

CHAPTER II

LITERATURE REVIEWS

Since the discovery of metallocene catalysts by Kaminsky and Sinn in 1980, the catalysts have been interested in the polymer industries due to their potential in producing tailor-made polymers. Metallocene catalysts have many advantages over conventional Ziegler-Natta (TiCl_4 supported on MgCl_2) and Phillips (CrO_3 supported on silica) catalyst, which have been used commercially to produce polyolefins in gas phase and slurry plants. The metallocene catalysts have been developed to replace the conventional heterogeneous catalysts by heterogenizing metallocenes on support.

There are many earlier attempts to heterogenize a soluble metallocene catalysts. Chien and Hsieh [7] prepared a series of catalyst systems containing R_4Ti , R_3TiCl ($\text{R} = \text{benzyl, p-methyl}$) and $\text{Cp}_2\text{M}(\text{CH}_3)_2$ ($\text{M} = \text{Ti, Zr, Hf}$) supported on alumina, zeolite, silica, $\text{Mg}(\text{OH})\text{Cl}$, $\text{Ca}(\text{OH})_2$ and polyvinyl alcohol and used them to polymerize ethylene as well as propylene. Other supported catalyst such as bis (cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) supported on silica gel to polymerize ethylene with $\text{AlEt}_n\text{Cl}_{3-n}$ as the cocatalyst was prepared by Slotfeldt-Ellingsen and co-workers [8].

In the last few years, a large number of studies have been devoted to transformation of soluble metallocene complexes into heterogeneous catalyst by supporting them on inorganic or organic carriers to polymerize olefins. Inorganic oxide, finely divided polymers or other high surface area materials have been used as supports. The main inorganic supports used are silica, alumina and magnesium compounds.

Kaminaka *et al.* [9], prepared the heterogeneous catalyst systems composed of Al_2O_3 - or MgCl_2 - supported $\text{Et}[\text{IndH}_4]\text{ZrCl}_2$ with an impregnation method. $\text{Al}(\text{CH}_3)_3$ or $\text{Al}(\text{C}_2\text{H}_5)_3$ as cocatalyst were used for propylene polymerization. These catalyst systems can produce isotactic polypropylene in a fairly good yield, whereas the system composed of SiO_2 - supported $\text{Et}[\text{IndH}_4]_2\text{ZrCl}_2$ was almost inactive. The

Al_2O_3 - supported $\text{Et}[\text{IndH}_4]_2\text{ZrCl}_2$ systems gave a narrow molecular weight distribution (MWD; M_w/M_n) about 2, while the MgCl_2 - supported $\text{Et}[\text{IndH}_4]_2\text{ZrCl}_2$ systems gave broader molecular weight distribution. It may be considered, therefore, that the active species in the Al_2O_3 - supported catalyst were uniform, whereas those in the MgCl_2 - supported catalysts were not uniform in chemical nature.

Soga *et al.* [10] reported that the catalyst prepared by supporting CpTiCl_3 (Cp = cyclopentadienyl) or Cp^*TiCl_3 (Cp^* = 1, 2, 3, 4, 5- pentadimethylcyclopentadienyl) on Al_2O_3 treated with $\text{Al}(\text{CH}_3)_3$ or $\text{Al}(\text{iC}_4\text{H}_9)_3$ catalyzed the syndiotactic polymerization of styrene by using common trialkylaluminums as cocatalyst. The catalytic activity was still very low. The use of $\text{Al}(\text{CH}_3)_2\text{Cl}$ for treating Al_2O_3 , on the other hand, gave only atactic polystyrene.

Moreover, Soga and Kaminaka [11] reported on propylene polymerization conducted with catalysts activated by common alkylaluminums. Several kinds of heterogeneous catalysts containing zirconocene were prepared by supporting $\text{Et}[\text{IndH}_4]_2\text{ZrCl}_2$, $\text{i-Pr}(\text{Flu})(\text{Cp})\text{ZrCl}_2$ and Cp_2ZrCl_2 on Al_2O_3 , SiO_2 , MgO , MgCl_2 , MgF_2 , CaF_2 and AlF_3 as supports. When Al_2O_3 , MgCl_2 , MgF_2 , CaF_2 and AlF_3 were used as carriers, the resulting catalysts were easily activated by common trialkylaluminums to give isotactic, syndiotactic and atactic polypropylene in fairly good yields. Whereas the other supported catalysts combined with common trialkylaluminums did not show any polymerization activity. Besides, it was found using Cl-containing alkylaluminums always killed the catalyst activity.

Then Kaminaka and co-worker (1997) [12] studied the six kinds of heterogeneous catalyst prepared by supporting $\text{i-Pr}(\text{Flu})(\text{Cp})\text{ZrCl}_2(1)$ (i-Pr = isopropyl; Flu = fluorenyl) and $\text{Cp}_2\text{ZrCl}_2(2)$ on Al_2O_3 , MgCl_2 and SiO_2 . Propylene polymerization was conducted with these supported catalysts using a common alkylaluminum, $\text{Al}(\text{CH}_3)_3$, as cocatalyst. For reference, the homogeneous 1/MAO and 2/MAO catalysts were also used. The results found the 1/ Al_2O_3 and 1/ MgCl_2 catalysts presented highly syndiotactic polypropylene and showed higher melting temperature (T_m) compared to that produced with the homogeneous 1/MAO catalyst

system whereas the $2/\text{Al}_2\text{O}_3$ and $2/\text{MgCl}_2$ catalysts produced atactic polypropylene and gave fairly good yields. In contrast, the SiO_2 - supported catalysts were found inactive for propylene polymerization.

As previous papers, it was known silica-supported systems were all inactive when TMA was used as a cocatalyst. This is consistent with the absence of strong Lewis acidic centers in SiO_2 , therefore no active sites were formed upon the absorption of zirconocene complex on SiO_2 . Because of unfavorable surface chemistry of silica, it is necessary to improve by pretreating support with chemical reagents before fixing the catalyst.

Collins *et al.* [13] investigated the use of partially dehydroxylated SiO_2 (PDS) and partially dehydroxylated Al_2O_3 (PDA) pretreated with TMA at a 0.8 mmol Al/g support ratio. It was then contacted with $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$ (1). The resulting 1/TMA/PDA has 2.3 times the activity of unmodified 1/PDA. The benefit of the TMA modification was much greater in the case of the PDS support, the activity increased was 40-fold. This was because the unmodified 1/PDS catalyst was only one-tenth as active as 1/PDA, and modification with TMA raised both catalysts to comparable activity of ca. 3.5×10^5 g PP/(mol Zr·h·atm) using MAO as cocatalyst. The properties of the polyethylene produced were essentially indistinguishable from that produced under homogeneous conditions with these same catalysts.

Soga and co-worker (1992) [14] have found the SiO_2 - supported catalyst prepared from the reaction between $\text{Et}[\text{IndH}_4]\text{ZrCl}_2$ and SiO_2 pretreated with a small amount of methylaluminoxane (MAO) can effectively catalyze isotactic propylene polymerization even with the use of common alkylaluminums as cocatalyst. Anyway, the catalyst showed fairly good yields. The polymerization activity was strongly dependent upon the cocatalyst used, it markedly increased in order: $\text{Al}(\text{C}_2\text{H}_5)_3 < \text{Al}(\text{CH}_3)_3 < \text{Al}(\text{iC}_4\text{H}_9)_3$. In case of the polymerization using $\text{Al}(\text{iC}_4\text{H}_9)_3$ as cocatalyst, the activity drastically increased with a decrease in its amount. However, the precise reason has not been clear. In addition, it was found that among the three kinds of alkylaluminum, $\text{Al}(\text{iC}_4\text{H}_9)_3$ gave the highest molecular weight. For the profile of

reactions among MAO, $\text{Et}[\text{IndH}_4]\text{ZrCl}_2$ and hydroxyl groups on SiO_2 may be considered as follows: MAO was chemically fixed to the SiO_2 surface accompanied with evolution of CH_4 . During the next step, $\text{Et}[\text{IndH}_4]\text{ZrCl}_2$ probably forms a stable, inactive complex with the MAO fixed on the SiO_2 surface. The last, the alkylaluminums used as the cocatalyst were supposed to activate the inactive complex.

A comparison of ethylene polymerized on metallocene compounds Cp_2ZrCl_2 supported on silica and on silica pretreated with MAO was reported by Sacchi et al [15]. The modified SiO_2/MAO -supported systems exhibit rather high activities, although still lower than homogeneous systems. However, the polyethylene molecular weight obtained with these systems remains low and nearly identical to those produced by homogeneous metallocenes. On the contrary, directly impregnated SiO_2 -supported systems present low activity but yield polymers with higher molecular weights. Besides, propylene was polymerized in the presence of isospecific $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$ (Et = ethylene, Ind = indenyl) and the aspecific $(\text{Ind})_2\text{ZrCl}_2$ complexes in solution and anchored to SiO_2 and SiO_2/MAO . From the stereochemical analysis of the obtained polypropylene samples it can be deduced that i) the same active species is formed when a metallocene is in solution and when it is anchored to the SiO_2/MAO support and ii) a completely different active species is formed when the metallocene is anchored to the silica. The fact that both systems $\text{Et}(\text{Ind})_2\text{ZrCl}_2\text{-SiO}_2$ and $(\text{Ind})_2\text{ZrCl}_2\text{-SiO}_2$ produced the same prevailing isospecific polymer suggests that only isospecific centers are formed in this case, independently of the metallocene stereochemical structure.

Recently, Lee *et al.* (1995) [16] prepared supported catalyst for ethylene polymerization. Silica was pretreated with trimethylaluminum (TMA) followed by supporting Cp_2ZrCl_2 . The partially hydrated silica (H-SiO_2) was chosen for reaction with TMA to prepare catalyst precursor and produce aluminoxanes in situ. The resulting $\text{HSiO}_2/\text{TMA}/\text{Cp}_2\text{ZrCl}_2$ systems were effective for ethylene polymerization when a common alkylaluminum was used as the cocatalyst. The catalytic activity of the supported catalyst was found to depend on the H_2O content of silica, the

H₂O/TMA ratio, the kind of metallocene and cocatalyst. Moreover, the polymerization activity strongly depended on the kinds of aluminum compounds treated on silica. In this study, these catalytic systems have been compared to MAO/SiO₂- and TMA/SiO₂- supported systems. TMA treated silica showed very low polymerization activity, while MMAO or PMAO (modified MAO) treated silica gave high yield.

In the case of H-SiO₂ supported catalysts, those obtained from H(16)-SiO₂ (16wt% water) exhibited higher activity than H(45)-SiO₂ (45wt% water) supported ones. This result was explained by a fast and uncontrolled reaction between TMA and water in H(45)-SiO₂.

The study of effect of H₂O/TMA ratio found that the catalytic activity increased in the case of using excess amount of TMA, whereas, small amount of the TMA, compared to water used, activity was the lowest. It can be suggested that excess water in SiO₂ might act as a poison to metallocene catalyst.

The effect of cyclopentadienyl (C_p) substituted in supported zirconocenes was also investigated. The catalysts with monoalkyl-substituted C_p, such as n-BuC_p, MeC_p showed higher activities than those with cyclopentadienyl or indenyl ligands. It was due to the alkyl substituents of the catalysts which increased electron density at metal and led to favoring ethylene coordination.

In addition, the types of alkylaluminum using as the cocatalyst have affected the ethylene polymerization activity which increased in the following order; diethylaluminum chloride (DEAC) < triethylaluminum (TEA) < triisobutylaluminum (TIBA) < trimethylaluminum (TMA). Alkylaluminum without halogen gave high activity and high molecular weight.

Ihm *et al.* [17] immobilized the metallocene compounds Cp₂ZrCl₂, Cp₂TiCl₂ and Cp₂HfCl₂ on modified SiO₂ pretreated with small amounts of MAO, AlEt₃, or (C₂H₅)MgCl. Ethylene polymerization was then carried out with these supported

catalysts using MAO or a common alkylaluminum as cocatalysts. Among the various supported catalysts examined, Cp_2ZrCl_2 supported on SiO_2 modified by MAO showed the highest activity, whereas titanocene-based systems showed the lowest. This latter result was attributed to the bimolecular deactivation of titanocene by aluminum compound. Likely, in relation to this, bimodal MWD was observed for titanocene supported on SiO_2/MAO or on $\text{SiO}_2/\text{AlEt}_3$ but not for $\text{SiO}_2/(\text{C}_2\text{H}_5)_2\text{MgCl}$. It was speculated that the interaction of titanocene and aluminum species (MAO and AlEt_3) affected the molecular weight distribution.

A few papers reported the use silane compounds as modifier for the supports. Soga *et al.* [18] prepared a silica gel modified with $\text{Cl}_2\text{Si}(\text{CH}_3)_2/\text{NaHCO}_3$ and subsequently contacted with MAO to be support for Cp_2ZrCl_2 . It was observed that the polymerization activity increased remarkably (2-3 times) with the modified SiO_2 and was strongly dependent on the nature of the alkyl aluminum ($\text{AlEt}_2\text{Cl} < \text{AlEt}_3 < \text{Al}(\text{i-Bu})_3 < \text{AlMe}_3$). The maximum activity was obtained when MAO fixed to modified silica gel (5550 kg of PE/(mol Zr.h)). Nevertheless, MAO-free catalysts composed of modified SiO_2 , Cp_2ZrCl_2 and $\text{Al}(\text{CH}_3)_3$ can also be activated by common trialkylaluminums (3490 kg of PE/(mol Zr.h)).

Iiskola and co-worker (1997) [19] have achieved a novel heterogeneous ethylene polymerization catalyst prepared by the immobilization of CpZrCl_3 on chemically modified silica support. The surface modification of silica was carried out by utilizing the saturated gas-solid reactions of a silane coupling agent with hydrocarbon spacer, $\text{Cp}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, and a partially dehydroxylate silica. In gas-solid reactions all reactive surface hydroxyl groups were utilized in bonding the silane coupling agent on silica. The immobilization of CpZrCl_3 on the cyclopentadienyl surface formed on the silica was done using liquid-phase reactions. The supported catalyst system has a high activity in ethylene polymerization and can be used to produce polyethylene with a narrow molecular weight distribution in the presence of methylaluminoxane. The activity was two times when CpZrCl_3 immobilized on cyclopentadienyl surface of SiO_2 compared with the activity of

CpZrCl_3 in homogeneous catalysis. However, the direct homogenization of CpZrCl_3 onto unmodified silica produced a catalyst with a very low activity.

Recently, Moroz *et al.* (1998) [20] have prepared supported catalysts for ethylene polymerization by interaction of Cp_2ZrX_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{X} = \text{Cl}$ or CH_3) with silica chemically modified by $(\text{CH}_3)_3\text{SiCl}$ (TMCS) or trialkylaluminum compounds, AlR_3 ($\text{R} = \text{C}_2\text{H}_5$ (TEA) and $i\text{-C}_4\text{H}_9$ (TIBA)). The interaction between the modifiers and the silica surface has been examined by ^1H -solid-state MAS NMR spectroscopy, DRIFTS and chemical analysis. The $\text{Cp}_2\text{Zr}(\text{CH}_3)_2/\text{SiO}_2\text{-TMCS}$ catalysts showed a fairly high activity in ethylene polymerization (30-300 kg PE/mol Zr.h.bar) even in the absence of any cocatalysts specially added. The addition of the cocatalyst (MAO or TIBA) led to a further increase in the activity of supported catalysts. Polyethylene obtained with the $\text{Cp}_2\text{Zr}(\text{CH}_3)_2/\text{SiO}_2\text{-TMCS}$ catalyst without any cocatalyst consisted of uniform polymer particles of spherical shape replicating that of the silica particles, whereas the shapeless aggregates of finely dispersed polymer particles similar to those usually obtained with homogeneous systems were produced with the same supported catalyst in the presence of the MAO cocatalyst.

Besides, highly isospecific supported metallocenes were synthesized by immobilizing aryl ligands on the support, followed by addition of metal salt such as zirconium, titanium and neodymium halides. This method was a new preparation method in which metallocene was more tightly attached to the support.

Soga [21] synthesized a highly isospecific metallocene catalyst to produce a highly isotactic polypropylene. Tetrachlorosilane or 1, 1, 2, 2-tetrabromoethane was reacted with the surface hydroxyl groups of silica gel and the resulting chemically modified silica gel was brought into contact with lithium salt of indene. The catalyst precursors thus prepared were then reacted with zirconium tetrachloride to obtain the immobilized heterogeneous metallocene catalysts.

Polymerization of propylene was conducted with them using either methylaluminoxane or common trialkylaluminums as cocatalyst. Since the catalysts

may contain a mixture of meso and racemic isomers which gave atactic and isotactic polypropylene, respectively, the polymer produced was fractionated by extracting with boiling heptane. It was found that the catalysts can be easily activated by ordinary trialkylaluminums to give highly isotactic polypropylene with the melting point as prepared using fluorene as ligand, which gave highly isotactic polypropylene.

Jin and co-worker [22] prepared SiO_2 -supported neodymocene catalysts to polymerize ethylene using alkylaluminums, MAO, BuLi and BuMgEt as cocatalyst. The silica gel support was reacted with SiCl_4 or MeSiCl_3 and then contacted with lithium salt of indene. The catalyst precursors were then reacted with neodymium trichloride to obtain supported metallocene catalysts. The lifetime of these catalysts was found to be very long. Catalytic activity as well as molecular weight of the produced polymer were strongly dependent upon kind and amount of cocatalyst used. With increasing polymerization temperature, the activity increased monotonously up to 80°C . The use of BuMgEt and $\text{Al}(i\text{-C}_4\text{H}_9)_3$ as cocatalyst showed the highest activity and highest molecular weight, respectively.

In recent time, zeolite was used as the support for metallocene. Ciardelli and co-workers (1994) [23] selected HY zeolite as a carrier to produce supported metallocene catalyst. When directly supported on thermally treated HY zeolite, Cp_2ZrCl_2 activated by trialkylaluminums displayed rather modest activity in ethylene polymerization. The activity was substantially improved with MAO as the cocatalyst. In the case of HY zeolite pretreated with AlMe_3 , considerably higher activities were obtained in the presence of MAO (2,800 kgPE/(g Zr.hr)). Cp_2ZrMe_2 supported on dealuminated HY pretreated with AlMe_3 ($\text{HY}^{**}\text{-AlMe}_3$) and associated with MAO gave comparable activity to the corresponding homogeneous metallocene.

In the recent years, Maria and co-worker (1997) [24] have synthesized zeolite-supported Cp_2ZrCl_2 catalysts by using Y zeolite obtained from dealumination with ammonium hexafluorosilicate as the support. The catalytic activities of the supported and homogeneous systems were compared for ethylene polymerization. The experimental result presented that the supported systems produced polyethylene with

higher molecular weight and a narrow molecular weight distribution the same as the homogeneous system but showed lower activity than the homogeneous ones. The most active of the supported catalyst was the one supported on the zeolite which has a high Si/Al value and a high external area.

However, a few papers referred to use of organic supports, such as cyclodextrin, polymeric support and polysiloxane derivatives for the olefin polymerizations.

Lee and Yoon (1993) [25] also used organic supported as α -cyclodextrin (CD) for preparing supported catalyst in order to perform ethylene polymerization. The cyclodextrin was previously treated with modified methylaluminoxanes (PMAO; Al = 7.56wt% or MMAO; Al = 12.5wt%) or trimethylaluminum (TMA), and then Cp_2ZrCl_2 was supported on the modified cyclodextrin by using triethylaluminum (TEA), TMA or MMAO as cocatalyst. When Cp_2ZrCl_2 was anchored on CD/PMAO, CD/MMAO or CD/TMA, polymerization could be initiated with the ordinary trialkylaluminum, such as TMA and TEA. From this study, it was found that the molecular weight (Mw) of polyethylene (PE) obtained with CD-supported catalysts were 30 times greater than with unsupported catalyst and molecular weight distribution (MWD; Mw/Mn) presented a narrow polydispersity index (2.3-2.5).

Nishida *et al.* [26] studied several polystyrene-supported metallocene catalysts prepared and used in the polymerizations of propylene and ethylene with methylaluminoxane (MAO) as cocatalyst. It was found that these catalysts are stable even at 70 °C. They display fairly high activities when the polymerizations were conducted at high temperature.

In the last five years many attempts were devoted to heterogenize metallocene complexes by anchoring to crosslinked polystyrene resins.

Hong and co-worker [27] have recently reported that $\text{rac-Ph}_2\text{Si(Ind)}_2\text{ZrCl}_2$ supported on poly(styrene-co-divinylbenzene) beads showed activity for ethylene

polymerization using MAO as a cocatalyst. At a polymerization temperature below 100 °C, the catalyst showed a very high activity to give polyethylene beads replicating the shape of the carrier.

Meng *et al.* [28] used crosslinked poly(styrene-co-4-vinylpyridine) having functional groups as the support for zirconocene catalysts in ethylene polymerization. Conditions such as time, temperature, Al/N (molar ratio), Al/Zr (molar ratio) and mode of feeding were found having no significant influence on the activity of catalysts, while the state of the support had a great effect on the catalytic behavior. The activity of the catalysts sharply increased with either the degree of crosslinking or the content of vinylpyridine in the support.



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