32]

### 1.4.3　Polymerization mechanism

The mechanism of polymerization by Phillips catalysts is still not so clear.　This is because of several steps including reduction by monomer, desorption of redox products and self-alkylation (that is, without a metal alkyl co-catalyst).　The alkylation step is particularly unclear.　Polymerization then involves propagation (monomer addition) and chain transfer by several different methods.　End-group analysis yields about one methyl and one terminal vinyl per chain [33].

1.4.3.1 Initiation mechanism

Phillips ethylene polymerization systems without activator do not contain an initial alkyl ligand.　Therefore, Phillips catalysts require additional initiation steps, which make an induction period in the ethylene polymerization.　The initiation steps include a reduction of Cr (VI) to lower-valent species and a formation of growing chain.　A step of desorption of the oxygenated redox products also proposed as one of the important initiation steps by some researchers.[1]　On the contrary, Liu et al.

identified that the oxygenated molecules coordinatively adsorbed on some of the active sites.[34]   The induction period can be shorten or eliminated by the addition of reducing agents, suggesting that the induction time seem to determine by a reduction step.   However, since even reduced catalysts still showed a gradual rise in polymerization rate, the initiation of growing chain was also believed as one of the important induction time determination steps.[1]

The mechanism of formation of the first growing chain is poorly understood. Some groups have suggested that surface silanols provide the source of hydrogen atoms (Scheme 1-4-2). [35, 36]   However, mechanisms involving silanols have been considered by some to be unlikely, since dehydroxylation of the catalyst usually improves activity and some completely dehydroxylated catalysts have shown high activity. [1]
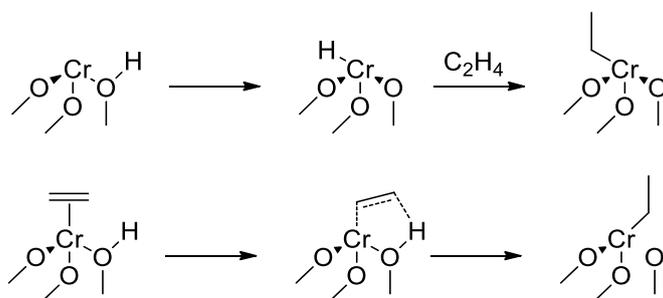
Scheme 1-4-2.

Matallacycle and alkylidene mechanisms do not require a source of additional hydrogen atoms.[37]   For example, two coordinated ethylene can form a metallacycle species (Scheme 1-4-3 a).[38]   The mechanism with repeated ethylene insertions into the metallacycle has been suggested as one of propagation steps.[37]   The metallacycle can undergo β-hydrogen elimination to generate a alkenyl species

(Scheme 1-4-3 b). Formation of vinyl species through dissociative adsorption of ethylene also has been proposed (Scheme 1-4-3 c). [39-44]
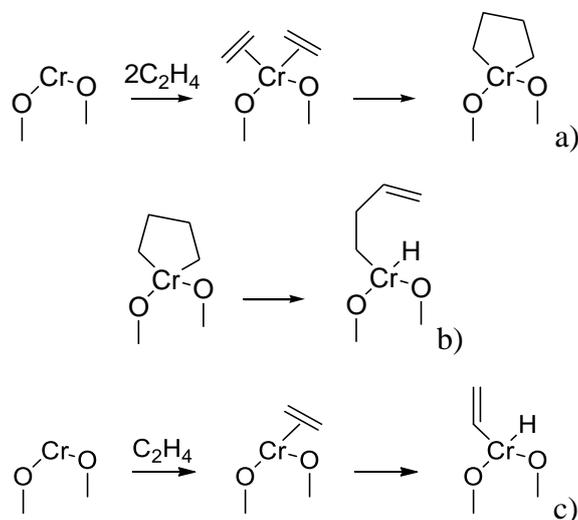
Scheme 1-4-3

Another possibility is the mechanism involving a generation of alkilidene-Chromium species. Some evidences for alkilidene species have been found. Ghiotti et al. reported that the metallacyclopentane could undergo β-hydrogen elimination on to an oxygen linking the Cr (Scheme 1-4-4 a). [45] It also has been suggested that coordination of ethylene may occur to form a ethylidene species (Scheme 1-4-4 b). [45-47]
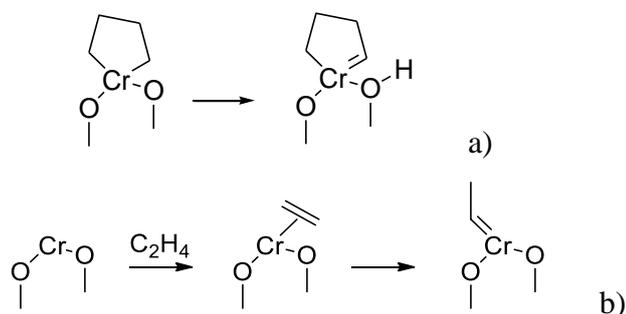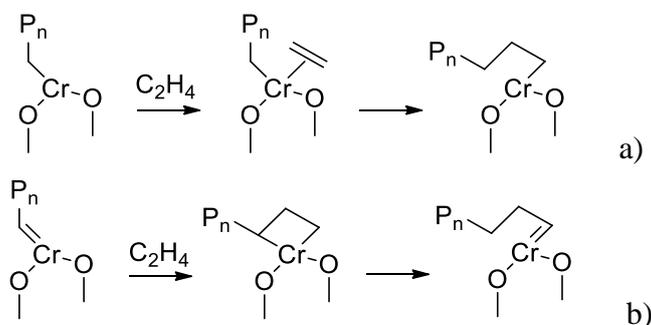

Scheme 1-4-4

Other features including a formation of bridge between two Cr were proposed. However despite the many investigations and much effort as shown above, little is

known certainly about the initiation mechanism.

1.4.3.2 Propagation mechanism

Despite the amount of related research, less general agreement concerning propagation mechanism exists. Two types of mechanisms are generally accepted for the propagation of olefin polymerization using transition-metal catalysts: the Cossee-Arlman (Scheme 1-4-5 a)[48, 49] and the Green-Rooney (Scheme 1-4-5 b)[50] mechanisms.

Scheme 1-4-5

Most of researchers have interpreted the behavior of Cr/Silica catalysts in terms of Cossee-Arlman mechanism, by analogy with d^0 alkyl metal catalysts. The barriers of olefin insertion to M−C for d^0 species are small due to a lack of metal d electrons. Since the active sites of Cr/Silica catalysts must have d^n ($n \neq 0$) configurations, it is potentially different. However, the absence of H/D scrambling during polymerization of partially labeled ethylene showed inconsistent with Green-Rooney mechanism.[50]

The structure of the active species of working catalyst in Cossee-Arlman mechanism has often been expected to be monoalkyl-Cr(III) as shown in Scheme

1-4-6 b.[52, 53]   The main problem is to explain the initiation mechanism of the first

chain in the absence of any activator.   Therefore, the ethylene insertion into the

dialkyl-Cr(IV) and chromacycle(IV) also has been proposed (Scheme 1-4-6) and

some recent experimental results suggested the possibility of them for the

propagation.[54-56]   On the contrary, Espelid et al. reported the difficulties of the

ethylene insertion into the dialkyl-Cr(IV) and chromacycle(IV) by them DFT

calculations.[57]
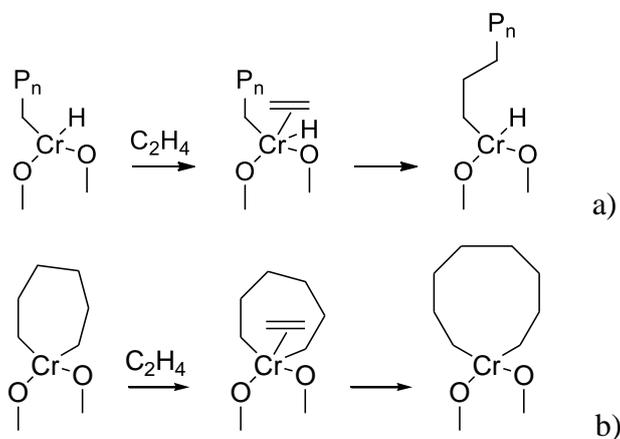
Scheme 1-4-6

1.4.3.3 Chain transfer and termination

In general, chain transfer is thought to proceed through elimination of an agostic

β-hydride to yield a vinyl end-group as shown in Scheme 1-4-7. A new chain then

starts on the same site with a methyl end-group and the process repeats. The MW of

the polymer is determined by the rate of chain growth relative to the rate of chain

termination or transfer, each of which can have a dependence on ethylene

concentration, if ethylene is involved in that step.
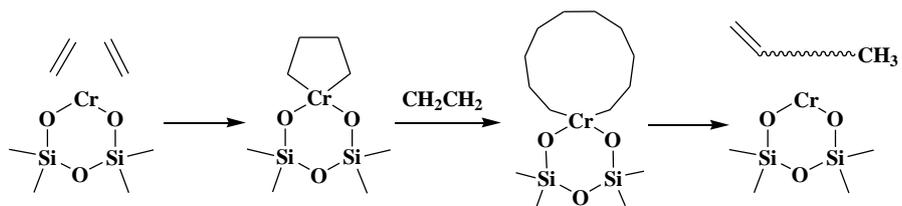
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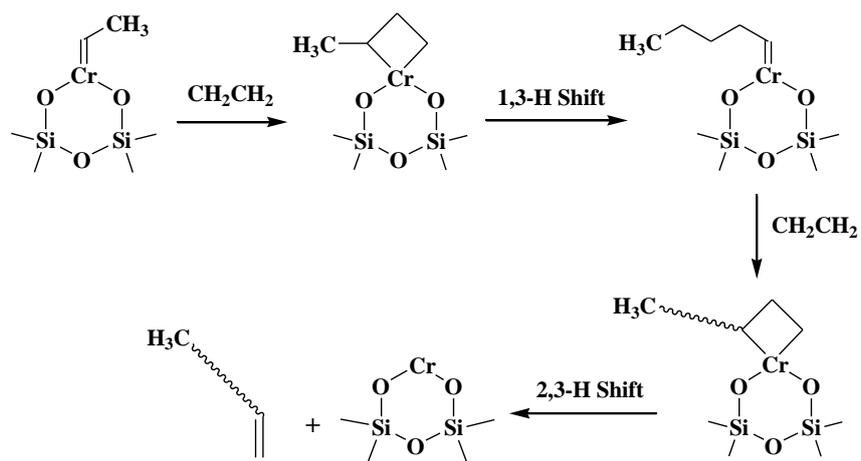
Scheme 1-4-8
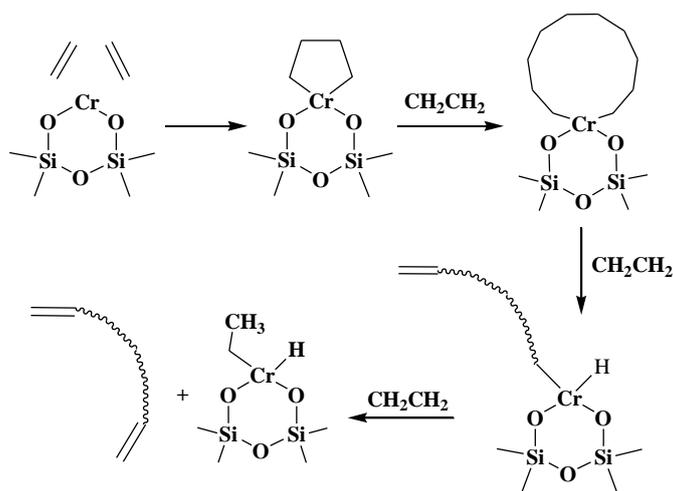
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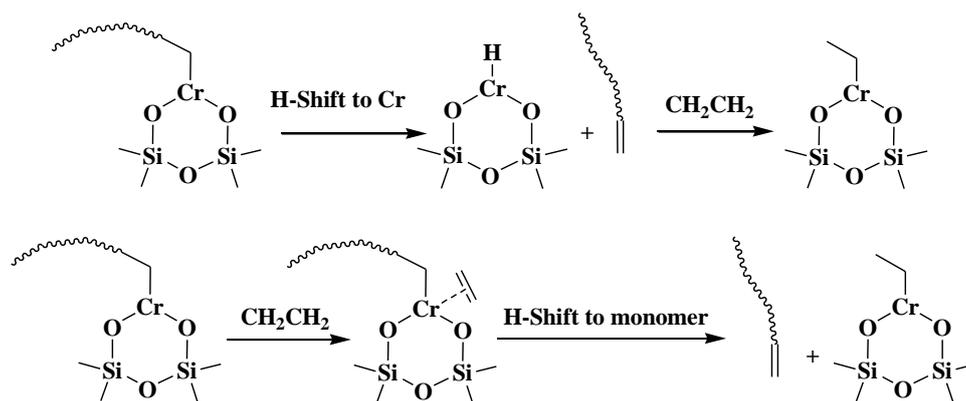
Scheme 1-4-10

H atom transfer can occur in either of the following ways: (1) H transfer to the chromium (Cr–H then begins a new chain in a separate step with ethylene addition) (2) H transfer directly to the incoming monomer.[58]

In the first case, H elimination to chromium is not dependent on the ethylene concentration. Therefore, the polymer MW should be proportional to the monomer concentration (i.e. a linear relationship between MW and ethylene concentration) in which MW extrapolates to zero at zero ethylene partial pressure. But it does not happen. In the latter case, H elimination to monomer is dependent on monomer concentration and because propagation is also first order in ethylene, there is no net dependence of the polymer MW on monomer concentration i.e. the MW should remain constant and there should be no dependence on the ethylene partial pressure. Again it does not happen.

The MW of polymer formed with the Phillips catalyst is not proportional to the ethylene concentration. This is because the actual response is neither first nor zero order, but in between, indicating that both mechanisms are in operation

simultaneously.[59]

1.4.3.4 Branching mechanism

Chain branching has been one of the most important characters of the Phillips catalyst

in the production of HDPE.

LCB formation probably occurs when the terminal vinyl of one chain becomes

incorporated into another growing chain.   LCB varies with Cr loading and

calcination temperature.   Recently, McDaniel et al. reported about the influences of

silica porosity for LCB formation and the some results showed the tendency that the

catalyst with smaller pore volume produced more branched PE.[60]   Perhaps local

active site concentration is relating to the frequency of LCB formation.

Among the SCB formations, two mechanisms have been proposed for the methyl

branching: the isomerization of growing chain (Scheme 1-4-10)[61] and the

copolymerization with propylene which produced by olefin metathesis (Scheme

1-4-12).[61]   The methyl branching by the isomerization of growing chain is well

known in the polymerization using late-transition metal based homogeneous catalysts.

However the β-hydrogen elimination in ethylene polymerization with Phillips

catalysts is known to hardly occur as a chain termination.[62]   The metathesis reaction

on the catalyst surface was strongly revealed by the direct transformation of ethylene

into propylene in a temperature programmed reaction work by Liu et al.[62]
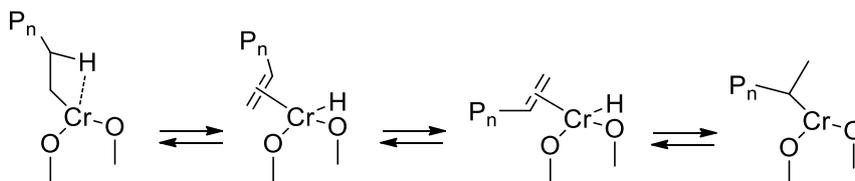
Scheme 1-4-11
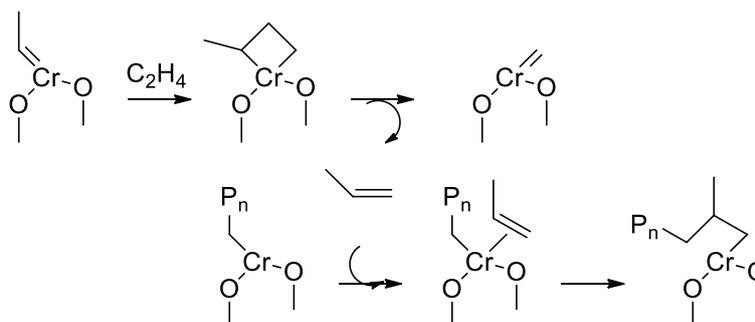
Scheme 1-4-12

The mechanism of SCB formations except methyl branching have been accepted in terms of copolymerization with in situ produced □-olefins. These olefins include 1-butene, 1-octene and especially 1-hexene. The α-olefins formation has been explained that the mechanism involve metallacycles as key intermediates. The key steps of this mechanism are coordination of ethylene, oxidative coupling to form a metallacycle, ethylene insertion to metallacycle and β-hydrogen elimination/reductive elimination (Scheme 1-4-13).[63, 64] The oligomerization mechanism has been believed by the results using homogenous Cr complex models. The mechanisms were elucidated using deuterium labeling and studies of reactions with α-olefin and internal olefins in the homogeneous systems. An experimental result on heterogeneous Phillips catalyst also suggested the possibility of this mechanism.[65-69]

21
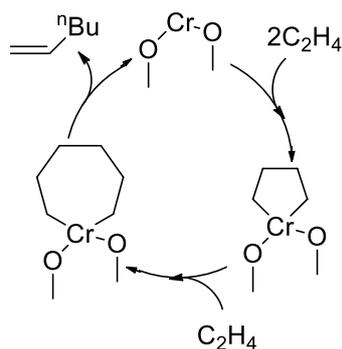
Scheme 1-4-13

1.4.4 Activation of pre-catalyst

Usually, Phillips catalysts are given as Cr(VI)/Silica which is pre-catalyst for ethylene polymerization, since Cr(VI) is not active site. For the Phillips ethylene polymerization, the reduction reaction for Cr(VI) to lower oxidation state should be the first step in the induction stage. Active site precursors of polymerization can be obtained after reduction reaction by CO in a separated pre-activation step, metal alkyl activator or by ethylene monomer during the initial stage of polymerization.

1.4.4.1 Activation by CO

Activation procedure using ethylene is most frequently carried out in the commercial processes. The usage of CO or metal alkyl activator as reduction agent may shorten or remove the induction stage. CO or metal alkyl activator is often utilized at the laboratory scale. Activation by ethylene, CO or metal alkyl activator creates a lower-valence active sites on which polymerization can occur. The molecular structure of reduced Cr active site always has been a matter of controversy in the

literature. The most of possible Cr valences have been proposed as the active sites, either alone or in combination. Among them, Baker et al.[70] reported that low-temperature treatment of Cr(VI)/Silica by ethylene could produce Cr(II) and formaldehyde was released as by-product. The by-product of formaldehyde was also confirmed by Liu et al. using temperature programmed desorption (TPD).[71] However, due to its strong Lewis acidity and coordinative instauration, Cr(II) undergoes reactions between SiO_2 surfaces.[72-74] Therefore, reduced chromium species, which are transient states between Cr(VI) and lower valence active species, exhibit a variation in the bonding and the interaction with surface oxygen. For example, UV-vis spectroscopy and XAS showed the presence of pseudo tetrahedral Cr(II), pseudo octahedral Cr(II) and pseudo octahedral Cr(III) on a reduced catalyst. A recent report by Gianolio et al.[75] showed a direct evidence of the coordination of surface siloxane ligands to reduced chromium species by the EXAFS, which is believed to be crucial for giving a variety of coordination environments around reduced chromium species.

Phillips pre-catalyst reduced by CO at 350°C can show instantaneous polymerization activity, once it contact with ethylene monomer. In IR studies by Zecchina et al.,[41] three types of reduced species were identified through the adsorption of CO and a variety of probe molecules.[76] These sites were considered to vary in the extent of their interaction with the SiO_2 surface. Some sites were identified as most reactive and active in ethylene polymerization, whereas some sites were found to be inactive. Anyway, Cr(II) must be one of active precursors.

However, the structure of active sites and them real precursors are still unresolved.

1.4.4.2 Activation by metal alkyls

The addition of small amount of metal alkyls can enhance the activity of Phillips catalysts.　Metal alkyls has been known to act on the catalysts in following ways: reduction Cr(VI) to the lower-valent species, alkylation of the Cr, removal of trace amount of poisons and chain transfer.[42]　The metal alkyls includes aluminum, boron, magnesium, zinc and lithium.　The various metal alkyls perform in the several ways to different degrees.

The metal alkyls were also known to affect the PE structures such as MW, MWD and branch structures.　For example, the addition of triethylaluminum caused the increase of the branching and MW of produced PE.　On the other hands, the addition of triethylborane or diethylzinc decreased MW, while increasing the branching.[42, 125, 126]

However, a difficulty arises from the fact that a variety of polymerization conditions affect the role of the metal alkyls on the polymerization behavior.　Also in the case of using metal alkyl for the activation of Phillips catalyst, its introduction in which stage had been reported to be crucial to affect the polymerization behavior as well as PE properties according to Blom et al.[127, 128]　Typically there are three stages for introduction of metal alkyl: catalyst preparation stage, catalyst aging or pretreatment stage in polymerization reactor just before introduction of monomer and polymerization stage with simultaneous interaction of catalyst with metal alkyl and

monomer.

1.4.5   Molecular weight control of produced polymer

Normally, Phillips catalyst fabricated the polyethylene with very long polymer chain.
Not like Ziegler-Natta catalyst, Phillips catalyst has no H_2 response for controlling the
MW of polymer.   The MW of the polymer chain namely the average chain length is
decided by the relative rate of between chain termination and chain propagation.
Another indication for MW of polymer is the melt index (MI).   At the same time, MI
is a criterion of the molten polymer fluidity.   Meanwhile the molten polymer fluidity
involves in its MW in turn.   Typically, the MI related to the MW with the inverse
fourth power and the higher MI attribute to a higher the relative polymer chain
termination rate.   In industrial, MI of polymer tends to be pay more attention than
MW, since MI is an indication of the flow of the molten polymer which is crucial for
polymer processing.

There are several factors which can control the MW of the produced
polyethylene.   When polymer chain initiation start which means polymerization
began.   If the temperature of polymerization was increased, the rate of polymer chain
termination can be significantly improved, because arising of the rate of termination
lead to the metal-polymer bond less stable and more tendencies for undergoing
β-elimination.   However, increasing of temperature gives a small influence in the
propagation rate as comparison with termination rate.   As a consequence, it can be
achieve the shorter polymer chains, resulting in increased MI.

Another factor is variation of the ethylene pressure, but it shows an opposite effect.   The polymer chain propagation extremely depends on ethylene pressure, however, the rate of termination less rely on ethylene pressure.   As a result, a rising the ethylene pressure improves the propagation without greatly changing on chain termination contributing to longer chains.

As mentioned above, for Phillips catalyst, the hydrogen response is negligible compared with others catalysts.   Interesting, hydrogenation on Phillips catalyst did not observed and hydrogen response should existed in some other still mysterious way for shortening the polymer chains.

1.4.6   Catalyst support

On Phillips catalyst support surface, free hexavalent CrO_3 decomposes into trivalent Cr_2O_3 and O_2 above 200°C.   However, when anchored on to the silica surface, various chromium species get stabilized even up to 900°C due to the formation of monochromate, dichromate or polychromate surface species.   Noticeably, neither of the chromate nor the silica shows activity towards ethylene.   The chromate is only active if it is anchored to the silica support, which means that the support itself is a part of the active site indicating the active catalyst is a new surface species.[77]

Silica as support for polyethylene catalysts is commercially available from several companies in a variety of catalyst grades.   These typically have high surface areas (300-600 m^2/g) and large pore volumes (1-3 mL/g). Silica is granular or spheroidal and is available in a range of average particle sizes, typically between

about 40 and 150 microns. Particle size distribution (PSD) must be controlled to avoid problems associated with overly large or small particles. The polymer particle usually grows in a way to replicate the morphology of the catalyst particle, which is referred as "replication," *i.e.,* a spherical catalyst results in a spherical polymer particle.

1.4.6.1 Surface chemistry of silica support

Phillips catalysts are outstanding examples of catalysts where the sites are formed by anchoring a Cr compound to the hydroxyl groups of the silica surfaces. For this reason, the silica support is not only a dispersing agent for the active chromium centers. Its properties also influence the catalyst behavior.

The rigid tetrahedron silica is the building block of all siliceous materials: from quartz, through micro-porous zeolites, to amorphous silica. The reason that such a relatives rigid unit is able to aggregate in so many different ways lies in the peculiar bond between two SiO_4 moieties. In contrast with the rigidity of the O-Si-O angle, the energetic costs needed to change the Si-O-Si angle in the 130-180° range are negligible. This result also explains, among the other things, like the high thermal stability of the amorphous phase. Because of such flexibility, amorphous silica is easily formed and shows a great stability. It consists of a new work of such building blocks with a random distribution of the Si-O-Si angle centered around 140°. Silica is classified as a nonmetallic covalent oxide, where the valence electrons are localized in strong covalent bonds between Si and O.

Peripheral silica group carry OH groups, which terminated the unsaturated valences. Different types of the surface hydroxyl have been identified, differing either by the number of hydroxyl group per Si atom or by their spatial proximity. Roughly, OH groups can be divided as following: a) isolated free (single silanols), b) germinal free (germinal silanols or silanediols), and c) vicinal or bridged, or OH group bond through the hydrogen bond (H-bonded single silanols, H-bonded geminals and their H-bonded combinations). On the silica surface, there also different exist surface siloxane groups or Si-O-Si bridges exposing oxygen atoms on the surface. The concentration of hydroxyl groups decreases with increasing temperature of the treatment and is accompanies by the parallel increase of strained siloxane groups. Zhuravlev has shown that the number of total silanol per 100A, when the surface is hydroxylated to the maximum degree, is around 49, irrespective of both the kind of silica and the method of preparation.

Silica has relatively unreactive siloxanes and a variety of hydroxyl sites. Lewis acid/base sites are absent unless the Silica is activated at very high temperatures,[78] and Brønsted acidity is also limited.[79] Thermal treatment of silica leads to the elimination of physisabsorbed water, then condensation of hydroxyl groups with concomitant formation of siloxane bridge (Scheme 1-4-14 a).[80] The partially dehydroxylated Silica has three types of hydroxyl groups: germinal, vicinal and isolated (Scheme 1-4-14 b). Vicinal and germinal hydroxyl groups cannot undergo internal condensation. Since dehydration and rehydration process reflects basic underlying features of the organization of hydroxyl sites on the silica surface, which

has been described as a heterogeneous assortment of crystalline domains, resembling these difficult crystal faces.[81-85]
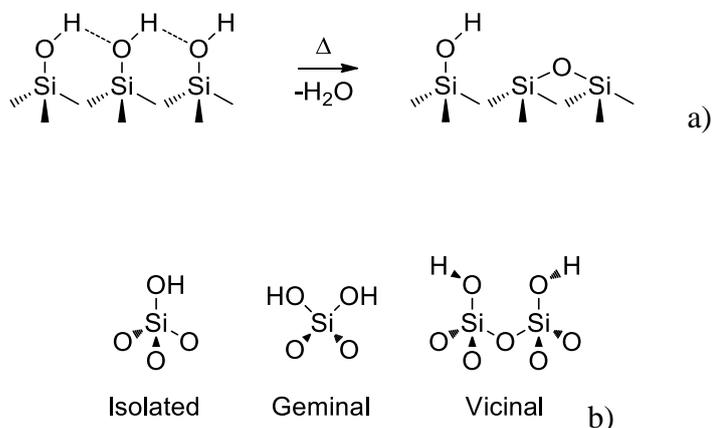
Scheme 1-4-14

Various crystal faces have been suggested as models for the amorphous SiO_2 surface, which has been described as a heterogeneous assortment of small crystalline domains, resembling these difficult crystal faces.

1.4.6.2 Support morphology

Most industrial catalysts need high surface area for high activity, and high strength to resist breakage. However, polymerization catalysts are radically different. Pores of the catalysts are filled with produced solid polymer and then the catalyst particles create smaller particle fragments by the particle rapture from the internal pressure. Thus, fragility is an important characteristic and given from high porosity.

The effect of the pore structure on activity is known to attribute to the varying abilities of the catalysts to fragment during polymerization. Especially, the pore

volume largely controls the fragility of the catalyst, which determines the degree of fragmentation.[86]

The porosity of Phillips catalysts also play a key role in MW and MWD of produced PE.[86] Pore diameter strongly affected to MW. McDaniel explained about the reason that it is attributed to how easily the polymer can escape from the interior of the fragment.

Other features including the effects for branching which described above were reported. Thus, the catalyst morphology affects the catalytic behavior. However, a variety of factors such as local monomer concentration, local heat accumulation, strength of hydrogen bonding between silanol groups etc is varied by the morphology, which makes discussions quite complicated.

1.4.6.3 Support acidity

Acid/base sites on the SiO_2 are limited. However, additions of acid sites are known to influence to catalytic properties due to their local electronic and spatial surroundings.

When a few percent titania is added to Phillips it serves as a strong promoter for the Cr, increasing its activity and lowering the PE MW, although titania itself functions poorly as support.[87] The addition of titania to SiO_2 enhances the Brønsted acidity, Cr becomes associated with the strongly acidic Brønsted sites. Cheng et al. found in XPS investigation that the acidity of silica-titania tends to lower the electron density on the Cr.[88] Although titania remains the industrial favorite as modifier,

other metal oxides, such as zirconia, tin oxide and alumina, also increase the Brønsted acidity of silica and influence the catalyst in similar.

1.4.7 Molecular weight versus porosity

Phillips catalyst also shows a close relationship between the silica porosity and the MW of the produced polyethylene. The relationship can be described like that a larger average pore diameter (PD) of the silica support imparts a lower the MW of produced polyethylene.

The cause for this phenomenon does not completely open. General consideration is that diffusion of ethylene monomer into the pores should affect polymerization performance. However, the truth is that the tendency runs as an opposite way, which is out of expecting. Other way to give the explanation is that starving the catalyst of ethylene might stay in small pores, which is considered as decreasing MW, not increasing it.

Another consideration is that long chain branching tend to exist in small pores since the active species are closer with each other. It means that the macro-monomer incorporation between two active species become more facility.

1.4.8 Modifications of Phillips catalyst

Typical modification of Phillips catalyst utilizes titanium compounds, since in the presence of small amounts titanium on Phillips catalyst does exhibit an enhancement

on both catalyst activity and chain termination rate. This good phenomenon probably originated from a change in the electronic environment on the chromium, since titanium maybe linked to chromium the after calcination leading to a rearrangement of electrons.

There are two methods for incorporating titania into Cr/silica catalysts, and each of them has its certain benefits. The one way is that the silica surface is covered by a layer of titania by having a reaction between a titanium ester and the hydroxyl groups on silica surface.

Co-precipitating by dropping titania along with the silica gel compose the second approach of incorporating titania into Phillips catalyst. It should be accomplished by addition of a water soluble titanium site into the silicate solution before gelation. This approach shows a higher degree of dispersion throughout the bulky catalyst. Some of the titania are exposed on the silica surface and during later calcination chromium can connect on it. Many specialty catalysts have been developed, which can fabricated polyethylene with a very narrow MWD as well as an extremely high environmental stress crack resistance (ESCR).[89-91]

Titania can improve the Phillips catalyst activity by decreasing the induction time and giving higher polymerization rates. The shortened induction time can achieved the easier reduction of Cr(VI) by titania, since the lower valence chromium active site comes to life much quickly. The activity improvement also come from a quick increasing of polymerization rate and an increasing of the active site population, even this is not evidence to confirm. Titania also can increase a termination rate.

Therefore, shorter MW chains were obtained.[92-94]

1.4.9   Model catalysts of Phillips catalyst

1.4.9.1 Homogeneous model catalyst

A major obstacle to better mechanistic understanding is the scarcity of well-defined models for Phillips catalysts.   In this light, some researchers have undertaken to prepare homogeneous models of the Phillips catalysts.

Feher et al. prepared a Cr-ester of a silsesquioxane and addition of two equivalents of AlMe$_3$ to this compound produced active species for ethylene polymerization under mild conditions (Scheme 1-4-15).[95]
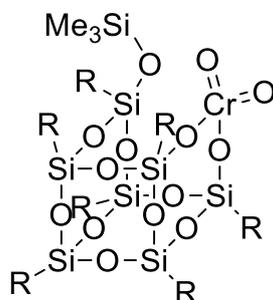
Scheme 1-4-15

These compounds seem to the available structural models of oxidized Phillips catalysts.   However no further information about the chemical nature of the active state in the systems was reported.

Baker and Carrick reported[96] a bistriphenylsilyl chromate which is a hexavalent chromate compound bearing two triphenylsilyl ligands as Scheme 1-4-16 can polymerize ethylene at elevated temperatures (over 130$^{\rm o}$C) and high ethylene

pressures (higher than 350 atm) in cyclohexane solution without adding any activator. Industrially, Phillips catalyst did not work at extremely rigorous polymerization conditions. Therefore, this bistriphenylsilyl chromate should be more extensively research for considering as a homogeneous model for the Phillips catalyst.
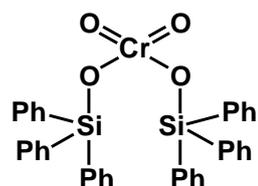
Scheme 1-4-16

Sullivan and his coworkers[97] prepared a spirocyclic Cr(II) siloxane homogeneous Phillips model catalyst for ethylene polymerization. They found that this catalyst gave no activity in the absence of Al-alkyl activator and very poor activity in the presence of $AlMe_3$ activator. This phenomenon was attributed to the homogeneous divalent model catalyst partial deactivation, resulting from ultrahigh sensitive catalyst structure to air and moisture.
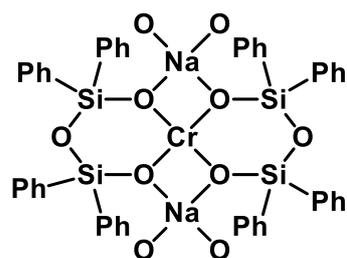
Scheme 1-4-17

Recently, a novel homogeneous chromium(II) model catalyst with a triphenylsiloxy bulk ligand was successfully synthesized and its ethylene polymerization behaviors was observed systematically.[98, 99] Model catalyst showed inactive for ethylene polymerization without Al-alkyl activator at 20 atm

ethylene pressure and room tempreture, then after increasing the temperature to 100°C for 16 h, which probably resulted from the existence of two strongly coordinated THF molecules in catalyst structure.   Therefore, an Al-alkyl activator was necessary for the ethylene polymerization using this model catalyst.
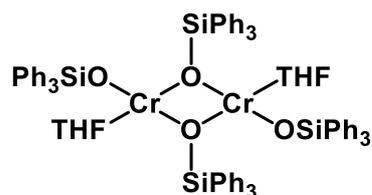
Scheme 1-4-18

Baker et al. reported that bis(triphenylsilyl)chromate catalyzed the ethylene polymerization at the pressure over 35 MPa in the absence of activator (Scheme 1-4-19).[100]   Furthermore, addition of alkyl aluminum to this catalyst caused onset of ethylene polymerization at atmospheric pressure.
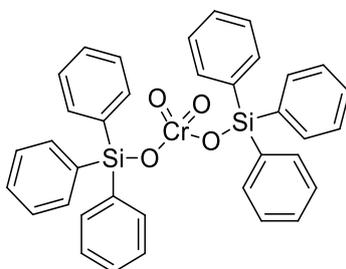
Scheme 1-4-19

Recently, Gambarotta et al. succeeded to isolate the active species for ethylene polymerization and oligomerization (especially trimerization).[102, 103]   They has elucidated a link between the metal oxidation state and the type of catalytic behavior in them systems: Cr(III) led to nonselective oligomerization, Cr(II) to polymerization and Cr(I) to selective trimerization (Scheme 1-4-20).

a)

b)
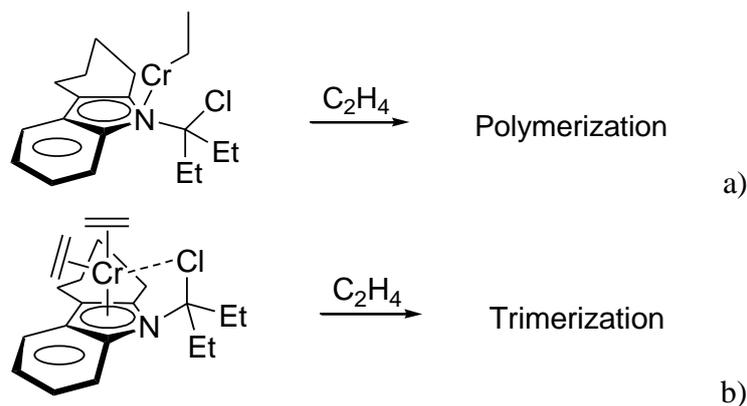
Scheme 1-4-20

One of the pitfalls in modeling heterogeneous chemistry with homogeneous systems is caused by the ignorance of the interactions with support surface. Since there are strong Cr-SiO$_2$ interactions in Phillips catalysts, well-defined models with the surface itself as a part of the ligand are important.

1.4.9.2 Heterogeneous model catalyst

The surface complexity of the conventional Phillips catalyst resulted from the following reasons: 1) the coexistence of mono-, di-, and polychromate species, 2) the lower oxidation chromium active species by a reduction reaction for surface chromate species from pre-catalyst, 3) the very low fraction of active chromate species in the all chromate loading, 4) the unclear and complicated reactions for the first monomer insertion during initiation.[103, 104] These factors mainly attributed to the surface complexity of the traditional Phillips catalyst. The surface complexity hinders an academic progress for basic understanding of this important commercial catalyst significant industrial polyolefin catalyst. Therefore, the nature of active sites and ethylene polymerization mechanisms for this significant industrial polyolefin catalyst

is still not open. During the last decades, various novel heterogeneous models catalysts having a uniform surface chromium species structure based on Phillips catalyst have been designed to study and understand in this field. Classical heterogeneous models which were reported for Phillips catalysts are discussed in here.

Several model chromium catalysts with uniform structures supported on SiO_2 have been designed in order to study the reactivity of their interactions with the surface.

For example, uniform hexavalent monochromate species[105] as showing in Scheme 1-4-21 firstly was synthesized by McDaniel and his colleagues through mild grafting at $200^{\circ}C$ of $CrClO_2$ onto silica with a thermal pretreatment at $400^{\circ}C$. This type of model catalyst showed a similar surface chromate structure and polymerization activity to the Phillips catalyst. However, they did not research the branching and MWD of produced polymer.
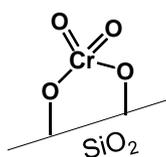
Scheme 1-4-21

Recently, Scott and her co-works[106, 107] designed a similar catalyst by the ambient anhydrous grafting of CrO_2Cl_2 onto silica with a thermal pretreatment at $200^{\circ}C$, $450^{\circ}C$ or $800^{\circ}C$. Through combination of IR, XANES, and EXAFS, it was explained that a higher polymerization activity obtained from CrO_2Cl_2 grafted onto silica thermal pretreatment at $800^{\circ}C$ is involved in the more strained chromasiloxane rings with a six-membered.

At the same time, it was also reported other model catalyst by Thune et al.,[108] a flat surface catalyst via impregnating aqueous CrO_3 onto a flat Si (100) substrate coated with an amorphous silica layer (Scheme 1-4-22). The flat catalyst coated with monochromate species showed ethylene polymerization activity at 160^oC. However, the divalent surface monochromate species with pre-reduced cannot polymerize ethylene resulting from its high sensitivity to air and moisture.[109]
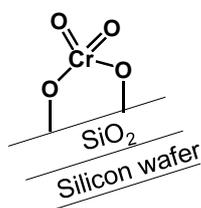
Scheme 1-4-22

Very recently, Kamiya et al.[110] conducted further research about highly air-sensitive divalent model of Phillips catalyst through CO reduction reaction as shown in Scheme 1-4-23. It were prepared two heterogeneous divalent models of Phillips catalyst by similar ambient anhydrous grafting of CrO_2Cl_2 onto silica with a thermal pretreatment at 500^oC or 800^oC, then followed by high temperature calcination and CO reduction at 300^oC. The catalyst obtained from Cr(II) supported on silica with a thermal pretreatment at $800\,^oC$ gave a higher ethylene polymerization activity than a one came from Cr(II) supported on silica with a thermal pretreatment at 500^oC without any induction period at room temperature. It indicated that different activities not only arise from heterogeneity of chromate species but also from heterogeneity of silica surface.
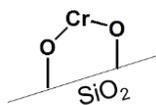
Scheme 1-4-23

In our previous research, we synthesized uniform mononuclear and dinuclear chromium species catalyst for ethylene polymerization.[111] The catalysts were prepared using the reaction between organochromium complexs (Cr(η^3-allyl)$_3$ or Cr$_2$(η^3-allyl)$_4$) and surface OH groups of partially dehydroxylated SiO$_2$ support (Scheme 1-4-24).[112-113] The uniform chromium species imparted very broad MWD as well similar to traditional Phillips catalyst.
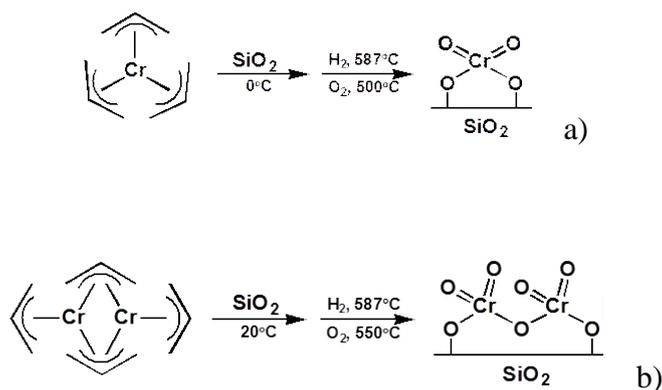
Scheme 1-4-24

Some groups have reported about the reactivity of SiO$_2$ supported η^3 - allyl-based organochromium species[114-116] and the model catalysts showed activity for ethylene polymerization. Among them, Bade et al. reported the comparison of Cr(η^3 - methallyl)$_3$ (methallyl = 2-methylallyl) grafted catalyst among that on SiO$_2$ pretreated at 200℃, 400℃ and 800℃. Cr(η^3-methallyl)$_3$ grafted on SiO$_2$ pretreated at 200℃ and 400℃ showed activity for the high pressure ethylene polymerization and that grafted on SiO$_2$ pretreated at 800℃ showed activity for ethylene oligomerization.

Considering the results, they suggested that bipodal chromium led to polymerization and unipodal chromium to trimerization (Scheme 1-4-25).

polymerization   a)

trimerization   b)
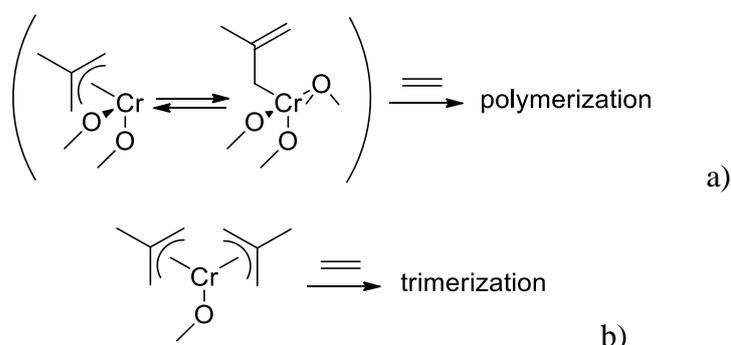
Scheme 1-4-25

McDaneal et al.[117] also reported similar tendency in the system using Cr(dmpd)$_2$ (dmpd = 2,4-dimethylpentadienyl) as a precursor and they identified similar links between catalytic behaviors and the structures. However, since less evidences made distinctions in their reports, direct links for catalytic properties and structures still deposit obscurities. Furthermore, some results that cast doubt to the suggestion also recently reported.[118-120]

Monoi et al. reported a catalyst supported on SiO$_2$, using a molecular precursor of Cr(N(SiMe$_3$)$_2$)$_3$.[121, 122] The catalyst showed high activity for ethylene polymerization with existence of alminoxane. As introduced in different systems, they also found that higher pretreatment temperature of SiO$_2$ produced oligomerization catalyst. Interestingly, the use of alminoxane with bulky alkyl effectively took place the active site to oligomerization. Monoi and Ikeda also prepared a catalyst with monoalkylated Cr(III) species, using Cr(CH(SiMe$_3$)$_2$)$_3$ (Scheme 1-4-26).[121-124] The catalyst performed high activity for ethylene polymerization without use of any activator. The behavior of the catalyst was

similar to the industrial Phillips catalysts, with respect to the effect of temperature on

the MW of PE, broad MWD and branching abilities. They revealed from the results

that main working sites on the Phillips catalysts were monoalkyl-Cr(III). However,

the critical problem in their report is absence of catalyst characterization.
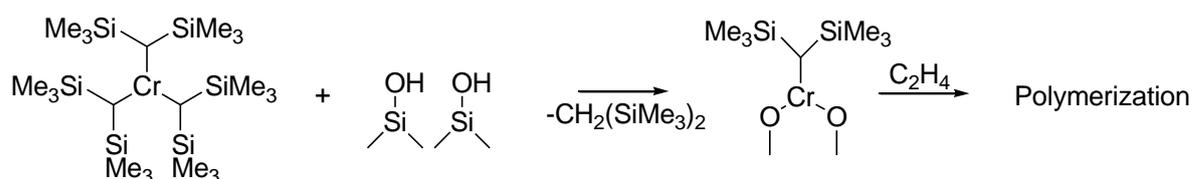
Scheme 1-4-26

1.5 Objective of this work

The industrial significance of the Phillips catalyst has attracted a great deal of

academic and industrial research round 60 years. Despite many efforts, the structure

of active site on Phillips type polymerization systems remained controversial. At the

same time, the Phillips polymerization mechanism is still not sufficiently understood.

The main difficulties preventing the deep understanding of the mechanism are the

complexity of catalyst system. It caused by the heterogeneous nature of Phillips

catalyst. Specifically, the conventional catalyst synthesized by an simple

impregnation method consist of a mixture of several types of potentially active Cr(VI)

species and inactive Cr_2O_3 clusters and a series of various coordination environments

for Cr(VI) species. Furthermore, reduced Chromium species, which are transient

states between Cr(VI) and lower valence active species, exhibit a variation in the

bonding and the interaction with surface oxygen. Therefore, it is very difficult to

dissolve the detailed relations between them and to draw out the nature of the

individual active sites independently from the integrated information. Model

catalysts with controlled active site structures are powerful for the former problem and there have been a number of precedent studies for model catalysts with uniform Cr structures. However these studies mostly only paid attention to Chromium species not on heterogeneous silica surface. Since the most attractive and irreplaceable nature of the Phillips catalysts is attributed to unique catalytic performance to produce branches and very broad MWD, disclosure of the control factors of the unique properties should be disclosed for establishing the pure unique catalysts.

Industrially, activators are not commonly utilized for Phillips ethylene polymerization system except for some specific polyethylene fabrication. Therefore, study about activator for Phillips ethylene polymerization less conducted. However, the activator is significant to tune the polymer structure and purify the polymerization system. The type of activator and its amount for polymerization is curial for Phillips ethylene polymerization performance due to a deactivation and not enough activation.

In this dissertation, firstly, the focus of this work was on various activators for Phillips ethylene polymerization to probe the deactivation during polymerization. A series of activator included modified one was investigated for Phillips ethylene polymerization in terms of polymerization activity and polymer properties. The information of microstructure of the polymers was obtained by GPC, NMR. The deactivation mechanism was further understood by accomplish the relationship between the structure of activators and the microstructure of polymer.

Secondly, this dissertation concerted with the fundamental matters of Phillips

catalysts, particularly the states of the active species. The strategy in this study is homogenous catalyst with a model of active site and silica support. The relationship between catalyst structure and catalyst behaviors was obtained. The deeper understanding of Phillips ethylene polymerization was achieved.

In general, the conventional Phillips catalyst was systematically studied from preparation to activation and polymerization. Based on the previous research, my final target in this study is to find the real reason why Phillips catalyst can produce polyethylene with unique properties. The new attempt for design and preparation of new grade of Phillip catalyst for polyolefin polymerization with high performance has been done.

The objective of this research is to produce a new class of PE by using bimetallic catalyst. In the present study, a series of metals were employed for preparing modified Phillips catalysts. Catalyst activity and polymer properties were investigated. Improved understanding of these catalysts may enable the development of bimetallic Phillips ethylene polymerization catalyst with improved catalyst performance in terms of catalyst activity and enhanced polymer properties.

This dissertation includes three parts of study. Effects of various activators on ethylene polymerization properties are descried in chapter 2. The importance of design of novel homogeneous Phillips catalyst using the model of trivalent and hexavalent chromium site and support is discussed in chapter 3 and 4. Finally, general conclusion is discussed in chapter 5.

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Chapter 2

Development of Hetero-Bimetallic Phillips Type Catalyst for Ethylene Polymerization

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2.1 Introduction

The Phillips catalyst[1] is one of the most important commercial olefin polymerization catalysts, producing more than 7 million tons of 100 different grades of high-density polyethylene (HDPE) and responsible for about 50% of the world HDPE market.[2] The Phillips catalyst is synthesized by the impregnation of chromium compounds (mostly chromium (III) acetate) onto amorphous silica gel and subsequent calcination under oxidative atmosphere, leading to a pre-catalyst with hexavalent chromium species attached onto silica. In spite of its simplest preparation procedure and chemical composition, the Phillips catalyst exhibits the following several unique features compared with other olefin polymerization catalysts such as Ziegler-Natta and metallocene catalysts:

1) The most important feature is the unique structure of produced PE such as ultra-broad (or bimodal) molecular weight distribution (MWD) as well as long- (and short-) chain branches (LCB and SCB respectively), being suitable for blow molding applications (bottles, drum, fuel tanks and other containers).[2, 3, 4] Interestingly, these features are attained only through ethylene homopolymerization in a single reactor, which indicates a highly multi-functional nature of the catalyst. The

chemical and geometrical heterogeneities of the supported chromium species are responsible for the mentioned multi-functionality.[5, 6]

2) The Phillips catalyst can be directly activated with ethylene without using any organometallic activator, on the contrary to most of other polymerization catalysts. However, organometallic activator can be also used to enable the activation under a mild condition and to modify polymer properties.[7]   It is believed that hexavalent chromium species in a pre-catalyst is once reduced into divalent species,[2] and then transformed into an active form, some alkylated chromium species.   Nowadays, monoalkyl-chromium (III) and Cossee-Arlman mechanism are believed as most plausible.[5, 8]

3) Phillips catalyst can be tailored in numerous ways for covering as many as 100 grades of HDPE.   Typical variables are the activation temperature, organometallic activator, support pore structures, and the addition of third components such as titanium oxide.[9, 10]

In these two decades, many efforts have been devoted to find out an alternative to the Phillips catalyst, since the ethylene polymerization activity of the Phillips catalyst is lower (3kg-PE/g-cat·h)[2] than other catalysts and the pre-catalyst contains toxic hexavalent chromium species.   Although some sort of metallocene,[11] supported metallocene[12] and constrained geometry catalysts (CGC)[13-15] of early transition metal and chromium have been extensively studied, these alternatives are still unable to compete with the Phillips catalyst in terms of the unique polymer properties.   As a consequence, the improvement of the polymerization performance

of the Phillips catalyst is one of the most realistic ideas to reduce the chromium concentration in the product.

In general, supported bimetallic catalysts have been used in many important catalytic reactions, because these catalysts show many improvements over monometallic ones, such as higher activity, selectivity, stability and tolerance.[16] Also, they often show significant synersism between two metal components, leading to catalytic properties completely different from those of the monometallic catalysts.[16] As for the Phillips catalysts, the modification of silica support by titanium compounds was successfully employed to improve the polymerization performance.[17-20] Titanium can be incorporated by the condensation reaction between titanium alkoxide and hydroxyl groups of silica,[18] and by the addition of $TiCl_4$ in the sol-gel synthesis of silica support.[19] The titanium components dispersed on the silica surface or in the bulk bring about several positive consequences for the polymerization performance such as easier activation, improved activity, broader MWD, and uniform distribution of SCBs over MWD.[2] These advantages are believed to come from not only the surface acidity increased by titanium oxide[2] but also the formation of new active Cr species with Cr-O-Ti bridging bonds.[21] The introduction of other transition metal such as zirconium and tin imparts similar (but smaller) effects on the polymerization performance.[2] In these previous studies, the second metal components were once immobilized onto silica support, followed by the immobilization of the chromium component: the catalyst preparation was conducted under an idea of support modification. Moreover,

most of previous studies did not systematically examine the effects of a series of metal components based on the sole preparation recipe.

In our previous paper, a variety of chemical modification such as impregnation of metal salts and reaction of metal alkoxides with surface silanol for both typical and transition metal components were applied to improve the polymerization performance of Phillips catalysts.[22]   Here, a series of bimetallic-type Phillips catalysts with different second metal components were prepared based on a co-impregnation method, expecting synergism between two metal components over conventional support modification.   It was found that a second metal with low electronegativity tended to improve catalyst activity (such as zirconium, zinc and vanadium).   Moreover, bimetallic Phillips catalyst gave higher branch level than monometallic Phillips catalyst owing to acidity of catalyst surface.

2.2 Experimental

2.2.1 Materials

Silica gel was donated by PQ Corporation (ES70X, 51 µm, 320 m^2/g). $Cr_3(OH)_2(CH_3COO)_7$, $Al(NO_3)_3 \cdot 9H_2O$, $TiO[CH_3COCH=C(O^-)CH_3]_2$, $ZrO(NO_3)_2 \cdot 1-2H_2O$, $ZrO(CH_3COO)_2$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $(NH_4)_6H_2W_{12}O_{40} \cdot 5-6H_2O$ were purchased from Wako Pure Chemical Industries, Ltd., while $Al(OH)_2(CH_3COO)$, $Mn(NO_3)_2 \cdot 1-2H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$ $Cu(NO_3)_2 \cdot 1-2H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Zn(CH_3COO)_2$ were from Sigma-Aldrich Corporation.   Tri-isobutyaluminum

(TIBA) was donated by Tosoh Finechem Corporation. Ethylene of polymerization grade was donated by Asahi Kasei Chemicals Corporation. Nitrogen and oxygen of research grade were used without further purification. Heptane was purified by passing through a column filled with 4 A molecular sieve followed by bubbling with nitrogen for 2 h.

2.2.2 Catalyst preparation

0.0422 g of $Cr_3(OH)_2(CH_3COO)_7$ (0.067mmol, corresponding to 1.0 wt%) and a specified amount of second metal salt were co-dissolved in 5.0 ml of distilled water at room temperature. The amount of the second metal salts was set to the Cr/M molar ratio of 3, since the best performance was obtained at Cr/V of 3 in our previous study.[23] The pH of the solution was adjusted to be 7 by adding NH_3, except for $Al(NO_3)_2 \cdot 9H_2O$, $Al(OH)_2(CH_3COO)$, $Cu(NO_3)_2 \cdot 1\text{-}2H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $ZrO(CH3COO)_2$, $ZrO(NH_3)_2 \cdot 1\text{-}2H_2O$ and $Zn(CH_3COO)_2$, which made precipitate at pH 7.

The solution was added onto 1.0 g of silica and impregnation was performed at 80°C for 2 h with gentle stirring. After that, the product was dried at 120°C and calcined under oxygen at 400°C for 2 h, followed by cooling under nitrogen. The metal loadings determined with UV/Vis spectroscopy (JASCO V670 UV-Vis spectrometer) were almost equal to the theoretical values (*i.e.* the added amounts).

2.2.3 Ethylene polymerization

Semi-batch slurry ethylene polymerization was performed for 30 min in a 1 L stirred autoclave at 70°C with continuous supply of ethylene at 0.5MPa.   TIBA (0.2 mmol) was added as scavenger in 200 ml of heptane.[6]   The polymerization was started by the addition of 40 mg of a catalyst and terminated after 30 min by the addition of ethanol.   The obtained polymer was filtered and dried in vacuum at 60°C for 6 h.

2.2.4 Polymer characterization

The branch frequency of PE was determined by ^{13}C-NMR at 75.46 MHz operated at 120°C with 30.0 μs (90°) pulses, 1.7s acquisition time and 2.0 s relaxation delay. The branch frequency of PE was determined by the previously reported method.[23] Gel permeation chromatography (GPC, Waters Alliance GPCV2000CV) with polystyrene gel columns (Shodex UT-806 M) was used to determine MWD of the obtained PE by using 1,2,4-trichlorobenzene as solvent at 140ºC.

2.2.5 Characterization of bimetallic catalysts

X-ray photoelectron spectroscopy (XPS) analyses of the pre-catalysts were performed on a Kratos Analytical-Shimadzu (AXIS Ultra DMD model) spectrometer equipped with a hemispherical electron analyzer working in the constant pass energy mode.   A monochromated Al Kα radiation was used as the X-ray source.   Low resolution survey scan was measured between 0 and 1200 eV with a resolution of pass energy 160 and step size 1.0 eV for a preliminary survey of all surface elements. High-resolution XPS scan was carried out with a resolution of pass energy 20 and step

size 0.01 eV.   All the binding energies (BE) were referenced to the Si 2p peak of the

support at 103.3 eV.   Each powder sample was attached on a carbon tape and fixed

on a sample holder under nitrogen.   The sample holder was then put into the air-tight

transfer vessel, through which the sample holder was loaded onto the instrument in an

inert manner.

2.3 Results and discussion

A series of bimetallic catalysts were prepared to survey effects of second metal

components on the catalyst activity and branching ability of the Phillips catalyst.

Table 2-3-1 summarizes the ethylene polymerization results for the bimetallic

catalysts.   It has been observed that on the introduction of second metal, the activity

and the branch frequency were changed as compared to the conventional Phillips

catalyst.   In the cases of bimetallic catalyst containing titanium, vanadium, zinc and

zirconium components as the second metal, both the activity and branching ability

were improved.   On the other hands, the introduction of aluminum, iron, cobalt,

nickel and copper components hardly affected the catalyst performances, and

manganese, molybdenum and tungsten components rather deteriorated the

performances.   These tendencies for different metal components will be discussed

later.   Table 2-3-2 summarizes the effects of the kind of precursors as a source of

second metal on the activity and branching ability of the resultant bimetallic catalysts.

Different precursors of the same second metal imparted similar catalyst activity and

branching ability, indicating that the presence of second metal components themselves

exerted the primary contributions while interaction balances of two metal precursors with silica during impregnation offered marginal contributions.

Table 2-3-1.　Effects of second metal on the ethylene polymerization activity and the branching frequency of obtained PE

Second metal precursor[a]	Activity (kg-PE/g-cat·h)[b]	$\geq$ Hex branch /1000C[c]
–	0.79	0.43
$Al(NO_3)_3$	0.78	0.48
$TiO(C_5H_7O_2)_2$	0.85	0.51
$V(C_5H_7O_2)_3$	0.87	0.56
$Mn(NO_3)_2$	0.53	0.35
$Fe(NO_3)_3$	0.78	0.47
$Co(NO_3)_2$	0.72	0.46
$Ni(NO_3)_2$	0.80	0.35
$Cu(NO_3)_2$	0.81	0.47
$Zn(NO_3)_2$	0.86	0.50
$ZrO(NO_3)_2$	0.92	0.52
$(NH_4)_6Mo_7O_{24}$	0.65	0.45
$(NH_4)_6H_2W_{12}O_{40}$	0.62	0.44

[a] The metal loadings were set to 0.067 mol-Cr /g-SiO$_2$ and 0.022 mol-second metal/g-SiO$_2$.

[b] The polymerization was carried out at 70°C and 0.5 MPa of ethylene pressure for 30 min.

[c] Measured by ^{13}C NMR.

Table 2-3-2.　Effects of second metal precursors on the ethylene polymerization

activity and the branching frequency of obtained PE

Second metal precursor	Activity (kg-PE/g-cat·h)	$\geq$ Hex branch /1000C
$Al(OH)_2(CH_3COO)$	0.77	0.53
$Al(NO_3)_3$	0.78	0.48
$V(C_5H_7O_2)_3$	0.87	0.56
VO_3NH_4	0.98	0.61
$VOSO_4$	0.89	0.63
$Ni(CH_3COO)_2$	0.75	0.35
$Ni(NO_3)_2$	0.80	0.43
$Zn(CH_3COO)_2$	0.84	0.52
$Zn(NO_3)_2$	0.86	0.50
$Zr(OH)(CH_3COO)_3$	0.89	0.55
$ZrO(NO_3)_2$	0.92	0.52

In our previous paper, we reported that the polymerization yield in the reactor

was highly correlated with the branch level in the resultant PE, where it was proposed

that the branch formation is owing to the *in-situ* co-monomer formation and

subsequent incorporation into the main chain.[6]　Accordingly, the branch levels for

the bimetallic catalysts are plotted against the polymer yields in Figure 2-3-1 with

reference data for the 30 and 60 min polymerization with the conventional Phillips

catalyst.　In accordance with our previous report,[6] the branch level enhanced as the

yield increased by doubling the polymerization time for the conventional catalyst.

Though a similar correlation between the yield and branch level was observed for the

bimetallic catalysts, the bimetallic catalysts tended to form more branched PE.

Especially the upward deviation from the trend was the most obvious for　the

vanadium-based bimetallic catalyst, which was further examined in another paper.[23]

Even though several reasons could be inferred such as easier formation of unipodal chromium species regarded as the co-monomer formation site,[24] reduced pore volume,[25] and a larger number of Lewis acidic points that keep α-olefin co-monomer around surfaces in the presence of the second metal, we believe that it simply arises from shorter Cr-Cr distance[2] due to the reduction of immobilization sites due to the addition of second metal components.
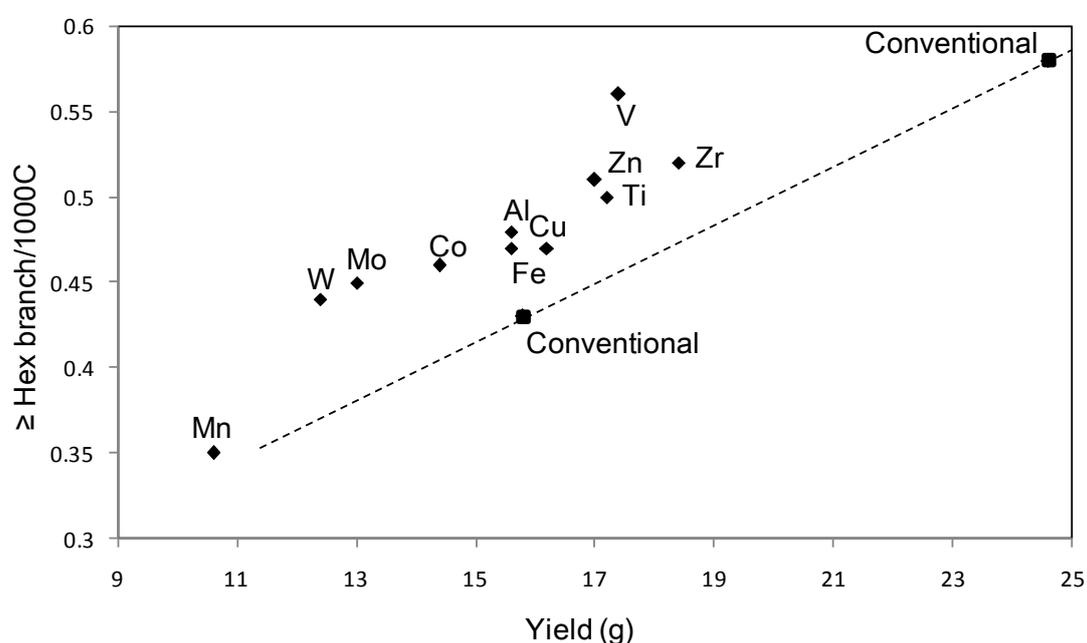
Figure 2-3-1.   Dependence of branching level on catalyst activity

Influences of the second metal components on MWD of produced polymer were examined for selected samples (Figure 2-3-1).   It is known that titanium-modification of SiO_2 support broadens MWD in a way to extend the low MW tail.[7]   The zirconium-based bimetallic catalyst resulted in similar consequences to those obtained by the titanium-modification.   Plausibly, stronger acidity of these metal components give rise to lower electron density on the chromium

species, thus relatively enhancing □-agnostic assisted chain transfer to ethylene.[2] On the other hand, the molybdenum component with much lower acidity hardly affected MWD, except a slightly enhanced bimodal feature.
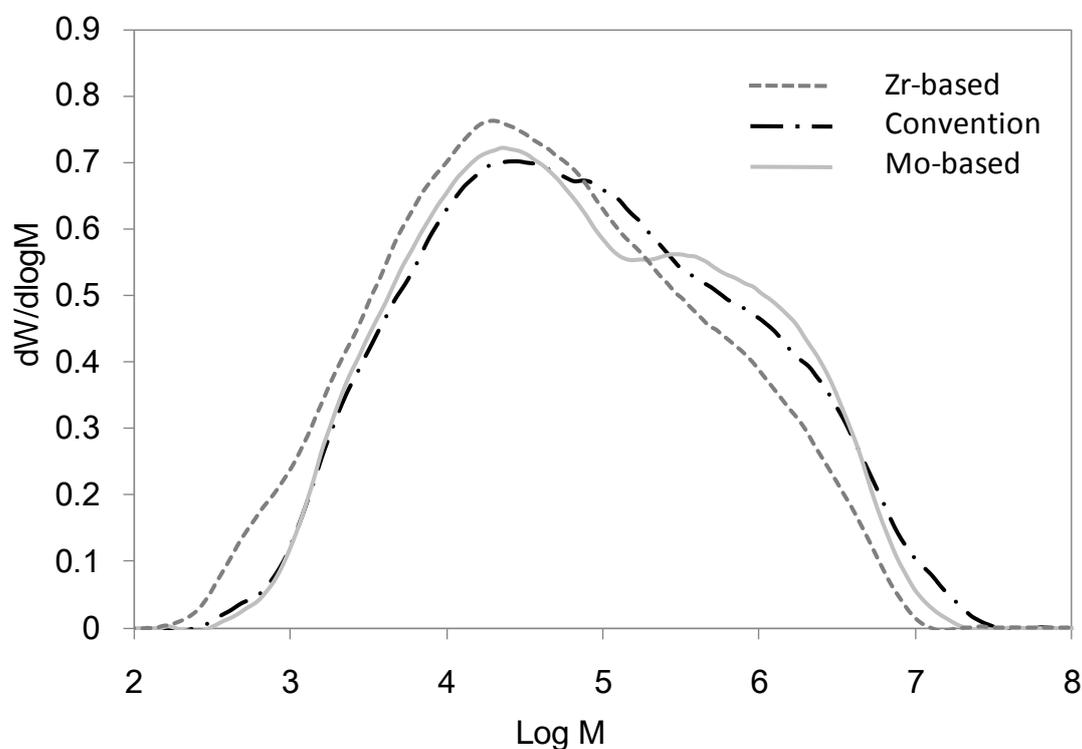
Figure 2-3-2. MWD of obtained PE for conventional Phillips catalyst (black dashed) and zirconium- (grey dot) and molybdenum-based (light grey solid) bimetallic catalysts.

XPS is one of the most powerful methods for the characterization of surface chromate species in the Phillips (pre-)catalyst.[26] Especially, the binding energies (BEs) of Cr (2p) have been used to discuss the electron density on chromate species, which is believed to be related to the catalyst performance.[27] The results of the XPS measurements on the BE of Cr (2p$_{3/2}$) as well as the atomic ratio of surface cationic components are summarized in Table 2-3-3. The deviation of the BE values

of Cr ($2p_{3/2}$) from the conventional catalyst correlated well with the electronegativity of the corresponding second metal as compared to the electronegativity of chromium: a larger BE value for metal with lower electronegativity while a smaller BE for metal with greater electronegativity. Only vanadium showed an exceptionally larger BE in spite of the similar electronegativity to that of chromium. It could be envisaged that the observed highest branching ability of the vanadium-based bimetallic catalyst originates not only from reduced Cr-Cr distances but also from enhanced α-olefin coordination to the electron-deficient chromium species. Figure 2-3-3 shows the relationship between the BE value of Cr ($2p_{3/2}$) and the polymerization activity, where a higher BE value, *i.e.* more electron-deficient chromium species tended to offer a higher activity in accordance with previous reports.[23] The surface metal concentrations were very similar among the bimetallic catalysts: slightly lower chromium concentrations than the conventional catalyst while 2.1-2.7 atomic% of the total metal contents (Cr + M).

Table 2-3-3.　XPS results for the bimetallic Phillips catalysts

Second metal	Electronegativity[a]	BE (Cr 2p$_{3/2}$)[b] (eV)	Surface metal content	
			Cr/(Cr+M+Si) (atomic%/atomic%)	M/(Cr+M+Si) (atomic%/atomic%)
–	1.65[c]	578.5	2.3	–
Al	1.61	578.9	1.5	0.9
Ti	1.54	579.6	1.7	0.4
V	1.63	580.5	1.8	0.3
Co	1.88	578.4	1.9	0.2
Zn	1.65	578.7	2.0	0.5
Zr	1.33	579.9	1.8	0.4
Mo	2.16	578.0	1.9	0.8

[a]Electronegativity shows the tendency of an atom to attract electrons towards itself

[b] The BE values were calibrated using Si (2p) peak at 103.3 eV.
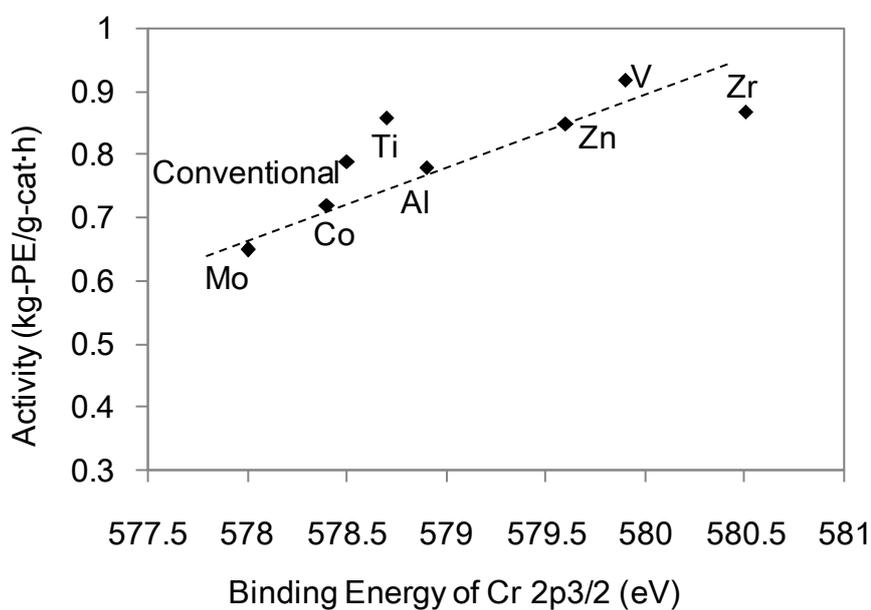
[c] The electronegativity of chromium.

Figure 2-3-3.　Correlation between binding energy of (Cr 2p$_{3/2}$) and catalyst activity

2.4 Conclusion

A series of Phillips-type bimetallic catalysts were prepared according to a co-impregnation method and their ethylene polymerization performances were examined. Second metal components in addition to the main chromium species improved the polymerization activity when second metal withdrew electron density from chromium species (for zirconium, zinc and vanadium). Oppositely, when the electron density of chromium species was increased by the addition of second metal, the activity was dropped (for molybdenum and tungsten). Though a higher activity of the catalysts tended to produce more branched PE due to the enhanced comonomer formation, the incorporation of the second metal components obviously enhanced the branching ability of the Phillips catalyst. Especially the vanadium-based bimetallic catalyst exhibited an exceptional branching ability as well as low electron density of chromium species, which is likely worth more detailed examination in the future.[23]

As conclusive remarks for the bimetallic approach, early transition metal as the second component offers improvements both in the activity and branching ability. The maximum performance improvements over the conventional Phillips catalyst are plausibly around several tens%. Interestingly, the addition of second metal components should alter the nature and density of surface hydroxyl groups similarly to the calcination temperature. However, the influences of the second metal components are much smaller than those of the calcination temperature. This fact may hide some key parameter(s) toward immense improvements of the catalyst performances.

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Chapter 3

Effects of Various Activators on
Ethylene Polymerization Properties

3.1 Introduction

The Phillips catalyst,[1] simply composed of chromium species supported on silica, is a

unique catalyst for industrial ethylene polymerization. It produces high-density

polyethylene (HDPE) featured with short- & long-chain branches (SCB & LCB) and

extremely broad molecular weight distribution (MWD), while the other catalysts such

as Ziegler-Natta or Metallocene generally fabricate linear polymer with narrower MWD

in homopolymerization. Due to the said uniqueness, the Phillips catalyst has still kept

the annual production volume of approximately 10 million tons of commercial HDPE.

It is well known that the Phillips catalyst can polymerize ethylene without the addition

of an aluminum alkyl activator, contrary to the Ziegler-Natta and Metallocene catalysts.

Though, the exact mechanism for the alkylation is yet unclear, researchers have reached

a consensus that hexavalent chromium species is activated and reduced into divalent

ones by ethylene with the emission of formaldehyde as a by-product. An external

reductant source such as aluminum alkyl is therefore essentially unnecessary for the

Phillips catalyst. Nonetheless, a few research groups[2,3] examined the activation of a

Philips catalyst by an aluminum alkyl activator and emphasized the benefit in

abbreviation of induction period by this type of activator. The proposed potential roles

of aluminum alkyl activator are in the followings:

1)   To reduce hexavalent chromium species to shorten or eliminate the induction time, as ethylene and other reductants such as hydrogen and carbon monoxide do;[4-7]

2)   To form chromium-alkyl species as a chain growth initiator;[8]

3)   To scavenge traces of poisons in a polymerization system;[9,10]

4)   To dissociate a Si-O-Cr bond by forming R-Cr and Si-O-M-R$_x$.[11]   Thus formed unipodal chromium species that has only one covalent bond with silica surfaces were proposed as oligomerization sites;[12,13]

5)   To promote a chain transfer reaction through ligand exchange, leading to terminally saturated polymer.[14]

In summary, it is believed that all or some of the roles cooperate to modulate the polymerization performance of the Phillips catalyst.

The usage of an aluminum alkyl activator is also useful for tuning the microstructure of polymer.   Various types of activators, such as AlEt$_3$, Al(i-Bu)$_3$ Et$_2$AlOEt,   Al(i-Bu)$_2$H, and their mixtures have been used for the Phillips catalyst.[4] The activator can be employed for the MW regulation of produced polymer.   As comparison to Ziegler-Natta catalyst, Phillips catalyst normally exhibits almost no H$_2$ response for controlling of MW.   However, in the presence of aluminum alkyl, Phillips catalyst becomes highly sensitive for H$_2$ resulting in obtained polymer with a low MW fraction like organochromium catalyst.   At the same time, just the introduction of aluminum alkyl contributed to the polymer having a high MW tail in

MWD owing to the formation of active sites with a greater propagation rate constant or time by aluminum alkyl reduction.[15,16]   Meanwhile, the short chain branch in polymer also can be increased by usage of aluminum alkyl due to improvement of α-olefin in polymerization.   The formation of light olefin is similar to organochromium active site formed from a reaction between chromium oxide catalyst and activator.   It was also reported that a typical activator significantly improves melt elasticity by enhancement of the long chain branch content.   Increment of long chain branch was attributed to an increase in the active site concentration as a key parameter for long chain branch production.[17]

In previous researches, it was observed that the type and the concentration of activators pronouncedly affect the catalyst performance, especially for the activity.[18-21]   Metal-alkyl is known to be a reducing agent for hexavalent chromium species and reaction is extremely facile even at a low concentration.   Asahi Kasei Corporation reported that when the activator was introduced excessively, deactivation became predominant, leading to a loss of the activity and increase of short and long chain branching.[22]   Deactivation just can be interpreted as a result of attack from activator to Si-O-Cr bond or coordination of the reduced chromium with activator leading to a loss of catalyst activity.   However, a clear mechanism of deactivation is still ambiguous and the systematical investigation of the activation and deactivation by aluminum for Phillips ethylene polymerization has never been reported.   An activator with a suppression of deactivation was highly expected, because of sensitivity of Phillips catalyst activity for ethylene polymerization in the presence of

activator. In this study, we have explored the activation and deactivation abilities of various aluminum alkyl activators including triethylaluminum (TEA), triisobutyaluminum (TIBA) and tri-*n*-octylaluminum (TNOA) in ethylene homopolymerization using a Phillips catalyst. The relation between activator concentration and polymer yield was discussed. 2,6-di-*tert*-butyl- 4-methylphenol (BHT) was also introduced to suppress the deactivation. Microstructures of the resultant PE were investigated by ^{13}C-NMR in terms of methyl branch and $\geq$ hex branches for understanding of deactivation, and molecular weight distribution profile of polymer was analyzed by GPC.

3.2 Experimental

3.2.1 Materials

Silica gel was donated by PQ Corporation (ES70X, 51 μm, 320 m^2 g^{-1}). Triethylaluminum (TEA) and triisobutylaluminum (TIBA) were donated by Tosoh Finechem Corporation. Tri-*n*-octylaluminum (TNOA) was purchased from Sigma-Aldrich Corporation. 2,6-di-*tert*-butyl-4-methylphenol (BHT) was purchased from Wako Pure Chemical Industries Ltd. Ethylene of polymerization grade was donated by Asahi Kasei Chemicals Corporation. *n*-Heptane was used after purification by passing through a column of 4A molecular sieve followed by nitrogen bubbling for 2 h.
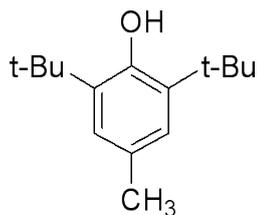
Figure 3-2-1.   Molecular structure: BHT

A Phillips catalyst was prepared based on impregnation of aqueous solution of CrO$_3$ onto silica gel followed by calcination in dry air at 600°C.   The catalyst sample was divided and stored in small glass ampoule bottles sealed under nitrogen atmosphere.   The chromium content in the catalyst was *ca.* 1.0 wt%.   A partially passivated activator was prepared by a dropwise addition of 5 mmol L^{-1} solution of BHT in heptane into 0.1 mol L^{-1} solution of TIBA in heptane.   The BHT/Al molar ratio was used at 1.0.

3.2.2 Ethylene polymerization

Semi-batch slurry ethylene polymerization was performed in a 1 L stirred autoclave at 70°C.   Heptane (200 mL) was used as solvent.   Followed by the addition of a specified amount of an activator, the polymerization was initiated by the addition of 40 mg of the catalyst.   Ethylene pressure was maintained at 0.5 MPa during the polymerization time of 30 min.   The obtained polymer was filtered and dried in vacuum at 60°C for 6 h.

3.2.3 Polymer characterization

The branching frequency of PE was determined by ^{13}C-NMR at 75.43 MHz using Varian Gemini-300 spectrometer operated at 120°C.   The samples were prepared by dissolving 240 mg of PE in 3.1 ml of 1,2,4-trichlorobenzene and benzene-d$_6$ (4:1 v/v). The branch frequency of PE was decided by the previously reported method.[23]   Gel permeation chromatography (GPC, Waters Alliance GPCV2000CV) with polystyrene gel columns (Shodex UT-806 M) was used to analyze MWD of the produced PE using 1,2,4-trichlorobenzene as solvent at 140°C.

3.3 Results and Discussion

It is generally known that the presence of small amount of metal alkyl activator can significantly alter the performance of Phillips ethylene polymerization.   The type and concentration of activator affect the enhancement and/or diminishment of polymerization performance and polymer properties in a self-contradictory way.   In this work, various types of aluminum alkyl activator were employed and theirs concentrations were carefully optimized to obtain a tradeoff between the activation and deactivation contributions and thus to maximize the polymer yield.   The relationships between activator concentration and polymer yield for TEA, TIBA and TNOA are shown in Figure 3-3-1a-c, respectively.   For all activators, the polymer yield increased with the increase of activator concentration and then began to decline after reaching the maximum value.   The optimal concentration to achieve the maximum yield was found to be dependent on the size of alkyl group, in which the lowest concentration is required for TEA followed by TIBA and TNOA, respectively.

At these optimal concentrations, the yield was inversely highest for TNOA followed by TIBA and TEA, which is in contrast to other polymerization catalysis systems where increasing the size of alkyl group often results in the decrease of polymerization activity.[24]   It is interesting to note here that the size of alkyl group not only affected the optimal concentration and polymer yield, but also the shape of relation curve between concentration and polymer yield was significantly changed. The width of the curve became noticeably wider with increasing the alkyl size. Likewise, the operating window to obtain relatively high yield before the declining of activity became less restrictive.   This result evidently emphasized that the reaction between aluminum alkyl activator as reducing agent and Cr(VI) as oxidant is rapid and sensitive to type and concentration of activator.   Whilst the activation by TEA could be done at a very low concentration, the over reduction of active sites from the attack of activator on the Cr-O-Si bond similarly progressed resulted in the deactivation of newly activated species.   Thus, polymerization performance is a result of balance between activation and deactivation of active sites.   The activator with bulky ligand exhibited higher yield most plausibly due to the suppression of deactivation.
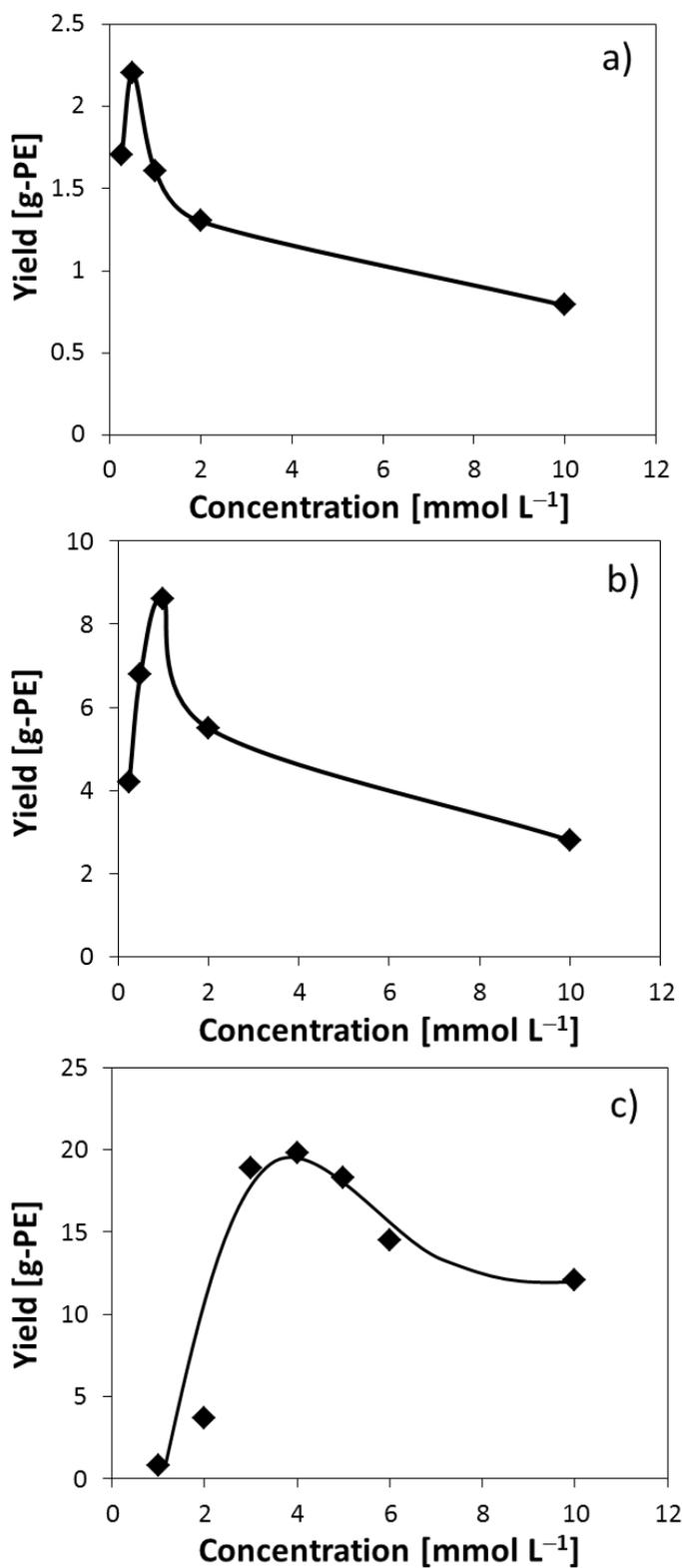
Figure 3-3-1.　Correlation between the activator concentration and polymer yield: a) TEA, b) TIBA, c) TNOA

In order to suppress the effect of deactivation, the modification of TIBA with a sterically hindered phenol was employed.   BHT has been successfully applied to passivate free aluminum alkyl presented in methylalumoxane,.[25]   The reaction of aluminum alkyl with BHT gives aluminum aryloxide species that has lower ability to interact with metal center,[26] thus reduces the free aluminum alkyl reactivity.   Hence it is also expected to assist the suppression of deactivation in Phillips ethylene polymerization.   The concentration of passivated TIBA (TIBA-BHT) was varied and the results were plotted against yield as illustrated in Figure 3-3-2.   Similar to other activators, the polymer yield increased with the increase of activator concentration before dropping down.   The maximum yield of TIBA-BHT was attained at the concentration of 2.0 mmol L^{-1}, higher than the optimal concentration obtained from TIBA, while the width of the curve became much broader.   The response curves between deterioration of polymer yield and activator concentration normalized by defining the maximum yield at 100% (Figure 3-3-3) revealed that TIBA-BHT gave much slower speed of decay than those of TIBA and slightly lower in the low concentration region than TNOA, underlining the effective suppression of deactivation by passivation.   However, the maximum yield turned to be lower than TIBA (Figure 3-3-2) suggested that the less reactive aluminum aryloxide species not only suppressed the deactivation, but the activation of chromium active center was also suppressed.   Thus, the optimization of polymerization performance though the selection of activator with bulky ligand is more preferable to maximize the performance.
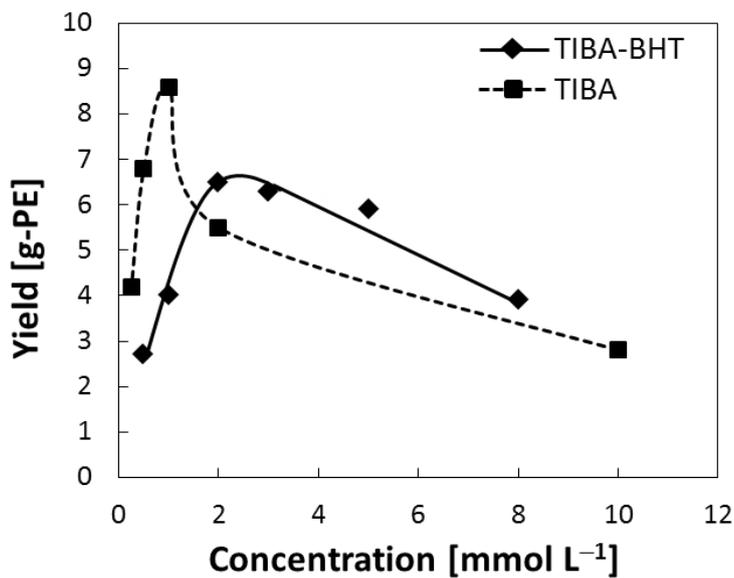
Figure 3-3-2. Influence of activator passivation on polymer yield: (dotted line) TIBA passivated BHT, (solid line) TIBA
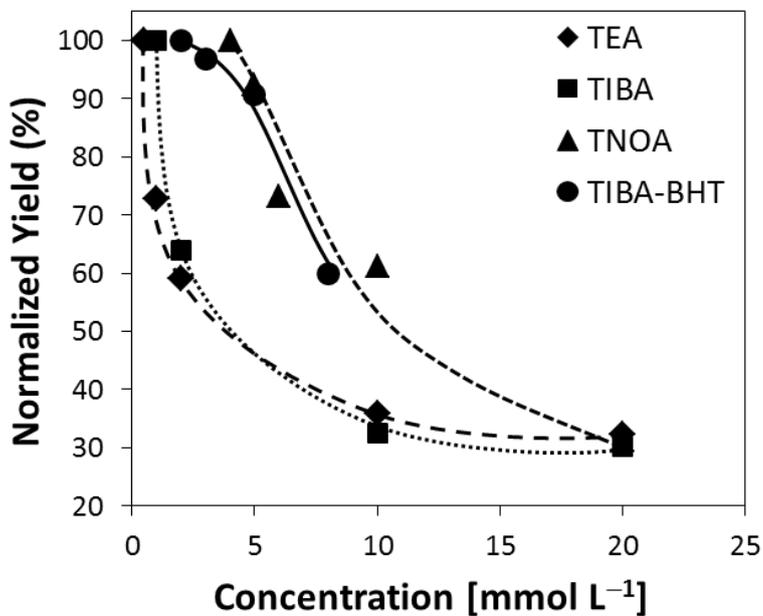

Figure 3-3-3. Deterioration of polymer yield

Branching level of polymer produced at the optimal aluminum alkyl concentration was measured by ^{13}C-NMR and the results are listed in Table 1. It has been considered that the branching in Phillips ethylene polymerization is formed by copolymerization with in-situ produced macro-monomer and α-olefins whose concentration increases with time in steady state polymerization.[21] This has been proved by the branches-yield curve correlation, where the frequency of branches (≥ n-butyl) was found to follow polymer yield at fixed activator concentration.[21] In our case, the frequency of the methyl branches in PE polymer obtained from different activators and concentrations was found to associate with the degree of deactivation. The highest frequency of methyl branches was observed when TEA was used, while the lowest methyl branches was obtained from TIBA-BHT, having the slowest rate of yield deterioration in normalized yield-activator concentration curve. This plausibly originated from the unipodal chromium sites formed from the attack of Cr-O-Si linkage by activator. Unipodal chromium is reported to be responsible for the ethylene oligomerization and particularly leads to a high propylene concentration during polymerization.[27-29] Moreover, aluminum alkyl with high reactivity might also help to accelerate propylene production by transforming chromium species into suitable sites for methathesis.[30] The copolymerization in the presence of high concentration of propylene took account for the high level of methyl branches under the prominent condition that deactivation and/or high reactivity activator participates. While the degree of deactivation corresponded to the formation of methyl branches, the frequency of ≥ hex branches more or less followed the polymer yield, in line with

our previous result.[21]   In perspective of highly active sites producing high polymer yield, the high level of α-olefin was also in-situ produced and subsequence incorporated into main chain.

Table 3-3-1.   Summary of ethylene polymerization performances at the optimal concentration of various activators

Activators	Concentration [mmol L^{-1}]	Yield [g-PE]	Methyl branches [1000C]	$\geq$ Hex branches [1000C]	Mw/Mn
TEA	0.5	2.2	0.53	0.45	40.7
TIBA	1.0	8.6	0.41	0.49	35.3
TNOA	4	19.8	0.32	0.68	38.3
TIBA-BHT	2.0	6.5	0.19	0.48	41.4

MWD of polymer produced at the optimal activator concentration was analyzed by GPC and the results are shown in Figure 3-3-4.   All of the activators gave a very broad molecular weight distribution profiles, demonstrating the variation of the coordination environment of active species.   TEA, TIBA and TNOA exhibited similar shape of distribution curve with a clear bimodal, while TIBA-BHT gave MWD with trimodal shape.   This might due to aluminum aryloxide species reacted with chromium site and became part of active site environment.   The mechanism in transformation or further reduction of these sites might be different and probably

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more difficult due to the bulkiness of ligand. This resulted in the suppression of deactivation as mentioned earlier and the high molecular weight fraction largely retained. This work clearly highlighted the pronounced effect of deactivation by aluminum alkyl in Phillips ethylene polymerization system, where the intrinsic stearic effect of ligand imparts in activation and deactivation of active sites and influences the polymer properties.
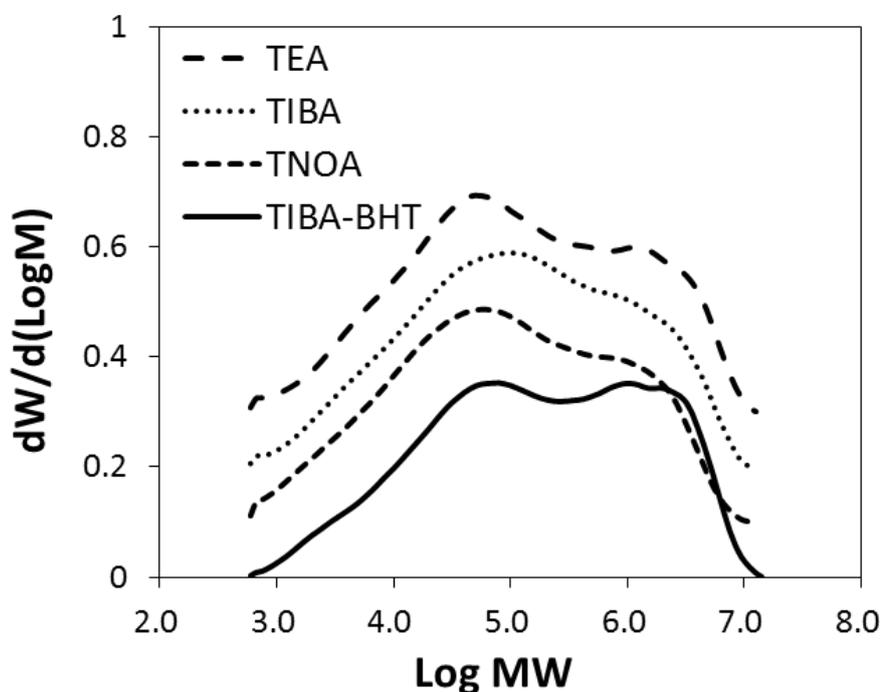

Figure 3-3-4.   Influence of the activator types on MWD of polymer

3.4 Conclusion

Various types of aluminum alkyl activator were employed to explore the performance of Phillips catalyst through the balance of activation/deactivation.   Polymer yield was found to be dependent on type and concentration of activator, whose bulkiness

enhanced the performance and extended the concentration-yield operating window by the suppression of deactivation. Frequency of methyl branches using different activators and concentrations was found to be associated with the degree of deactivation, plausibly originated from unipodal chromium and/or activator assisted the formation of suitable metathesis sites for the production of propylene, while $\geq$ hex branches formed from the incorporation of in-situ α-olefin followed polymer yield. The environment of active site could be altered by activators though activation/deactivator mechanism, leading to the differences in active site behaviors and polymer properties.

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Chapter 4

Design of Novel Homogeneous Phillips Catalyst Using the Model of Trivalent Chromium Site and Support

4.1 Introduction

Phillips catalyst[1] (Cr/SiO$_2$) discovered by J. P. Hogan and R. L. Banks in the early 1950s is very important commercial catalyst for polyolefin manufacture, roughly producing half of the high density polyethylene (HDPE) over the world, owing to its versatility and ease of preparation and handling.[2]   It consists of silica support and a chromium compound, and conventional method for preparation is that a chromium compound is deposited onto silica surface by wet impregnation leading to heterogeneous catalyst.   Due to the existence of various chromium species and the chromium species situated in different coordination environment on catalyst support, it makes difficult to investigate the nature of active site and, the structure of active site and its relationship with polymer properties.   Despite several decades of research efforts, the nature of the active site and the role of coordination environment of chromium species in ethylene polymerization have yet to be directly observed.

To develop this significant industrial polyolefin catalyst, an understanding of the relationship between active site structure and its performance in terms of polymer properties and catalyst activity is important.   Nowadays, a surface organometallic chemistry has been focused on proposing a well-defined approach to the conception

and synthesis of heterogeneous catalyst.[3, 4] A single site heterogeneous catalyst had

been prepared by grafting organometallic compound.[5] A understanding of the

relationship between structure of the active site and catalyst performance have been

expected. As a consequence, the most direct method is to use uniform chromium

active site as a model catalyst. In the previous researches, the model catalyst with

uniform chromium structure grafted on silica surface was investigated for insight into

relationship between the chromium species and catalyst performance. For example,

in our previous work, uniform chromate and dichromate species on silica surface were

synthesized.[6] Scott et al also synthesized mononuclear chromium species on silica

to mimic polymerization performance if the commercial Phillips catalyst .[7]

However, these model catalysts with uniform active site as well as produced the

polymer with broad molecular weight distribution.   It is still a big challenge to

design a model catalyst with a well-defined structure to deeply understand Phillips

catalyst.   Recently, through density function theory (DFT) calculation,[8] our group

have clarified that a broad molecular weight distribution of HDPE produced by the

Phillips catalyst comes from not only the existence of various chromium species but

also their situated in different coordination environments owning to the heterogeneity

of surface hydroxyl groups including isolated, vicinal and germinal hydroxyl groups.

The hydroxyl groups on silica surface are considered as a key role for Phillips catalyst,

not only fixing chromium compound but also participating in ethylene polymerizing.

There are three reasons that show the significance of hydroxyl groups as following: at

first, an simple chromium compound does not gave any activity for ethylene

polymerization;[9] second, the hydrogen atom by introduction of hydroxyl groups is proposed to participate in a reaction during the initiation stage, hence the methyl group is presumably formed as end group;[10, 11] third, some researchers have been reported that active site is involved in hydroxyl groups which coordinated with the chromium site according to IR measurement.[12, 13]   However, until now without a clear understanding of the interaction between the hydroxyl groups of the silica and chromium compound, the relationship between Phillips catalyst structure and polymer properties is not likely to be achieved.   Therefore, it also prompts us to research the different coordination environments for chromium active sites in Phillips ethylene polymerization resulted from interaction between the hydroxyl groups on the silica surface and a chromium compound.

In this research, other strategy is proposed for study the heterogeneous Phillips catalyst, which is model both chromium active site and its various coordination environment on silica surface in one homogeneous catalyst to obtain the analogue for not only active sites but also its coordination environment on the silica surface. Isolated, vicinal and germinal hydroxyl groups on silica surface will be modeled by various polyhedral oligomeric silsequioxane (POSS) which contain different amount and types of siloxy groups in one POSS cage.   It is well accepted that POSS is a close molecular analogue of silica and silica derivatives to mimic hydroxyl groups on silica's surface.[14, 15].   POSS with a cage-like structure and reactive silanol group can be obtained by model ligands like monosiloxy, polysiloxy and the siloxy family.   In this work, not only the chromium active site but also hydroxyl groups on silica surface

are uniform in one homogeneous catalyst, namely single chromium active site and POSS support providing uniform coordination environment compose the homogeneous catalyst.   Moreover, a homogeneous catalyst in computational study for theoretical molecular modelling can achieve easily and it is relative facility of characterization of a well-defined catalyst structure, which makes tuning of the catalyst structure possible.   Especially in spectroscopic study it is likely to shed more light for an understanding of the relationship between catalyst structure and its performance.

In this study, trivalent chromium (III) complex was selected for insight into relationship between catalyst structure and catalyst performance in terms of polymer properties and catalyst activity and trivalent catalysts (Cr(III)/POSS-2OH, Cr(III)/POSS-2OH-OSiMe$_3$ and Cr(III)/POSS-3OH) were synthesized for ethylene polymerization to obtain catalyst performance.   Because Ikeda and Monoi reported that tris[bis(trimethylsilyl)methyl]chromium(III) support on silica without calcination can lead to much high catalyst activity indicating that trivalent chromium is active species for ethylene polymerization.[16]   In this time, a very broad MWD of obtained polymer was gained, probably because active site changed during polymerization owing to a reaction between catalyst and activator, or trivalent homogeneous catalyst is ultrahigh sensitivity to air and moisture.   All the trivalent homogeneous catalysts showed a low activity compared with heterogamous one, because of a facile deactivation during polymerization.

4.2 Experimental

4.2.1 Materials

1,3,5,7,9,11-Octaisobutyltetracyclo[7,3,3,15,11]octasiloxane-endo-3,7-diol[$(C_4H_9)_8Si_8$ $(OH)_2O_{11}$] (POSS-2OH), 1,3,5,7,9,11,14-Heptaisobutyltetracyclo[7,3,3,15,11] heptasiloxane-endo-3,7,14-triol [$(C_4H_9)_7Si_7(OH)_3O_9$] (POSS-3OH) and tri-n-octylaluminum (TNOA) were purchased from Sigma-Aldrch Corporation. Tetrahydrofuran (THF), triethylamine (TETN), chloro(trimethyl)silane (TMCS), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), 2,6-di-tert-butyl-p-cresol (BHT), chromium oxide (Cr(VI)) and magnesium sulfate ($MgSO_4$) were purchased from Wako Pure Chemical. Benzene-d_6 (C_6D_6) and carbon tetrachloride (CCl_4) were purchased from Kanto Chemical Corporation. Tris[bis(trimethylsilyl)methyl] chromium (Cr(III)) was donated by Japan Polyethylene Corporation. Ethylene of polymerization grade was donated by Asahi Kasei Chemicals Corporation. Hexane, heptane and toluene were distilled from dark purple solutions of sodium benzophenone under nitrogen for organic syntheses. Heptane was used after purification through a column of 4 A molecular sieve followed by bubbling under nitrogen for 2 h for ethylene polymerization. CCl_4 was purified by 4 A molecular sieves bubbling under nitrogen for 4 h.
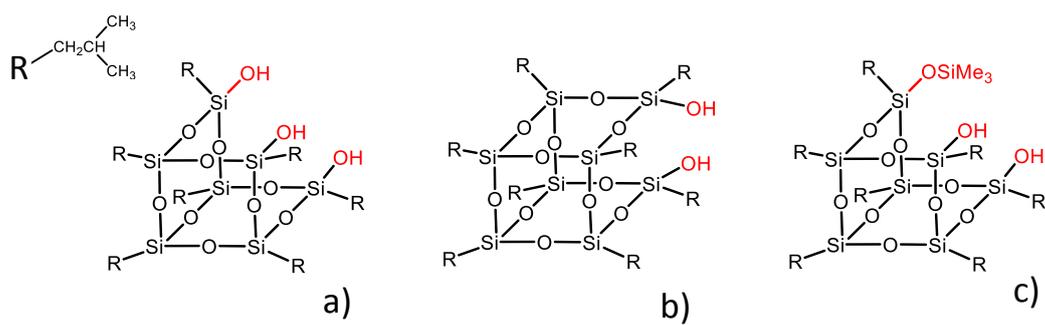
Figure 4-2-1. Molecular frameworks of various POSS: a) POSS-2OH, b) POSS-2OH-OSiMe$_3$, c) POSS-3OH
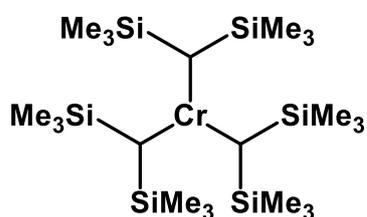

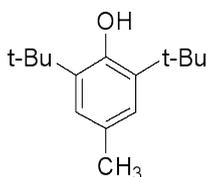Figure 4-2-2. Molecular structure of tri-valent tris[bis(trimethylsilyl)methyl] chromium

Figure 4-2-3. Molecular structure of BHT

4.2.2 Synthesis of POSS-2OH-OSiMe$_3$

TMCS was added dropwise to a THF solution of mixture of POSS-3OH and TETN (Molar ratio: TMCS/POSS-3OH=1 TETN/POSS-3OH =10).[17] Triethyl-ammonium hydrochloride began to precipitate immediately after mixing. It was removed by filtration after 18 h of stirring at room temperature. Remove of the volatiles in vacuo

and then the white solid was extracted with hexane, filtered and concentrated to by distillation.[18]   After one week, a big crystal was obtained in solution.   The product of crystal was gained by removed the solution.

4.2.3 Synthesis of modified TIBA activator (TIBA-BHT)

Solution of BHT (0.5 mmol, optimized molar ratio of BHT/Al=1)[19] in heptene (100 ml) was slowly added to TIBA (0.50 mmol) in heptane (5 ml) at 0°C in ice bath, which stirred for 3 h.   After of the reaction completion, products were stored under N$_2$.

4.2.4 Cr(III)/POSS catalyst preparation

Solution of POSS-2OH, POSS-2OH-OSiMe$_3$ or POSS-3OH in heptene (15 ml) was slowly added to tris[bis(trimethylsilyl)methyl] chromium in heptane (45 ml).   (Molar ratio: Cr(III)/POSS=1).   It was kept for stirring in a water bath at 40°C for 6 h.[16] After the reaction, heptane was removed in vacuo until no volatiles appeared.

4.2.5 Catalyst characterization

^{1}H-NMR

^{1}H-NMR ^{13}C-NMR and ^{29}Si-NMR[20] spectra were recorded on a Bruker AVANCE-III spectrometer using benzene-d$_6$ solvent.   The experiments were carried out at room temperature operating at resonance frequencies of 400 MHz. ^{1}H-NMR

spectra were measured with the 30.0 $\square$s pulses, with 2 s delay time and 100 scans. However, the [13]CMR and [29]SiMR spectra were measured with 4 s delay time 2000 scans and 20 s delay time 2000 scans respectively. Chemical shift is recorded in ppm relative to C_6D_6 (δ 7.16, ^{1}H), C_6D_6 (δ 128.06, ^{13}C) and tetramethylsilane (δ 0.00, [29]Si).[21]

IR spectroscopy

The spectra of all the POSS and all the homogeneous catalysts were recorded using a JASCO FT-IR 6100 with a background of carbon tetrachloride (CCl4). The sample was prepared by using liquid cell with a CaF_2 window prepared inside a glove bag which was kept a low water concentration (200 ppm). The spectra were obtained in range of 4000-1000 cm with resolution of 4 cm and 80 times scanning.

4.2.6 Ethylene polymerization

Semi-batch slurry ethylene polymerization was performed in a 1 L stirred autoclave at different temperatures (40, 50, 60, 70 and 80°C). Heptane (200 ml) was used as a solvent. Ethylene pressure was kept at 0.5 MPa. TNOA or TIBA modified by BHT was added as an activator (1 mmol/L). The polymerization was started by the addition of the catalyst with different stirring condition. After 30 min polymerization, ethanol was added to quench the reaction. The produced polymer was filtered and dried in vacuum at 60°C for 6 h.

4.2.7 Polymer characterization

The branching frequency of PE was determined by ^{13}C-NMR at 75.43 MHz using Varian Gemini-300 spectrometer operated at 120°C. A sample was prepared by dissolving 240 mg of PE in 3.1 ml of 1,2,4-trichlorobenzene and benzene-d_6 (4:1 v/v). The branch frequency of PE was decided by the previously reported method.[22] Gel permeation chromatography (GPC, Waters Alliance GPCV2000CV) with polystyrene gel columns (Shodex UT-806 M) was applied to determine MWD of the produced PE using 1,2,4-trichlorobenzene as solvent at 140°C.

4.3 Results and discussion

To understand the Phillips ethylene polymerization, homogenous tiravalent chromium catalysts (Cr(III)/POSS-3OH, Cr(III)/POSS-2OH and Cr(III)/POSS-2OH-OSiMe$_3$) were synthesized with the different POSS as a support and a trivalent chromium complex. Support POSS-2OH-OSiMe$_3$ was synthesized by using a POSS-3OH precursor. The structure of POSS-2OH-OSiMe$_3$ was clarified by the characterization of NMR and solution IR. As a comparison, a heterogeneous catalyst Cr(III)/SiO$_2$ with silica as a support was prepared from the same trivalent chromium complex. Catalyst characterization based on NMR and solution IR indicated that the Cr(III) precursor was reacted with two hydroxyl groups to bear the (Me$_3$Si)$_2$CH-Cr(-O-Si-)$_2$ structure for all the POSS (POSS-3OH, POSS-2OH and POSS-2OH-OSiMe$_3$), as the scheme 4-3-1 was shown.
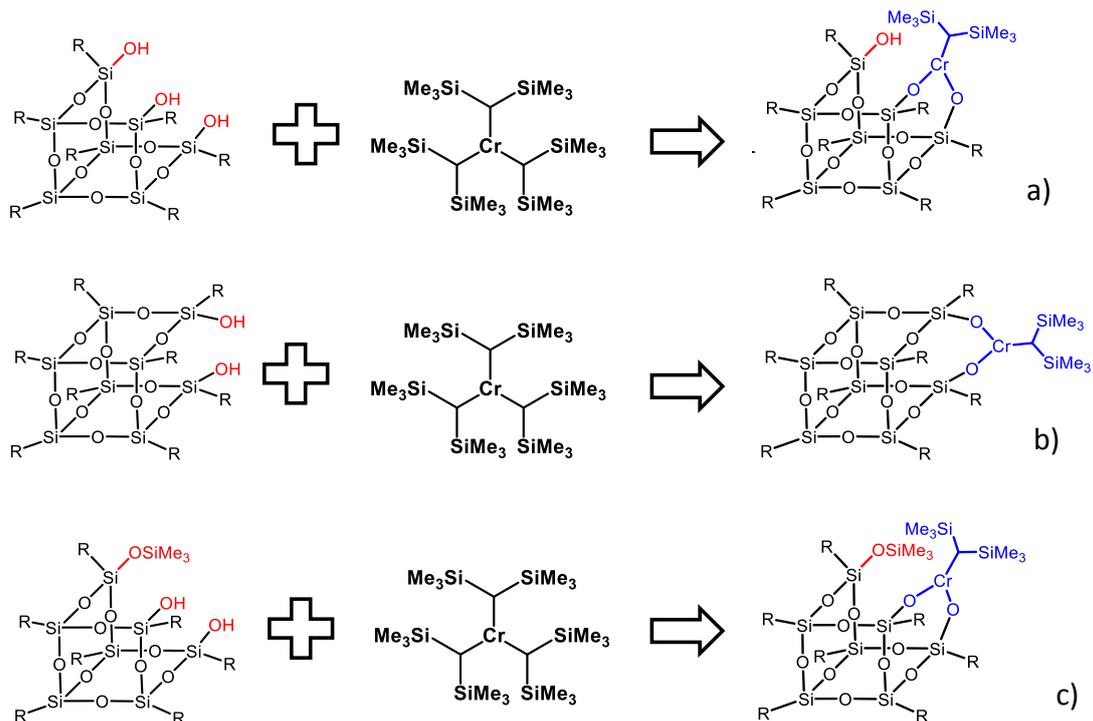
Scheme 4-3-1. The reactions between POSS and tris[bis(trimethylsilyl)methyl] chromium: a) POSS-3OH, b) POSS-2OH, c) POSS-2OH-OSiMe$_3$

Figure 4-3-4 shows the ^{1}H-NMR spectrum of trivalent homogeneous catalysts. In Figure 4-3-4 a), a small peak appeared around 3.1 ppm which was assigned to the proton originated from one hydroxyl group in catalyst Cr(III)/POSS-3OH structure. However, in Figure 4-3-4 b) and c) there is no peak responded to proton originated from one hydroxyl group in catalyst Cr(III)/POSS-2OH and Cr(III)/POSS-2OH-OSiMe$_3$structure.
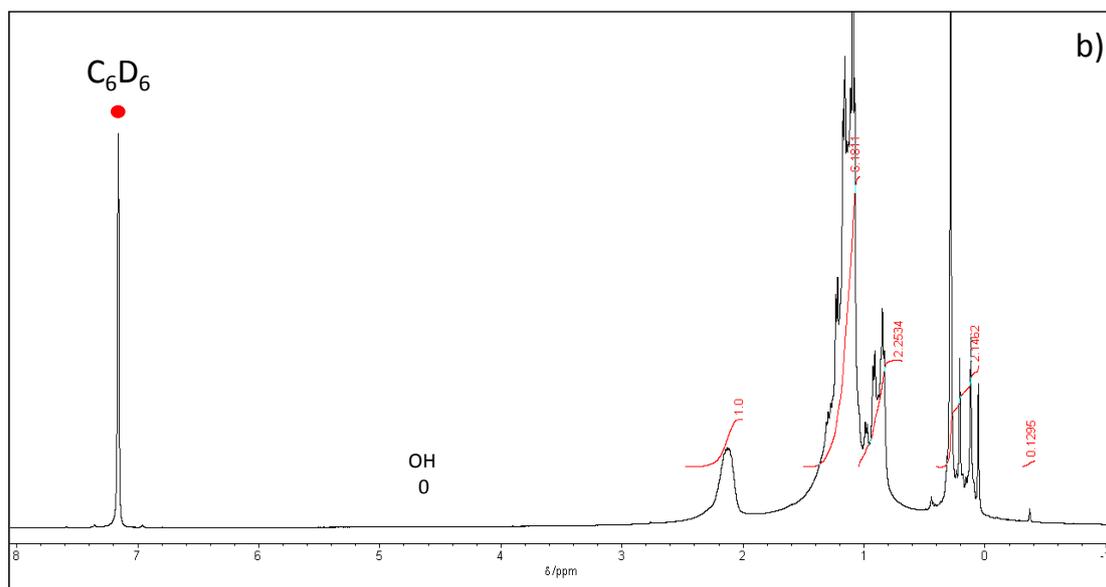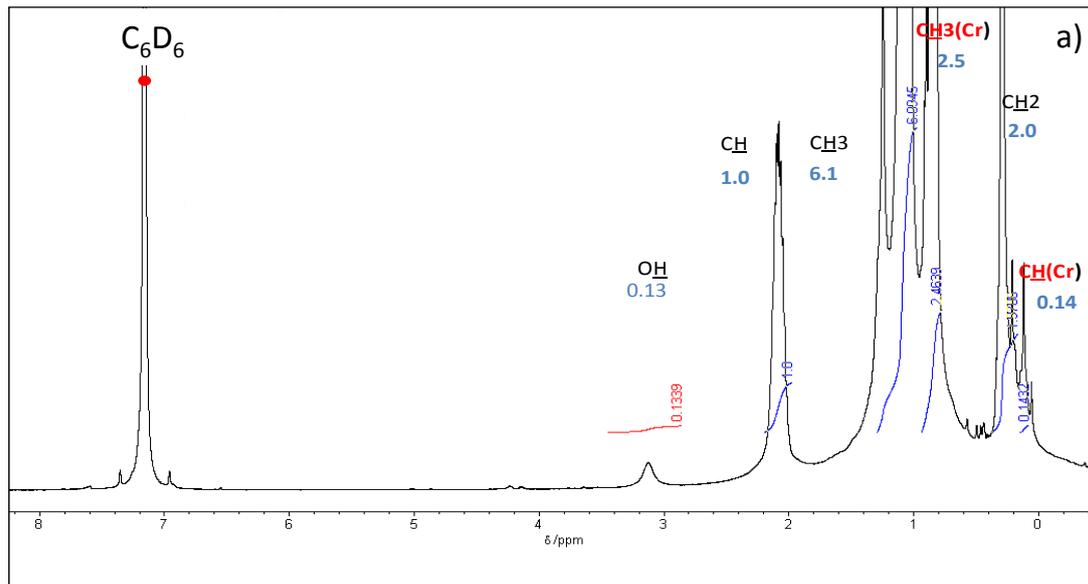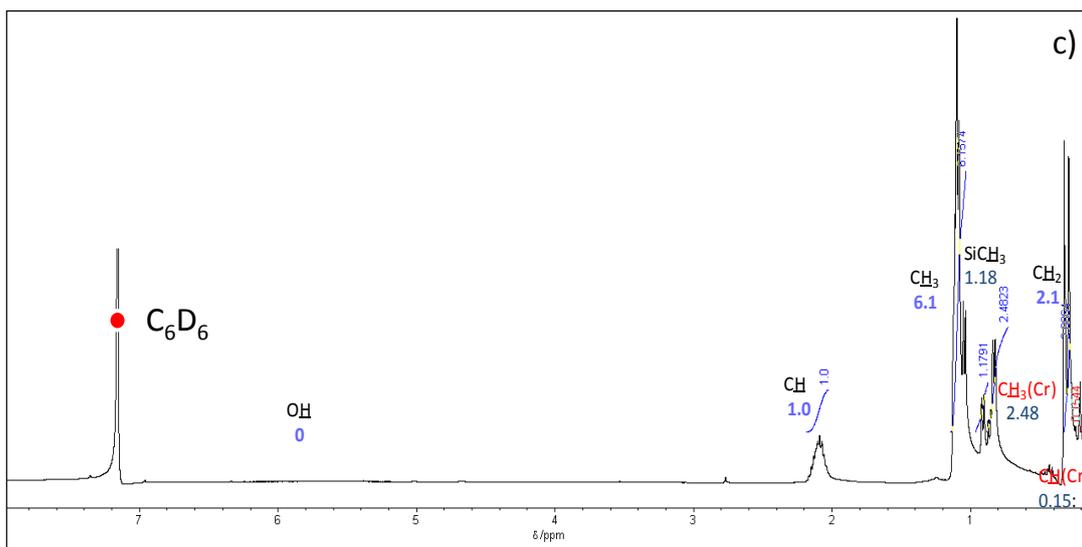
Figure 4-3-4. ^{1}H-NMR spectrum of homogeneous catalysts: a) Cr(III)/POSS-3OH,

b) Cr(III)/POSS-2OH and c) Cr(III)/POSS-2OH-OSiMe$_3$

The hydroxyl group in all the homogeneous catalyst structures was also confirmed by solution IR.   In Figure 4-3-5 a), an abroad peak appeared around 3200 cm^{-1} which came from three hydroxyl groups with hydrogen bond in POSS-3OH structure.   Compare with POSS-3OH, there is an isolated hydroxyl groups without hydrogen bond in structure of catalyst Cr(III)/POSS-3OH as Figure 4-3-5 b).   For catalyst Cr(III)/POSS-2OH structure, no peak was observed in IR spectrum, because both of hydroxyl group in POSS-2OH structure were reacted with chromium precursor, similar to the structure of catalyst Cr(III)/POSS-2OH-OSiMe$_3$.
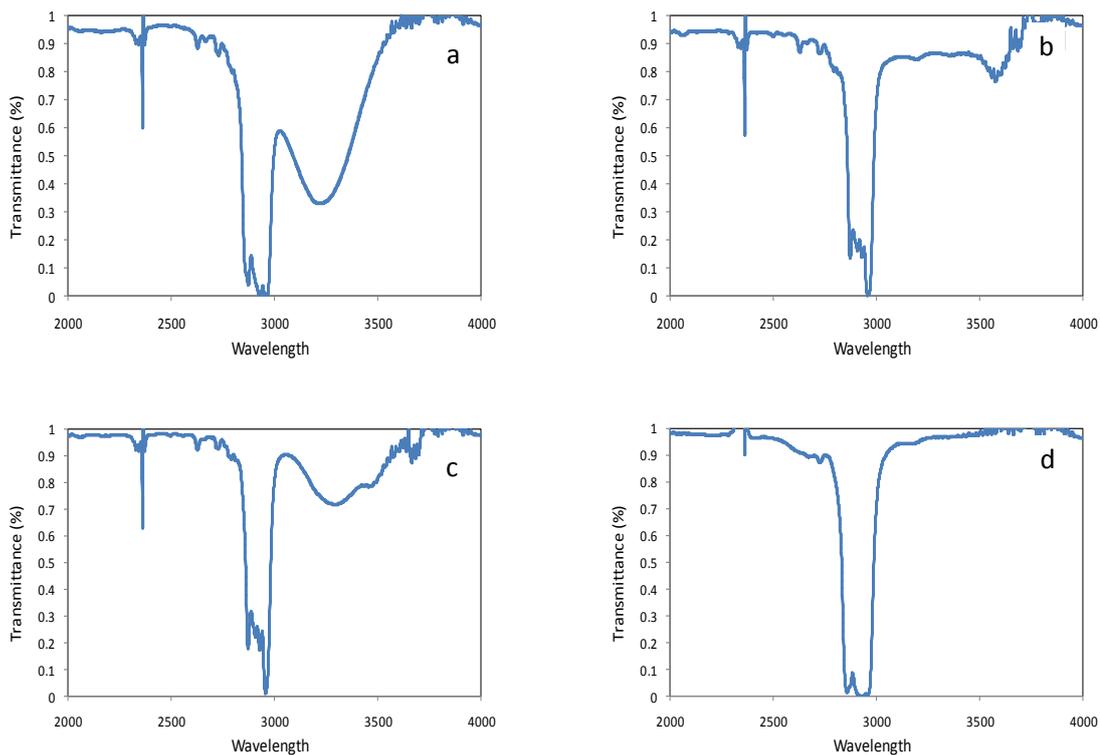
Figure 4-3-5. Solution IR spectrum of POSS and homogeneous catalysts: a) POSS-3OH, b) Cr(III)/POSS-3OH, c) POSS-2OH and d) Cr(III)/POSS-2OH

Table 4-3-1 shows the activity of ethylene polymerization which was performed at the various optimized temperatures with different catalysts using different activators.   All the homogeneous catalysts and heterogeneous catalysts had an ability of   ethylene   polymerization.   Catalysts   Cr(III)/POSS-2OH   and Cr(III)/POSS-2OH-OSiMe$_3$ without hydroxyl group in catalyst structure can polymerize ethylene.   Cr(III)/POSS-2OH-OSiMe$_3$ lead to a lower catalyst activity than Cr(III)/POSS-2OH, since ethylene insertion was hindered by a bulky ligand of SiMe$_3$ in catalyst structure .   However, the catalyst Cr(III)/POSS-3OH with a hydroxyl group imparted the highest catalyst activity among all the homogenous

catalyst. It indicated that a hydroxyl group has positive effect for trivlent homogeneous ethylene polymerization.

A heterogeneous catalyst contributed to a very higher catalyst activity than all the homogeneous catalysts due to a more stable catalyst with silica support in ethylene polymerization.

Meanwhile, ethylene performance was investigated using different activators for checking the MWD of produced polymer. The effect of different activator on MWD of produced polymer will discussed later in terms of GPC profile. Compared with TNOA, TIBA modified by BHT resulted in a lower catalyst activity consistent with my previous study in chapter 2.

Table 4-3-1. Activity of trivalent catalysts for ethylene polymerization without stirring

Catalysts	Activator	Temp.(^{o}C)	Activity(g-PE/mmol-Cr·h)
Cr(III)/POSS-3OH	TNOA	50	60
Cr(III)/POSS-2OH	TNOA	70	50
Cr(III)/POSS-2OH-OSiMe$_3$	TNOA	60	48
Cr(III)/SiO$_2$	TNOA	70	10000
Cr(III)/POSS-3OH	TIBA+BHT	50	414
Cr(III)/POSS-2OH	TIBA+BHT	70	41
Cr(III)/SiO$_2$	TIBA+BHT	70	3300

At the optimized temperature

Figure 4-3-6 exhibits the GPC profile of produced polymer by trivalent chromium catalysts using TNOA as an activator at 1 mMol/L. All the trivalent homogeneous catalyst gave a very clear MWD with the tri-model. However, heterogeneous catalysts gave a narrower MWD of produced polymer. The main peak in GPC profile of the produced polymer by all trivalent chromium catalysts appeared at low molecular weight around 10^3-10^5. In the case of catalyst Cr(III)/POSS-2OH-OSiMe$_3$, TNOA did not decrease the MW, because bulk ligand SiMe$_3$ protected Cr center from a reaction with TNOA. This very broad MWD originated from homogenous catalyst probably resulted from a reaction between catalyst and activator during polymerization leading to a new active species. To study the effect of the reaction between catalyst and activator on MWD, TIBA modified by BHT which is a passivated activator at 1 mMol/L was utilized for fabrication of polyethylene. Similarly, tri-model MWD of produced polymer was obtained using TIBA modified by BHT as an activator, as Figure 4-3-7. However, all the main peaks in GPC profile appeared at high molecular weight around 10^5-10^7. The broad MWD should result from the different active sites during polymerization. In the case of TONA, the polymer at lower molecular weight may attribute to a new active species which came from a strong reaction between catalyst and TNOA and the polymer at higher molecular weight may result from an unreactive active species. Due to a strong reaction between catalyst and TNOA, the new active species become more than originated active species, which lead to main peak of GPC occurred at the low molecular weight. Compared with TNOA, TIBA modified by BHT imparted o

main peak of GPC appeared at the high molecular weight which gave by unreactive

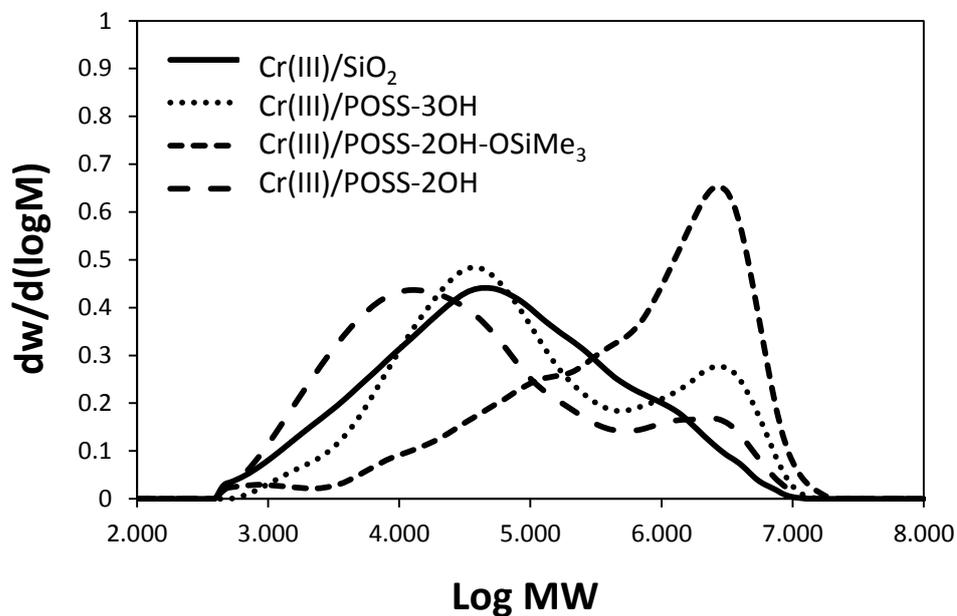active species due to week reaction between catalyst and TIBA modified by BHT.

Figure 4-3-6.　Comparison of MWD obtained from different trivalent homogeneous
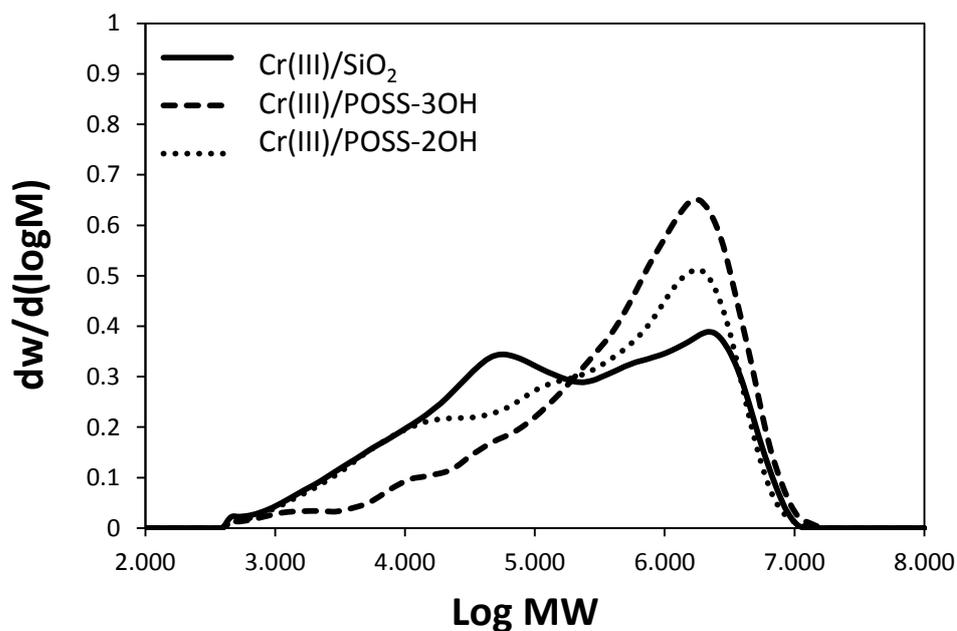
catalysts and with an activator of TNOA

Figure 4-3-7.　Comparison of MWD obtained from different trivalent homogeneous

catalysts with an activator of TIBA+BHT

Figure 4-3-8 shows a GPC profile of polymer obtained from different concentrations of TNOA and polymerization time. With the concentration of TNOA increasing, the polymer with high molecular weight gradually transfers to the polymer with lower molecular weight. Because amount of new active site become increasing, while the TNOA concentration was increasing owing to the reaction between catalyst and TNOA. The new active site fabricated the low molecular weight polymer. Similarly, when polymerization time was prolonged from 5 min to 30 min, the new active sties was increased due to a long reaction time for catalyst and TNOA.
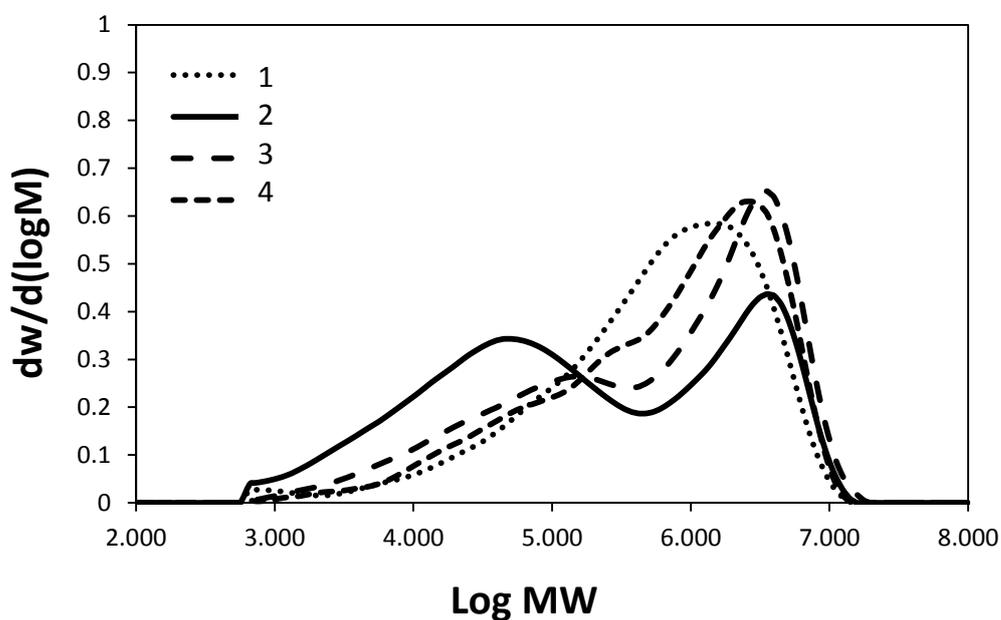

Figure 4-3-8. Comparison of MWD gave by different activators concentration and polymerization time: 1) 5 min polymerization time with a 1 mMol/L TNOA, 2) 30 min polymerization time with a 0.5 mMol/L TNOA, 3) 30 min polymerization time

with a 1 mMol/L TNOA, 4) 30 min polymerization time with a 2 mMol/L TNOA

Table 4-3-2 gives the branching information of polymer produced from various catalysts measured by ^{13}C-NMR. Homogeneous catalyst tend to produced more methyl branching as a comparison to heterogeneous one, the proposed reason is that a unstable homogeneous catalyst easily reacted to TNOA leading to the new active sites which can made propylene for copolymerization with ethylene, agreement with the results of chapter 3. Especially for catalyst Cr(III)/POSS-2OH, moreover, it may increase methyl branching by the isomerization of growing chain due to a proper structure.[24, 25] Heterogeneous catalyst facilely fabricated the polymer with long chain branching and the branching longer than methyl branching, since it was easy for heterogeneous catalyst without bulk ligand to co-polymerize a macro-monomer and a long chain with the terminal vinyl group.

Table 4-3-2. Comparison of branching gave by different catalysts with a TNOA as an activator at concentration of 1 mMol/L

Catalysts	Methyl	Ethyl	Propyl	Butyl	Long
Cr(III)/POSS-3OH	0.3	-	-	-	trace
Cr(III)/POSS-2OH	1.3	0.1	-	0.2	-
Cr(III)/POSS*	0.3	-	-	-	-
Cr(III)/SiO$_2$	trace	0.3	0.1	0.5	0.2

* Cr(III)/POSS-2OH-OSiMe$_3$

4.4 Conclusions

In short, it was found that homogenous catalyst Cr(III)/POSS-3OH, Cr(III)/POSS-2OH and Cr(III)/POSS-2OH-OSiMe$_3$ without hydroxyl group also gave an ethylene polymerization activity, indicating that hydroxyl group is not necessary for Phillips ethylene polymerization. At the same time, POSS supported homogeneous catalysts lead to a very broad MWD as well, because of a reaction between catalyst and activator during ethylene polymerization. Compared with heterogeneous catalyst, homogeneous catalysts resulted in a low ethylene polymerization activity due to an easy deactivation in polymerization.

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Chapter 5

Design of Novel Homogeneous Phillips Catalyst Using the Model of Hexavalent Chromium Site and Support

5.1 Introduction

Phillips catalyst based on chromium supported silica is one of the most important industrial catalyst, which produces more than one third of high-density polyethylene (HDPE) all over the world.[1]   Produced HDPE is characterized by ultra-broad molecular weight distribution (MWD), and long- and short- chain branches (SCB and LCB), giving fine mechanical properties and high melt tension suitable for blow molding applications.[2-4]   Phillips catalyst possesses clear multi-functionality to produces not only PE but also a wide range of co-monomers which lead to a variety of branching.[5-8]   This multi-functionality originates from the heterogeneous nature of Cr species supported on silica.

However, academic progress to understand the Phillips catalyst is much slowly than a successful industrial application, even tremendous efforts have been carried out, the nature of the active site including the oxidation state of chromium active sites and the structure of chromium active sties, relationship between the structure of active site and its unique ethylene polymerization performance and Phillips ethylene polymerization mechanism specially initiation mechanism still have not get consensus. These issues encountered in the determination of the structure of the active sites of the

real catalyst should be resulted from the following reasons: 1) only a small part of the chromium species are real active species for ethylene polymerization. As a result, even some characterization results are reported, it is not directly associated with the actives species of the catalyst, 2) because of the complexity of heterogeneous Phillips catalyst, there is a mixture of multiple oxidation states of chromium specie and various coordination environments in catalyst.[9, 10]

As a consequence, a deeper understanding of the unique Phillips polymerization behaviors, solving the existed problems in Phillips ethylene polymerization and opening the mystery of Phillips ethylene polymerization and was highly required for development this significant commercial polyolefin catalyst,. Nowadays, model catalyst was attracted the attention of researches who work not only in academic field but also industrial field and a lot of model catalysts containing homogeneous and heterogonous one were design to mimic Phillips catalyst polymerization. Based on previous study on Phillips catalyst, both heterogeneous and homogeneous model catalysts shed the light for studying this heterogeneous catalyst.

There are two groups of heterogonous model catalyst have been developed for an essential and fundamental research of Phillips ethylene polymerization behaviors, respectively the heterogeneous catalysts having a surface hexavalent chromate site and with a low oxidation state surface chromate site.[11-15] It have been demonstrated that a uniform and well-defined structure of surface chromium site for heterogeneous catalyst is a powerful strategy to research a basis of Phillips catalyst. Whereas the complexity resulting from a heterogeneous of the catalyst surface is an obstacle to

deeply study Phillips ethylene polymerization. The heterogeneous of the catalyst surface must be originated from an amorphous silica support.[9]

Amorphous silica acted as a support for several transition metal ions, leading to a great number of catalytic systems which play the key roles in both academic and industrial levels. Phillips catalyst is an excellent example of the catalyst where the chromium sties formed by anchoring a chromium compound onto the hydroxyl group of the silica surface. In this respect, the catalyst support not only works as a dispersing agent for the active chromium species but also its properties gives an effect on the catalyst activity and produced polymer properties. In the other words, the structure of active sites directly relies on the surface structure and chemical properties of the silica support. On the basis of these considerations, it is evident that a brief description of the structure of silica together discussion of the surface models is of vital important to understand the chromium localization.

Meanwhile, very recently our group has clarified that the broad molecular weight distribution of HDPE produced by the Phillips catalyst arises from not only the existence of various chromium species but also chromium species situated in different coordination environments by Density Function Theory (DFT) calculation.[10] To understand the nature of the active site of Phillips catalyst and the relationship with its unique ethylene polymerization performance, a completely uniform structure of chromium species are required. For these reasons, it forces researches to explode other approach which is homogenous catalyst. During the last several decades, the different type of homogeneous model catalysts has been design to mimic and simplify

the conventional Phillips catalyst with a heterogeneous catalyst surface.[11-15]   At the same time, the well-defined homogeneous catalyst sutures give a good understanding for studying the molecular model by other spectroscopic approach especially in-situ or operando technique.[16, 17]

In previous studies, various homogenous model catalysts have been synthesized for research Phillips ethylene polymerization.[18-21]   It can be mainly summarized three groups which have a divalent, trivalent and hexavalent oxidation state of chromium species.   Because CO reduced Phillips catalyst with divalent chromium species show no induction time for polymerization and for a while, divalent chromium species are consider as an active site.   In the case of homogenous model catalysts with trivalent oxidation state, recently, it was proposed an active site for Phillips ethylene polymerization.   However, there is no direct observation support it. Meanwhile, during polymerization the reactions among catalyst, activator and monomer are complex, the nature of active species and their transformation behavior does not clarify yet.   Other group is homogenous model catalyst with hexavalent chromium state which composes industrial pre-catalyst.

To mimic industrial Phillips catalyst with the different coordination environments round chromium species and hexavalent chromium species, POSS supported hexavalent chromium catalyst was designed for ethylene polymerization.[20]   As a consequence, in this study a novel and more realistic homogeneous Phillips catalyst was developed for investigation of the nature of active site and the relationship with its ethylene polymerization performance.

In last chapter, trivalent chromium homogeneous catalysts with POSS as a support were prepared for study Phillips catalyst. The homogenous catalysts gave a very abroad MWD and without induction time in polymerization may be due to a reaction between catalyst and activator and the catalyst living time is very short probably owing to an extremely air and moisture sensitivity of the trivalent catalyst. The nature of active site and the relationship with its ethylene polymerization performance does not clarify by trivalent chromium homogeneous catalysts. The more stable homogeneous catalyst structure was necessary for obtaining the nature of active site and the relationship with its ethylene polymerization performance. Therefore, in this chapter, chromium trioxide (CrO_3) as a precursor also was utilized for preparation of the relative stable hexavalent homogeneous catalyst. Hexavalent catalysts (Cr(VI)/POSS-2OH, Cr(VI)/POSS-2OH-OSiMe$_3$ and Cr(VI)/POSS-3OH) were synthesized for ethylene polymerization to gain catalyst behaviors. Different chromium oxidation states imparted various ethylene polymerization behaviors. In this time, a very broad MWD of obtained polymer was gained as well, probably because active site changed during polymerization owing to a reaction between catalyst and activator. All the hexavalent homogeneous catalysts showed a higher activity compared with trivalent one, maybe because of a relative stable hexavalent homogeneous catalyst structure.

5.2 Experimental

5.2.1 Materials

1,3,5,7,9,11-Octaisobutyltetracyclo[7,3,3,15,11]octasiloxane-endo-3,7-diol[$(C_4H_9)_8Si_8$

$(OH)_2O_{11}$] (POSS-2OH), 1,3,5,7,9,11,14-Heptaisobutyltetracyclo[7,3,3,15,11]

heptasiloxane-endo-3,7,14-triol [$(C_4H_9)_7Si_7(OH)_3O_9$] (POSS-3OH) and

tri-n-octylaluminum (TNOA) were purchased from Sigma-Aldrch Corporation.

Tetrahydrofuran (THF), triethylamine (TETN), chloro(trimethyl)silane (TMCS),

sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), 2,6-di-tert-butyl-p-cresol

(BHT), chromium oxide (Cr(VI)) and magnesium sulfate ($MgSO_4$) were purchased

from Wako Pure Chemical. Benzene-d_6 (C_6D_6) and carbon tetrachloride (CCl_4) were

purchased from Kanto Chemical Corporation. Ethylene of polymerization grade was

donated by Asahi Kasei Chemicals Corporation. Hexane, heptane and toluene were

distilled from dark purple solutions of sodium benzophenone under nitrogen for

organic syntheses. Heptane was used after purification through a column of 4 A

molecular sieve followed by bubbling under nitrogen for 2 h for ethylene

polymerization. CCl_4 was purified by 4 A molecular sieves bubbling under nitrogen
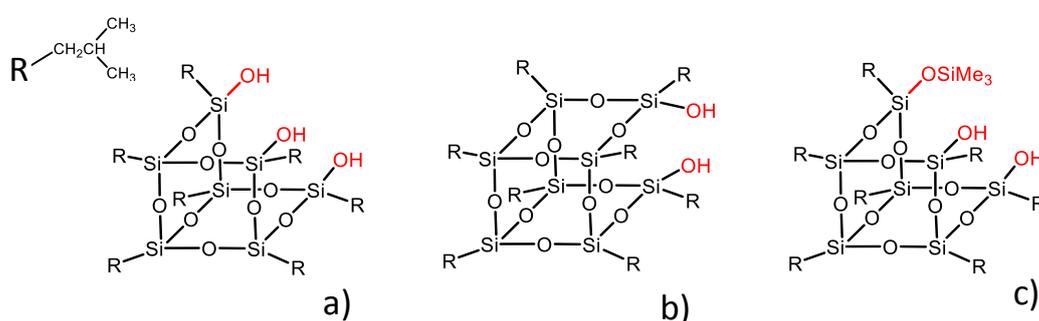
for 4 h.

Figure 5-2-1. Molecular frameworks of various POSS: a) POSS-3OH,
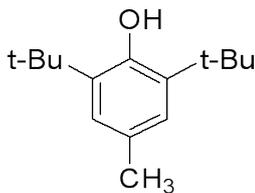
b) POSS-3OH, c) POSS-2OH-OSiMe$_3$

Figure 5-2-2.   Molecular structure of BHT

5.2.2 Synthesis of POSS-2OH-OSiMe$_3$

TMCS was added dropwise to a THF solution of mixture of POSS-3OH and TETN (Molar ratio: TMCS/POSS-3OH=1 TETN/POSS-3OH =10).[21-22]   Triethyl-ammonium hydrochloride began to precipitate immediately after mixing.   It was removed by filtration after 18 h of stirring at room temperature.   Remove of the volatiles in vacuo and then the white solid was extracted with hexane, filtered and concentrated to by distillation.[23]   After one week, a big crystal was obtained in solution.   The product of crystal was gained by removed the solution.

5.2.3 Synthesis of modified TIBA activator (TIBA+BHT)

Solution of BHT (0.5 mmol, optimized molar ratio of BHT/Al=1)[24] in heptene (100 ml) was slowly added to TIBA (0.50 mmol) in heptane (5 ml) at 0°C in ice bath, which stirred for 3 h.   After of the reaction completion, products were stored under N$_2$.

5.2.4 Cr(VI)/POSS catalyst preparation

In a typical reaction, a mixture of POSS-3OH, POSS-2OH or POSS-2OH-OSiMe$_3$, excess CrO$_3$ and MgSO$_4$ in CCl$_4$ was stirred overnight in the dark.　After the reaction, filtration and evaporation of the volatile material at room temperature in the dark gave the catalysts.

5.2.5 Cr content in catalyst by UV-vis measurement

Diffuse reflectance UV-vis spectroscopic measurements of all the three catalysts were recorded on a JASCO V670 UV-VIS-NIR spectrometer.　The spectra were collected at 200-800 nm with a 1 nm resolution.　UV-vis spectrum for the Cr content of catalyst was obtained using a Shimadzu UV-2401-PC spectrophotometer.　The sample was prepared as follows.　Catalyst 1 ml was weighed and stirred in a solution of 5 mL 5 M NaOH(aq) and 30% H$_2$O$_2$ at 80ºC for 5 h.　The mixture was diluted with deionized water to 50 mL.　The absorbance of the CrO$_4^{2-}$ peak of the solution at λ_{max} = 373 nm was converted to concentration using a calibration curve (Abs/l = $(4530 \pm 50)\cdot C - (0.0078 \pm 0.0058)$), where Abs is the absorbance, l is the path length, and C is the concentration).

5.2.6 Ethylene polymerization

Semi-batch slurry ethylene polymerization was performed in a 1 L stirred autoclave at different temperatures (40, 50, 60, 70 and 80ºC).　Heptane (200 ml) was used as a

solvent. Ethylene pressure was kept at 0.5 MPa. TNOA or TIBA modified by

BHT was added as an activator (1 mmol/L). The polymerization was started by the

addition of the catalyst with different stirring condition. After 3, 10 or 30 min

polymerization, ethanol was added to quench the reaction. The produced polymer

was filtered and dried in vacuum at 60°C for 6 h.

5.2.7 Polymer characterization

The branching frequency of PE was determined by ^{13}C-NMR at 75.43 MHz using

Varian Gemini-300 spectrometer operated at 120°C. A sample was prepared by

dissolving 240 mg of PE in 3.1 ml of 1,2,4-trichlorobenzene and benzene-d_6 (4:1 v/v).

The branch frequency of PE was decided by the previously reported method.[25] Gel

permeation chromatography (GPC, Waters Alliance GPCV2000CV) with polystyrene

gel columns (Shodex UT-806 M) was applied to determine MWD of the produced PE

using 1,2,4-trichlorobenzene as solvent at 140°C.

5.3 Results and discussion

To understand the Phillips ethylene polymerization, homogenous tiravalent chromium

catalysts (Cr(VI)/POSS-3OH, Cr(VI)/POSS-2OH and Cr(VI)/POSS-2OH-OSiMe$_3$)

were synthesized using the different POSS as a support and a chromium trioxide, as

scheme 5-3-1 is showing. The structure of catalyst Cr(VI)/POSS-2OH-OSiMe$_3$ was

concluded by the combination of multinuclear NMR data and a single–crystal X-ray

diffraction study in previous woks by Feher et al.
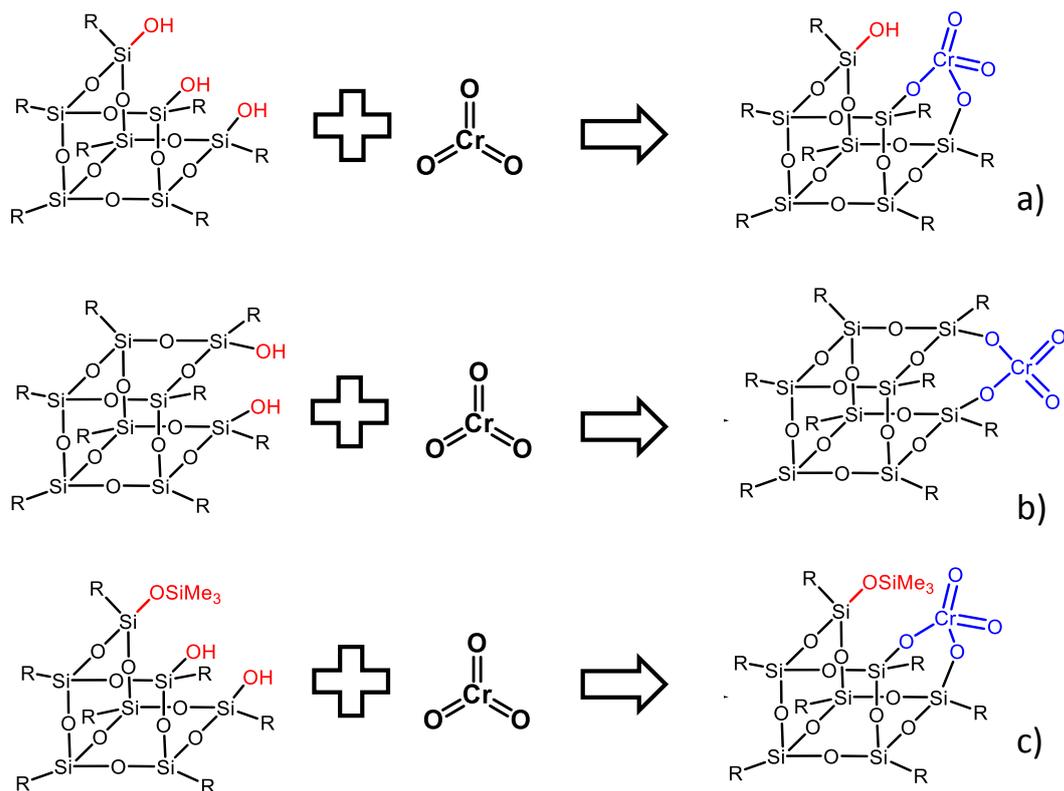
Scheme 5-3-1.   A reaction between POSS and chromium trioxide: a) POSS-3OH,

b) POSS-2OH, c) POSS-2OH-OSiMe$_3$

In addition to his conclusion, all the catalyst structures were supported by measurement of UV-vis for Cr content of catalysts.   As Table 5-3-1 was shown, the Cr content observed in experiment is similar to the value resulted from theoretical bipodal structure.

Table 5-3-1.   Cr content in catalysts by UV–vis measurement

Catalysts	Theoretical bipodal (Crwt%)	Experiment (Crwt%)
Cr(VI)/POSS-3OH	5.12	5.10
Cr(VI)/POSS-2OH	4.85	4.83
Cr(VI)/POSS-2OH-OSiMe$_3$	4.72	4.71

Table 5-3-2 displays the activity of ethylene polymerization which was conducted at the various optimized temperatures with different catalysts using different activators.   All the hexavalent homogeneous catalysts and heterogeneous catalyst with silica as a support have an ability of ethylene polymerization.   At the same time, the hexavalent catalysts Cr(VI)/POSS-2OH and Cr(VI)/POSS-2OH-OSiMe$_3$ without hydroxyl group in catalyst structure can polymerize ethylene.   It agrees with the results in last chapter.   Catalysts Cr(VI)/POSS-2OH and Cr(VI)/POSS-2OH-OSiMe$_3$ without hydroxyl group in catalyst structure can polymerize ethylene, it indicated that hydroxyl group is not necessary for Phillips ethylene polymerization.   It agreed with the phenomenon which is that dehydroxylation of Phillips catalyst improved catalyst activity and some completely dehydroxylated catalyst had shown high activity.[26] Cr(VI)/POSS-2OH-OSiMe$_3$ resulted in a lower catalyst activity than Cr(VI)/POSS-2OH, probably because ethylene insertion was hindered by a bulky ligand of -SiMe$_3$ in catalyst structure similar to trivalent homogeneous catalysts. However, the catalyst in hexavalent catalyst group imparted a higher activity than

corresponded catalyst with the same POSS as a support in trivalent catalyst group, probably due to a more stable hexavalent catalyst structure. A heterogeneous catalyst contributed to a higher catalyst activity as comparison to all the homogeneous catalysts because of a more stable heterogeneous catalyst with silica support and an easy deactivation of homogeneous catalysts in ethylene polymerization. Moreover, ethylene performance was investigated using different activators for studying the MWD of produced polymer. The effect of different activator on MWD of produced polymer will discussed later in terms of GPC profile. Compared with TNOA, TIBA modified by BHT resulted in a lower catalyst activity consistent with my previous study in chapter 2 and 3.

Table 5-3-2. Activity of hexavalent catalysts for ethylene polymerization without stirring

Catalysts	Activator	Temp.(^{o}C)	Activity(g-PE/mmol-Cr·h)
Cr(VI)/POSS-3OH	TNOA	60	410
Cr(VI)/POSS-2OH	TNOA	50	830
Cr(VI)/POSS-2OH-OSiMe$_3$	TNOA	40	460
Cr(VI)/SiO$_2$	TNOA	70	5800
Cr(VI)/POSS-3OH	TIBA+BHT	60	390
Cr(VI)/POSS-2OH	TIBA+BHT	50	820
Cr(VI)/SiO$_2$	TIBA+BHT	70	2800

At the optimized temperature

Figure 5-3-3 showed the polymer yield which gained from ethylene polymerization with different polymerization time and hexavalent homogeneous catalysts. From 10 min to 30 min of polymerization time, the polymer yield only had little increase for all the hexavalent homogeneous catalysts indicating that all the catalysts easily deactivated. After 10 min polymerization time, the catalysts lose almost activity. It confirmed that catalyst is facilely deactivated and lose an ability of ethylene polymerization.
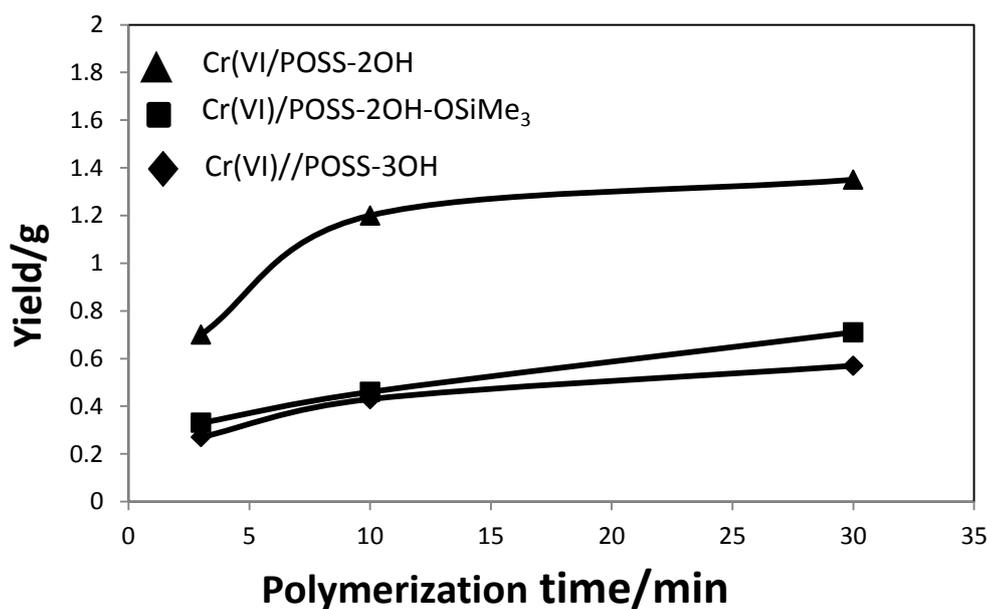

Figure 5-2-3. Effect of different polymerization time on polymer yield at the optimized temperature

Figure 5-3-5 shows the GPC profile of produced polymer by hexavalent

chromium catalysts by using TNOA as an activator at 1 mMol/L. All the hexavalent homogeneous catalysts lead to a very clear tri-model MWD. However, heterogeneous catalysts gave a narrower MWD of produced polymer. Similar to trivalent catalysts, tri-model MWD should result from different active sites during polymerization which maybe came from a reaction between hexavalent homogeneous catalyst and TNOA. To examine the influence of the reaction between catalyst and activator on MWD, a mild TIBA modified by BHT at 1 mMol/L was used to produce polyethylene. Tri-model MWD of produced polymer also was obtained by using TIBA modified by BHT, as Figure 5-3-5. However, TIBA modified by BHT tend to impart the polymer with high molecular weight. Probably because TNOA preferred to have a reaction with hexavalent catalysts leading to an active site which fabricated low MW polymer. Compared with TNOA, TIBA modified by BHT imparted the polymer with high molecular weight which gave by originated active species due to week reaction between catalyst and TIBA modified by BHT.

Compared with trivalent homogeneous catalysts in last chapter, Hexavalent homogeneous catalysts tend to less react with TNOA similar to industrial Phillips catalyst.
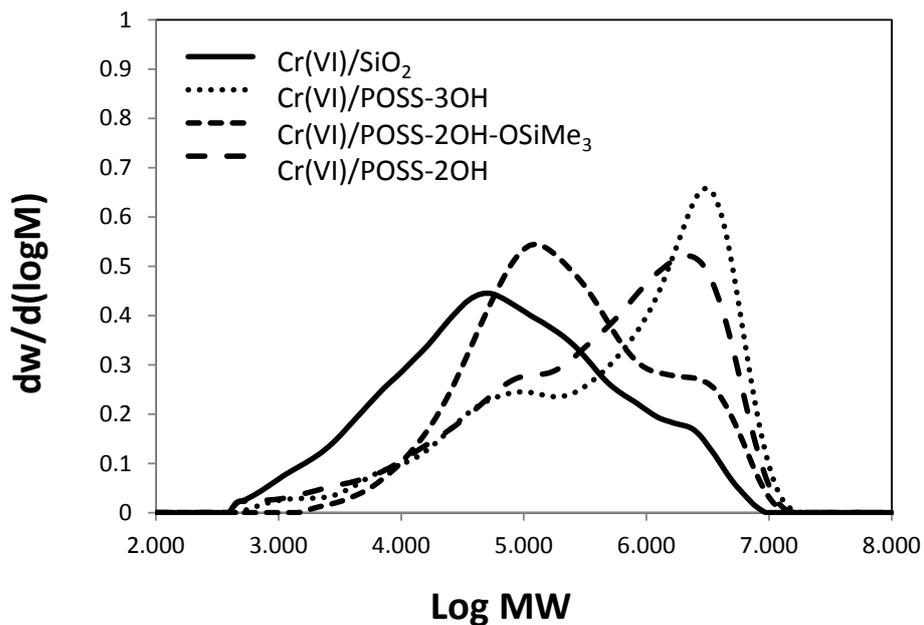
Figure 5-3-4. Comparison of MWD obtained from different hexavalent homogeneous catalysts with an activator of TNOA
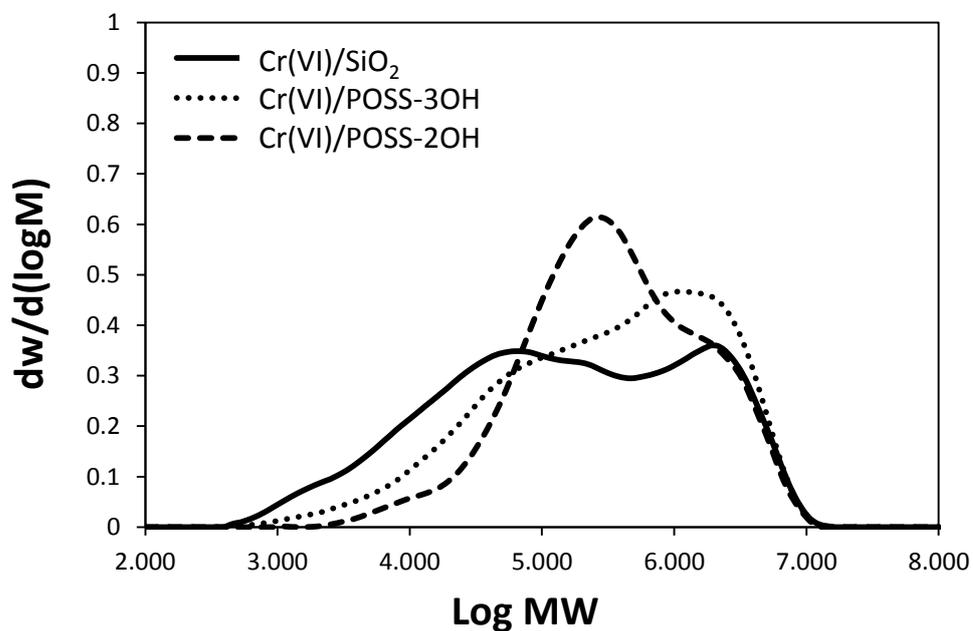

Figure 5-3-5. Comparison of MWD obtained from different hexavalent homogeneous catalysts with an activator of TIBA-BHT

Figure 5-3-6 shows a GPC profile of polymer obtained from different concentrations of TNOA and polymerization time. With the concentration of TNOA increasing, the polymer with high molecular weight gradually transfers to the polymer with lower molecular weight. Because amount of new active site become increasing, while the TNOA concentration was increasing owing to the reaction between catalyst and TNOA. The new active site fabricated the low molecular weight polymer. Similarly, when polymerization time was prolonged from 5 min to 30 min, the new active sties was increased due to a long reaction time for catalyst and TNOA.
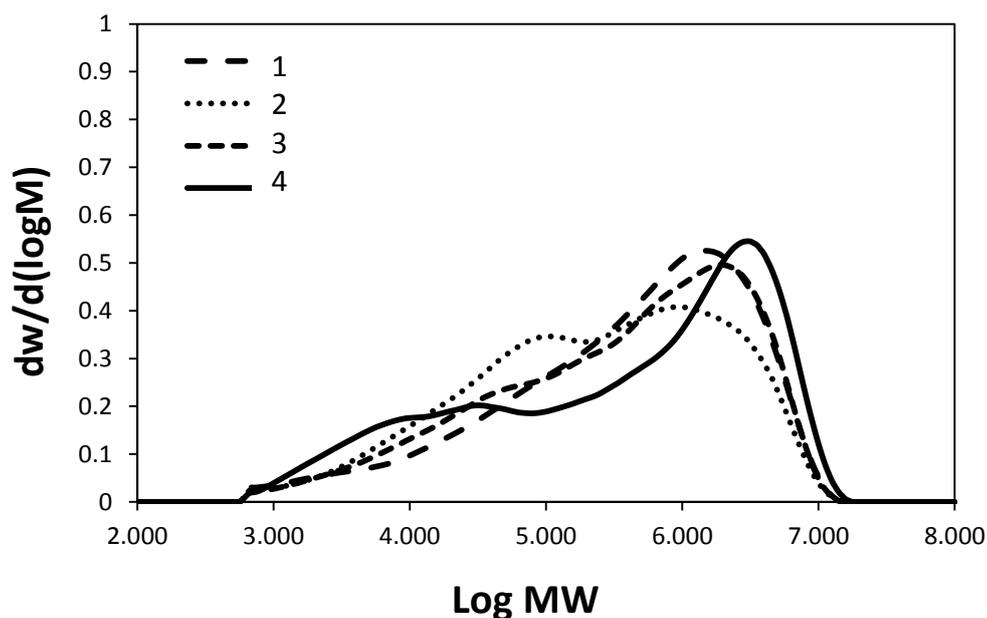

Figure 5-3-6. Comparison of MWD gave by different activators concentration and polymerization time: 1) 5 min polymerization time with a 1m mMol L^{-1}, 2) 30 min polymerization time with a 0.5 mMol L^{-1} TNOA, 3) 30 min polymerization time with a 1 mMol L^{-1} TNOA, 4) 30 min polymerization time with a 2mMol/L TNOA mMol L^{-1}

Figure 5-3-7 exhibited a GPC profile which originated from polymer produced by different heterogeneous catalysts and activators. The MWD mainly affected by activator for ethylene polymerization using heterogeneous catalyst with different chromium oxidation state. Compared with TIBA modified by BHT, TNOA almost gave a lower MW. And TIBA modified by BHT imparted a distinct two peaks on GPC trace. The proposed reason is that the TNOA with stronger reducibility can react with all the active site on heterogeneous catalyst surface, which lead to low MW polymer. However, in the case of TIBA modified by BHT with mild reducibility, only partial active site reacted with it. At the same time, the active site without reaction with activator can produced high MW polymer. Therefore, activator had most contribution on MWD for heterogeneous catalysts not chromium oxidation state.
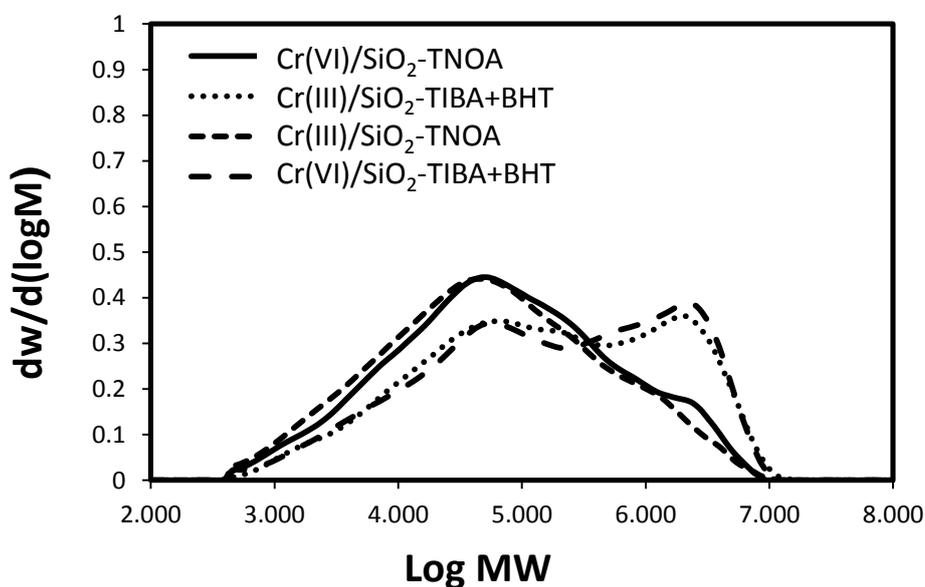

Figure 5-3-7.   Comparison of MWD obtained from various catalysts and different activators

Table 5-3-3 shows the branching information of polymer obtained by the catalysts with different ligand measured by ^{13}C-NMR. Compared with Cr(VI)/POSS Cr(VI)/SiO$_2$, Cr(VI)/POSS can easily co-polymerized propylene leading to a methyl branching owing to a strong deactivation. Cr(VI)/SiO$_2$ can fabricate the polymer with long chain branching and the branching longer than methyl branching, since it was difficulty for homogeneous catalyst with a bulk ligand to co-polymerized a macro-monomer or a long chain with the terminal vinyl group.

Table 5-3-3. Comparison of branching gave by different catalysts with a TNOA as an activator at concentration of 1 mMol/L

Catalysts	Methyl	Ethyl	Propyl	Butyl	Long
Cr(VI)/POSS-3OH	0.1	-	-	-	-
Cr(VI)/POSS-2OH	0.1	-	-	-	-
Cr(VI)/POSS*	-	-	-	-	-
Cr(VI)/SiO$_2$	0.1	0.2	-	0.4	0.2

* Cr(III)/POSS-2OH-OSiMe$_3$

5.4 Conclusions

In brief, it was found that all the homogenous catalysts Cr(VI)/POSS-3OH,

Cr(VI)/POSS-2OH and Cr(VI)/POSS-2OH-OSiMe$_3$ without hydroxyl group also gave an ethylene polymerization activity, indicating that hydroxyl group is not necessary for Phillips ethylene polymerization. At the same time, POSS supported all the homogeneous catalysts imparted a very broad MWD, probably because of a reaction between catalyst and activator during ethylene polymerization. Homogeneous catalysts lead to a low ethylene polymerization activity due to an easy deactivation in polymerization.

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Chapter 6

General Conclusion

6.1 General summary

This dissertation discussed the relationship between the catalyst structure and the type of activator, and their ethylene polymerization performance, according to the activity, branching abilities and production of MWD shed the new light for precise design of the Phillips ethylene polymerization system. Meanwhile, bimetallic Phillips type catalysts were developed for ethylene polymerization with an improvement on Phillips catalyst.   The results obtained are summarized briefly as follows.

In chapter 2, a series of bimetallic Phillip-type catalysts were synthesized by co-impregnation approach to investigate the catalyst performance in terms of catalyst activity and polymer properties including branching level and MWD. Catalyst activity and branching ability of the catalysts were enhanced by the introduction of zirconium, zinc and vanadium, while deteriorated by the introduction of molybdenum and tungsten.   When zirconium precursor was added into co-impregnation solution, the obtained polymer displayed a similar MWD to conventional Phillips catalyst. MWD was broadening by the introduction of molybdenum into Phillips catalyst showing a very clear bi-model style.   On the other hand, the structure of metal salt precursors did not greatly affect the catalytic performances.   XPS clarified a tendency that second metal with lower electronegativity decreased the electron density

on chromium species, resulting in higher polymerization activity of the bimetallic catalysts plausibly due to enhanced ethylene activation. On the other hand, the branching ability of the catalyst improved as the catalyst activity increased due to more facile formation of α-olefin co-monomer.

In order to understand the deactivation behaviors and alleviate it in Phillips ethylene polymerization at high concentration, various activators were investigated according to the ethylene polymerization yield and the produced polymer properties in chapter 3. At high activator concentration, excess activator react with catalyst resulted in a loss of polymerization performance. TNOA can decrease a deactivation due to a mild reducibility as comparison to TIBA and TEA. TIBA modified by BHT also shows a performance of alleviate a deactivation as comparison to TIBA, due to a passivated effect. In brief, a mild activator can alleviated the reaction contributed to a decreased deactivation. Meanwhile, DEZ and DEAC lead to a serious deactivation contributed to a more methyl branching and broader molecular weight distribution, probably because a serious deactivation resulted in the new active sites which come from a reaction between activator and Cr-O-Si bond. The new active sites can fabricate a new type of polymer chain or propylene for co-polymerization with ethylene leading to high methyl branching.

Relationships between the homogeneous model catalyst and ethylene polymerization properties are discussed in chapter 4 and 5. To mimic industrial Phillips catalyst and obtain a deeper understanding of industrial Phillips ethylene polymerization, the performances of the model catalyst with POSS as a support were

investigated compared with that of the industrial heterogeneous Phillips catalyst. The structures of model catalysts were confirmed by NMR and solution IR and UV-vis. The obtained model catalysts were employed in ethylene polymerization. All the model catalysts showed an activity for ethylene polymerization. The catalyst Cr(III)/POSS-2OH-OSiMe$_3$ with bulky POSS support than Cr(III)/POSS-2OH show a poor catalyst activity and branching ability. Both of them without hydroxyl group in catalyst structure have an ability of ethylene polymerization, it suggested that hydroxyl group is not necessary for ethylene polymerization. Moreover, Cr(III)/POSS-3OH with hydroxyl group showed the highest catalyst activity than other two, the hydroxyl group in trivalent homogeneous catalyst can imparted a positive effect on Phillips ethylene polymerization. All the homogeneous catalysts lead to a very broad MWD, maybe due to a reaction between catalyst and activator, because a passivated activator, a shorten polymerization time and a decreasing of activator concentration can narrow the MWD. The effect of different chromium oxidation state on catalyst behaviors also was studied. The chromium catalyst with different chromium oxidation state gave the similar polymer, however the hexavalent catalyst imparted an activity than trivalent one probably due to a stability of hexavalent catalyst during polymerization.

6.2 Conclusions

The Phillips catalyst have been utilized for commercial polyolefin production more than 6 decades, which discovered by Hogan and Banks at Phillips Petroleum Company. The irreplaceable unique characters of the Phillips catalyst are both broad MWD and adequate amounts of SCBs and LCBs incorporated. In spite of more than half century of research efforts, the real oxidation state, chemical structure and composition of the active site are the most controversial problem, and polymerization mechanism still remain unclear. Researches in this field are still ongoing and have led to new way to modification the catalyst and to tailor PE structure. A series of investigations were attempted in this work: 1) the bimetallic Phillips catalyst was developed for HDPE with a unique polymer chain structure, 2) the activators were studied for alleviated a deactivation of Phillips ethylene polymerization, 3) the specific model catalyst system having a controlled active site structure was employed for deep understand of Phillips catalyst. From the series of results, it can be conclude as follows.

Bimetallic Phillip-type catalysts with the zirconium, zinc or vanadium can improve catalysts activity and branching ability as comparison to conventional Phillips catalyst. XPS gave a reason that second metal with lower electronegativity decreased the electron density on chromium species, contributing to a higher polymerization activity of the bimetallic catalysts probably because of enhanced ethylene activation. At the same time, the branching ability of the catalyst improved as the catalyst activity increased owing to more easy formation of α-olefin

co-monomer.

A alleviate deactivation in polymerization for Phillips ethylene polymerization was achieved by using mild TNOA and a passivated BHT modified TIBA as an activator at a high concentration, because a reaction between catalyst and activator was weaken. A deactivation is proposed as a reaction between excess activator or a strong activator and catalyst leading to a change of active species. The new active sites can fabricate a new type of polymer chain and propylene resulted in the polymer with broad MWD and more methyl branches.

At last, the homogeneous model catalysts with uniform structure prepared using POSS as support was studied to understand industrial Phillips catalyst. The homogeneous model catalysts without hydroxyl group in catalyst structure can produce polymer, it indicated that hydroxyl group is not necessary for Phillips ethylene polymerization. Meanwhile, they can make the polymer with very broad MWD, plausibly it originated from the reaction between catalyst and activator. The homogeneous model catalysts with different oxidation state showed a similar ethylene polymerization performance on polymer properties. A hexavalent catalyst imparted a higher activity is more stable than trivalent one during polymerization. The POSS support also affected catalyst performance based on the POSS cage structure. The catalyst with a bulky POSS cage ligand leads to a low activity and branching ability. Because the bulky POSS cage ligand bury the chromium active site and hindered a copolymerization between ethylene and co-monomer.

Thus obtained discussion in this work suggests for development of new type of

Phillips catalysts to control a molecular weight, branching and their distribution in obtained polymer. The results and discussion in this dissertation will be benefited for improvement of the world wide used catalyst and in development for novel oxide based olefin polymerization catalysts.

Achievements

Publications

Original Articles

(1) Hetero-Bimetallic Phillips Type Catalyst for Ethylene Polymerization

Yanning Zeng, Akanksha Matta, Sumant Dwivedi, Toshiaki Taniike and Minoru

Terano

Macromol. React. Eng., 2013, *7*, 663-712.

(2) Development of effective co-catalyst for decreasing deactivation of Phillips

ethylene polymerization

Yanning Zeng, Toshiaki Taniike and Minoru Terano,

in preparation

(3) Design of novel homogeneous Phillips catalyst using the model of active site and

support,

Yanning Zeng, Toshiaki Taniike and Minoru Terano

in preparation

Awards

➢ Best poster award, International Workshop on Catalytic Olefin Polymerization
and High Performance Polyolefin, Shanghai, Oct. 20-26.

➢ Inorganic Chemistry Frontiers Poster Prize, Asian polyolefin workshop, Beijing,
Oct. 15-19.

Presentations

International Conferences

1. Design of novel homogeneous catalyst with silsequioxane support to understand Phillips catalyst

Y. Zeng, T. Taniike, M. Terano

International Workshop on Catalytic Olefin Polymerization and High Performance Polyolefins, Shanghai, China, Oct. 22-25, 2014.

2. Design of Novel Homogeneous Phillips Type Catalyst with Silsequioxane Support

Y. Zeng, T. Taniike, M. Terano

International Symposium of Advanced Material, Kanazawa, Japan, Nov. 22, 2013.

3. Design of Novel Homogeneous Phillips Catalyst with Uniform Active Species and Support

Y. Zeng, T. Taniike, M. Terano

Asian Polyolefin Workshop 2013, Beijing, China, Oct. 15-19, 2013.

4. Development of Hetero-Bimetallic Phillips Catalyst for Ethylene Polymerization.

Y. Zeng, A. Matta, T. Taniike, M. Terano

7th International Symposium on High-Tech Polymer Materials, Xi'an, China, Jun. 17-21, 2012.

5. Development of Hetero-bimetallic Phillips catalyst for Ethylene Polymerization

Y. Zeng, A. Matta, T. Taniike, M. Terano

8th International Colloquium on Heterogeneous Ziegler-Natta Catalysts, Kanazawa, Japan, Mar. 27-30, 2012.

6. Development of Hetero-Bimetallic Phillips Catalyst for Ethylene Polymerization

Y. Zeng, A. Matta, T. Taniike, M. Terano, Poster Presentation

International Symposium on Catalysis and Fine Chemicals 2011, Nara, Japan, Dec. 4, 2011.

Domestic Conferences

1. Design of Novel Homogeneous Phillips Catalyst with Uniform Active Species and Support

Y. Zeng, M. Akanksha, T. Taniike, M. Terano

44th Petroleum-Petrochemical Symposium of JPI, Asahikawa, Japan, Oct. 16-17, 2014.

2. Improvement of Polyethylene Microstructure Produced by Modified Phillips Type Catalysts

Y. Zeng, M. Akanksha, T. Taniike, M. Terano

42th Petroleum-Petrochemical Symposium of JPI, Akita, Japan, Nov. 11-12, 2012.

3. Effects of Various Transition Metals on Ethylene Polymerization Performance of Phillips Type Bimetallic Catalysts

Y. Zeng, M. Akanksha, T. Taniike, M. Terano

60th SPSJ Symposium on Macromolecules, Okayama, Japan, Sept. 28-30, 2011.

4. Development of New Phillips Type Bimetallic Supported Catalysts with Chelating Ligand

Y. Zeng, M. Akanksha, T. Taniike, M. Terano

60th SPSJ Annual Meeting, Osaka, Japan, May 25-26, 2011

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A study of the early stages of Phillips ethylene polymerization by oligomer analysis

by

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1. Introduction

Commercial polyethylene (PE), which is produced by Ziegler-Natta and Phillips chromium catalysts, is the most widely used commodity plastic. The Phillips catalyst[1] (Cr/SiO$_2$), consisting of chromium oxide supported on silica, accounts for a large share of the world's high density polyethylene (HDPE).[2] Since the Phillips catalyst was discovered by J. P. Hogan and R. L. Banks in the early 1950s the Phillips catalyst has been tailored in numerous ways for many specialized applications, because of ease of preparation and handling. The conventional method for preparation of the Phillips catalyst involves deposition of a chromium compound onto the silica surface, leading to a heterogeneous catalyst. Since various chromium species are located at different sites on the amorphous silica, their characterization is a complex and difficult task. For this reason, despite numerous investigations that have been performed, the true structure of the active sites and their ethylene polymerization mechanism, especially the initiation mechanism, are still mysterious.

An understanding of the initiation mechanism of ethylene polymerization is highly deseired in both industrial and academic research endeavors. Because the Phillips catalyst polymerizes ethylene without an activator, the monomer plays a key role in the initiation stage, reducing hexavalent chromium to divalent in the immediate precursor to the active site. The ensuring initiation of ethylene polymerization involves alkylation of the divalent chromium species. An induction period is always observed after the introduction of ethylene at usual operating temperatures (ca. 100 ^{o}C). This induction time represents a major problem for the production of ultrahigh

molecular weight polyethylene (UHWM PE), which is used in applications where extreme toughness is desired, such as in ski bottoms, artificial limbs, gears and bullet-proof vests. UHMW PE is more resistant to abrasion than steel.[2] Consequently, a better understanding of the initiation mechanism and is highly desired by polyethylene producers. At the same time, the mechanism of alkylation of divalent chromium by ethylene, followed by growth of the first polymer chain, is one of the most interesting and significant unsolved academic questions.

Numerous studies regarding the initiation mechanism on Phillips ethylene polymerization have been carried out, and various mechanisms has been proposed based on either pure speculation or controversial evidence. They include Cossee-Arlman[3, 4], Green-Rooney[5-8] and Metallacycle[9] mechanisms. Hogan[10] hypothesized a hydride transfer from the β–carbon of a growing polymer chain to the active metal center on the catalyst surface. Subsequent Cossee-Arlman insertion of another monomer into the C-H bond to form an ethyl group provided the means for initiating a new chain, and also explained the appearance of a vinyl group at the end of the polymer chain. However, this explanation did not account for the formation of the initial chain, which required an external source of hydrogen.[11] An alternative possibility via Green-Rooney chain initiation involves the interaction of two adsorbed ethylene molecules on a single chromium site to form an alkilidene species.[12] The polymer chain would then grow by insertion at the Cr-allyl bond. Such a hydride could also be involved in initiating a secon of polymer chain. These hypotheses are in agreement with the available IR and NMR evidence, [10-12] according to which each

polymer chain contains one vinyl group and one methyl end-group. Ghiotti et al[13]

proposed chain initiation by the formation of a metallacyclobutane from two

chemisorbed ethylene molecules, followed by propagation via an alkylidene structure.

The involvement of the latter species was supported by IR studies.[13, 14] They

attributed the weak broad absorption band at 2750 cm^{-1} to the ν (CH) mode of a

carbene group interacting with the metal center.[13] The carbene was formed initially

by migration of a CH_2 proton to a surface oxygen atom. The catalytic cycle is

completed by a proton shift from this new hydroxyl group back to the originating

carbon atom, thereby eliminating hydrogen scrambling. According to this

mechanism, no hydrogen shift occurs during propagation. Al-Mashta et al.[15, 16]

presented spectral evidence for a formation of an ethylidene species during the early

stages of ethylene polymerization on sulfated anatase. They assumed that these

species were related to initiation and were formed from ethylene itself without the

need for an extra hydrogen atom.[15] Because Ghiotti et al.[13] failed to observe IR

spectral evidence indicating the presence of either vinyl or methyl end-groups in the

growing polymer chains, they believed that terminal groups were not present. This

could occur, if the chains formed cyclic structures with both ends attached to the metal

centers. Vikuiov[17] also showed that ethylene polymerization is preceded by rapid

initial adsorption of monomer. Although spectral evidence was lacking, the

explanation[18] offered was that carbenes are formed from chemisorbed ethylene

molecules on two neighboring chromium sites. Unfortunately, there is as yet no

consensus for any of the above hypotheses, because of low abundance, the short

life-time and ambiguous spectroscopic signatures of the very active species formed

during the initiation.
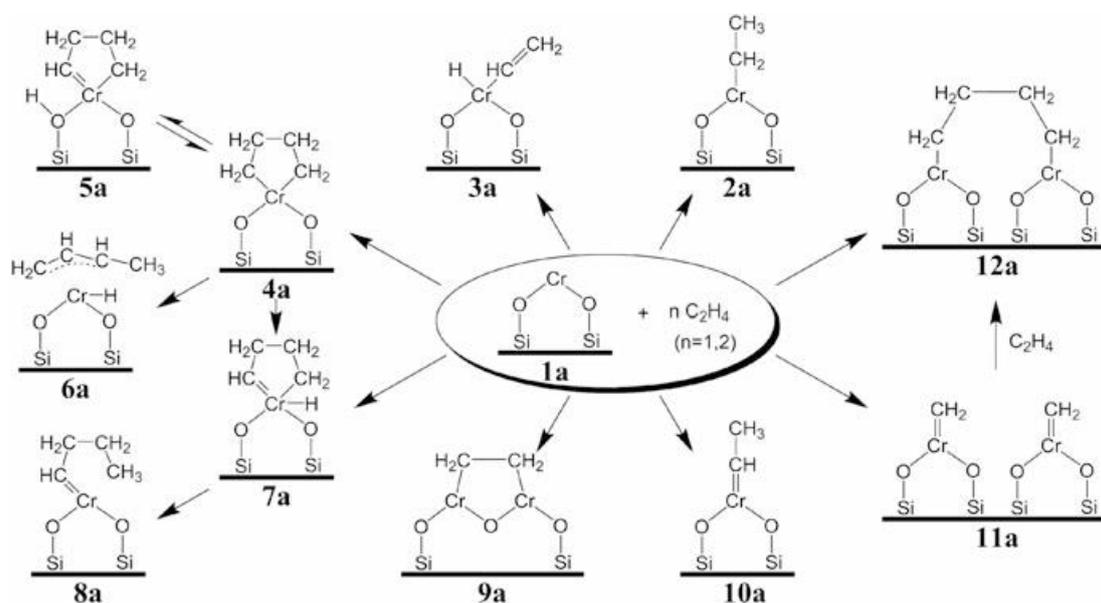
Scheme 1   Proposed three kinds of initiation mechanisms: 2a, 3a, 6a) Cossee-

Arlman, 5a, 7a, 8a, 10a, 11a) Green-Rooney and 4a, 9a, 12a) Metallacyclic

To shed light on the initiation mechanism for ethylene polymerization on Phillips

catalyst and to promote further development of this significant polyethylene catalyst, a

simplified version of the catalyst was used, because of the beginning of research in

this field, obtained by reduction of the supported chromate precursors with CO at

350°C.[19, 20]   In this way, the starting oxidation state of chromium is well defined and

uniform, mainly as Cr(II).   More importantly, the reduction phase is well-separated

formed the polymerization or oligomerization phase.   However, the major challenges

in fundamental studies of the initiation mechanism are still present in the

encapsulation of the active sites by the polymer product, and the very short lifetimes

of the growing polymer chains due to very fast polymerization.   Vikulov observed

spectra relevant to the initial steps by decreasing reaction rate in this manner. In this study, our strategy is to use ethylene at low pressure to obtain oligomers and to analyze their structures in order to explain the mechanisms of initiation of the first growing chains.

2. Experiments

2.1 Materials

Manipulations of air-sensitive materials were performed using a high vacuum line (10^{-4} Torr). The non-porous silica (Aerosil380, denoted A380) was provided by Evonik. $Cr_3(OH)_2(CH_3COO)_7$ (99.9 %) was purchased from Fisher Scientific. $CO(g)$ (99.99%), $O_2(g)$ (99.99%) and ethylene (g) (99.99%) were purchased from Praxair. Each was stored in a glass bulb over activated molecular sieves which had been dried dyed at $150^{o}C$ for 24 h.

2.2 Preparation of catalyst precursor

$Cr_3(OH)_2(CH_3COO)_7$ (0.0211 g) was dissolved in distilled water at room temperature. The solution was added onto silica (0.5 g, corresponding to 1.0 wt% chromium) and impregnation was performed at $80°C$ for 2 h with gentle stirring. Furthermore, the solid powder was dried at $120°C$.

2.3 Activation of catalyst precursor and reduction of grafted Cr(VI) to Cr(II)

The powdered catalyst precursor was pressed into self-supporting pellets (ca. 20 mg, 16 mm diameter) at 1000 psi, which were mounted in a quartz sample holder and thermally treated as described below. Because of the extreme air-sensitivity of the

reduced catalyst, thermal treatment of these pellets, to form chromate sites with or without CO reduction to Cr(II), was performed in a single glass batch reactor to avoid contamination during sample transfer. First, the reactor containning the catalyst precursor pellets mounted in a sample holder was evacuated. $O_2(g)$ (100 Torr) was transferred into the reactor at room temperature via an all-glass vacuum line. After this step, the catalyst precursor pellets was heated at either 500 or 800^oC under $O_2(g)$ in for 18 h, to activate catalyst precursor. During this step, the color of the pellets changed gradually from pale green to light orange (at 500^oC activation) and the color of the pellets did not change (at 800^oC activation). After activation catalyst precursors, the reactor was evacuated again to remove O_2 gas at the calcinations temperature for 2 h, then was cooled down to room temperature. Some of the catalyst pellets were reduced by heating in 100 Torr CO(g) for 2 h at $350\ ^oC$. Final evacuation of CO(g) was performed at the reaction temperature, to obtain CO-free sites.

2.4 IR spectroscopy

A custom-built quartz cell equipped with polished KCl windows (International Crystal Laboratories) affixed with TorrSeal (Varian) was used to record IR spectra of self-supporting pellets in transmission mode. A Shimadzu IR Prestige spectrometer equipped with a DTGS detector was purged with CO_2-free dry air from a Balston 75-52 Purge Gas Generator. For in situ IR experiments, spectra were obtained by pressing self-supporting pellets (ca. 20 mg, 16 mm diameter) at 1000 psi, mounting the pellets in a sample holder (made from quartz) and thermally treating them as

described above. Spectra were collected with 2 cm^{-1} resolution by averaging 32 scans.

2.5 Ethylene oligomerization

Due to the extreme air-sensitivity of the activated catalyst, it was necessary to evaluate ethylene oligomerization activity in situ to avoid contamination during sample transfer. Grafting of $Cr_3(OH)_2(CH_3COO)_7$ onto the silica, subsequent heating to form chromate sites, with or without subsequent CO reduction to Cr(II) were all performed in a single glass batch reactor, according to the procedures described above. After a final evacuation at 300°C for 2 h and cooling to room temperature, approx. 30 Torr dry ethylene was expanded from a storage bulb into the reactor and eated to 100 ^{o}C. After 2 h, the volatile reaction products were removed to a schlenk tube using a liquid nitrogen trap. Toluene was added to dissolve the of oligomers for analyss by Gas Chromatography-Mass Spectrometry (GC-MS).

Figure 1.   Pellet holder (left), Reactor for IR, activation and ehtylene oligomerization (right)

2.6 Gas chromatography-mass spectrometry (GC-MS)

A Shimadzu GC-2010 Gas Chromatograph coupled with a   QP2010 Mass

Spectrometer (GC-MS) was used for the analysis of oligomer prducts, with ionization achieved by electron impact at 70 eV. The operating conditions were injection port temperature, 280°C; interface temperature, 280°C; column oven temperature, 75°C for 3 min, followed by a temperature ramp at 5°C min^{-1} to 150°C, then 2.5°C min^{-1} to 210°C, then 10°C min^{-1} to 290°C with a 10 min hold; helium carrier gas (flow rate of 2.3 mL min^{-1} at 75°C); 0.2 μL injection volume. For identification purposes, the mass spectrum of each peak was recorded in total ion current mode. Preliminary identification of compounds was achieved using the mass spectral database, and was confirmed by comparing the mass spectra and retention times of the chromatographic peaks with those of authentic samples.

3. Results and Discussion

Figure 2 shows the IR spectra of catalyst pellets activation at different temperatures (500°C or 800°C). The left two curves which originated from the pellet active at 500°C before or after reacted with ethylene are same. It declared that catalyst pellet did not react with ethylene. It is likely to come from the contamination in reactor due to my poor experiment technique for high vacuum line and low activity of catalyst itself in low ethylene pressure without activator. The right spectrum arose from catalyst pellet active at 800°C after ethylene oligomerization. The band at 3080 cm^{-1} is assigned to C=HO vibration in olefins.[21] It indicated that catalyst pellet reacted with ethylene. A band at 3747 cm^{-1} in all the curves is attributed to hydroxyl groups. However, the former band is broader low-wavelength shoulder involved in

H-bonding interactions.　　The latter which did not include the vicinal OH group of Si_2

rings is a narrow intense band, which are not capable of mutual H-bonding, as a

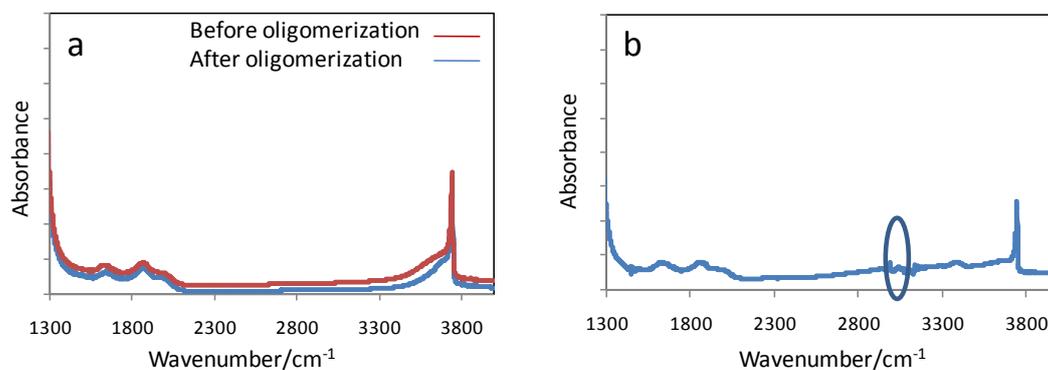results of high activation temperature of catalyst pellet.[22]

Figure 2　　IR spectra of the Phillips catalyst pellets a) activation at 500°C b)

activation at 800°C

Figure 3 displays the spectra of GC-MS of oligomers produced in the gas-phase

reaction of the catalyst after CO reduction.　　The two peaks at early stage of retention

times (< 2 min) of GC are due to ethylene and water, respectively.　　In the GC

spectrum, the series of peaks with-long retention times (> 5 min) arose from toluene

solvent and its impurities which came from solvent of liquid sample.　　To avoid

solvent effect on GC spectrum, preparation of gas sample also was conducted for

GC-MS analysis.　　However, this experiment failed during polymerization stage,

owing to some contaminations which come from my poor experiment technique for

high vacuum line.　　In addition, according to this GC-MS spectrum, five various

types of ethylene oligomers were identified; 2-methyl-pentane, 3-methyl-pentane,

hexane, 1-methyl-cyclopentane and methylenecyclopentane respectively, produced by

conventional Phillips catalyst reduced in CO. The first three are acyclic alkanes (C_6H_{14}) that originate from ethylene trimerization. The major peak is the linear chain, as expected, while the branched chains require isomerization (chain-walking). However, the fact that they are saturated alkanes raises the question of where the additional H comes from. Methylcyclopentane has the same H content as three ethylenes (C_6H_{12}), while methylenecyclopentane is dehydrogenated relative to ethylene (C_6H_{10}).

This result suggests that the Phillips catalyst is capable of hydrogenation/dehydrogenation in addition to polymerization, and that the former is important during the early stages of the reaction. It is interesting to note that further dehydrogenation could give rise to a methyl-substituted cyclopentadienyl ligand. Using HCl, Schmidt[23] extracted a trimethylcyclopentadienyl complex with formula [CpCrCl$_2$] or CpCrCl$_2$·D in donor solvents, from the Phillips catalyst. Furthermore, the Union-Carbide ethylene polymerization catalyst is made by depositing Cp$_2$Cr on silica. Our observations are consistent with in situ formation of Cp complexes via hydrogen transfer during initiation.
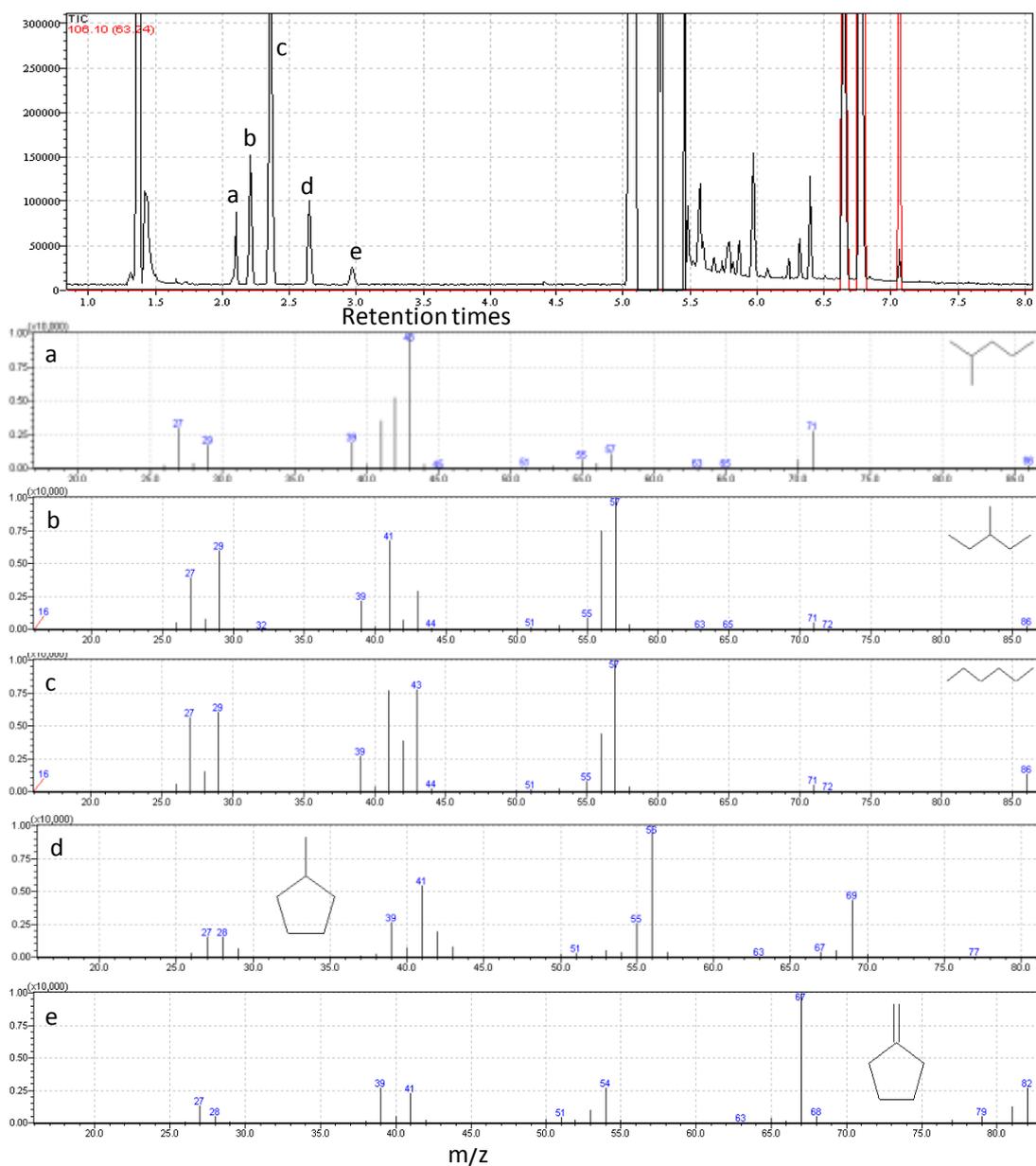
Figure 3. GC-MS of oligomers produced by the Phillips catalyst after CO reduction

Figure 4 shows the GC-MS spectra of oligomers obtained from a conventional Phillips catalyst without prior CO reduction. The results are qualitatively and quantitatively similar to those in Figure 3, suggesting that the products are characteristic of the Phillips catalyst itself and do not depend on the activation procedure.
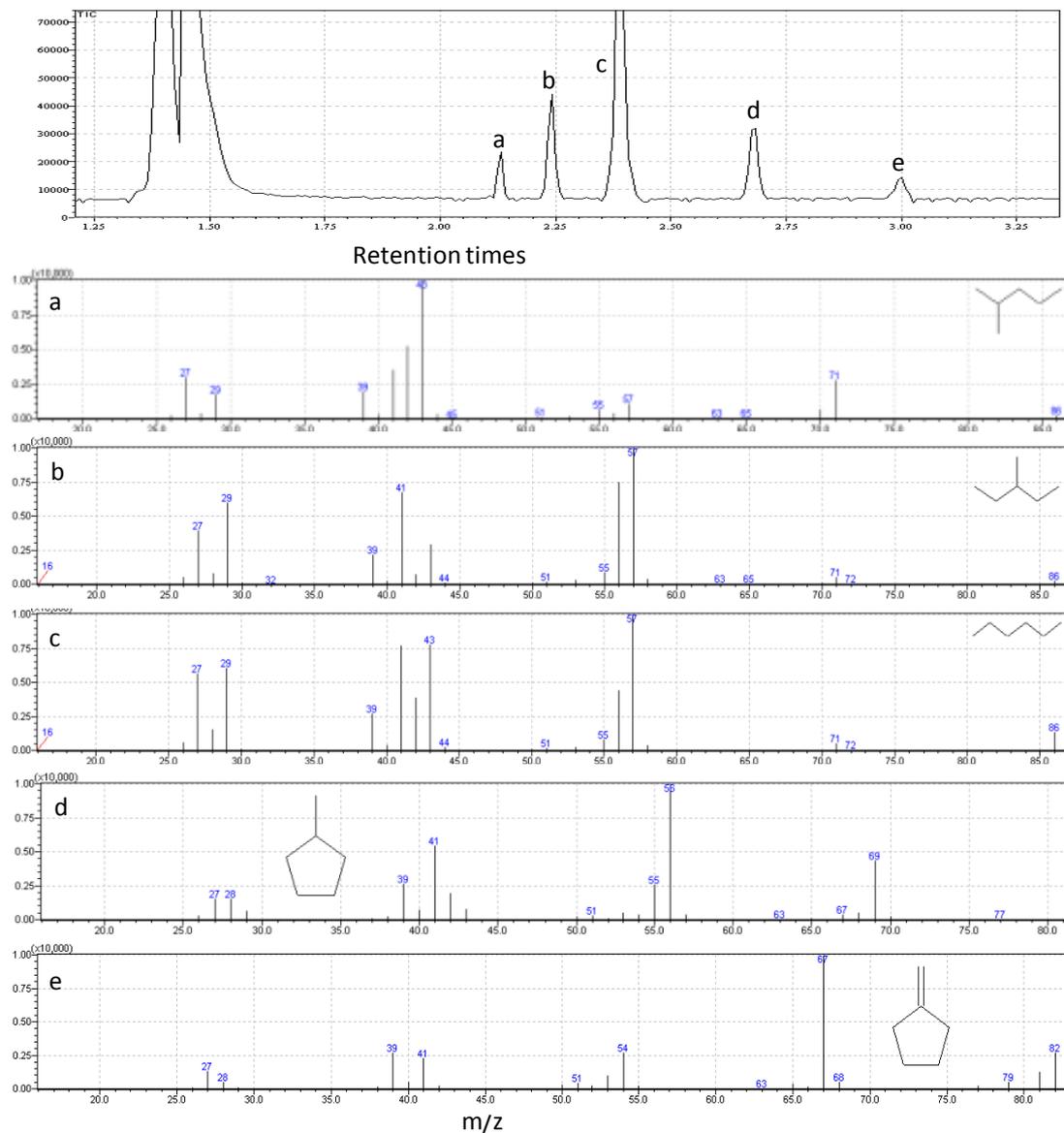
Figure 4. GC-MS of oligomers produced by the Phillips catalyst without CO reduction

4. Conclusion

In this research, GC-MS was used to identify several oligomers produced by a conventional Phillips catalyst during gas-phase activator-free oligomerization proceeding system with low ethylene pressure. In addition to the expected hexanes,

methylcyclopentane and methylenecyclopentane were observed. They may come from active species of (Cp-Cr-O), in agreement with the observation by Schmidt.

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