Original Communication

Effects of various metal chlorides-SiCl$_4$ on Mg(OEt)$_2$-based catalyst

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ABSTRACT

The modification of Mg(OEt)$_2$-based Ziegler-Natta catalysts with various metal chlorides were examined on ethylene homopolymerization and copolymerization with 1-hexene. One of the selected metal chlorides (FeCl$_2$, ZnCl$_2$ and MnCl$_2$) was added together with SiCl$_4$ in the chlorination stage of Mg(OEt)$_2$. It was found that the introduction of metal chlorides affect the exposure of Ti on the surface as well as the catalyst surface area. The homopolymerization activity correlated well with the surface Ti, in the order ZN-Fe > ZN-Si > ZN-Zn > ZN-Mn > ZN-none, while the copolymerization activity was independent of the surface Ti/Mg atomic ratio and increased in the following order; ZN-Fe > ZN-Zn > ZN-Mn > ZN-Si > ZN-none. The results showed that among various metal chlorides, the addition of FeCl$_2$ could enhance both the Brenauer-Emmett-Teller (BET) specific surface area and the surface atomic ratio of Ti/Mg, leading to the highest activity in both ethylene homo- and copolymerization. The exposure of Ti species on outer surfaces could be thought as a sign of easier mass transfer phenomena leading to the improvement of catalyst performances.

KEYWORDS: Ziegler-Natta catalyst, Mg(OEt)$_2$, ethylene polymerization, comonomer incorporation

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INTRODUCTION

Nowadays polyolefins are indispensable plastics in our daily lives, covering a huge range of applications such as garbage containers, films, sheets, automobile parts, kitchen helpers, water pipes, bottle plastic bags, agricultural materials, electronic parts, and so on [1]. Especially, polyethylene (PE) has a lot of advantages including good chemical resistance, high impact strength, and stiffness even at low temperatures [2]. There are three main types of ethylene polymerization catalysts: Ziegler-Natta (ZN), Phillips and metallocene catalysts. In particular, ZN catalysts have been mainly used for the production of high-density and linear low-density PE due to their distinct features such as high productivity [1-2], broad molecular weight distribution (MWD) [3-4], and good morphology controls [5-6].

A general ZN catalytic system comprises of titanium tetrachloride supported on a magnesium chloride (TiCl$_4$/MgCl$_2$), which is activated by alkylaluminum. Extensive efforts have been devoted in academic and industrial fields not only for better understanding of catalytic mechanisms, but also for specific targets including higher activity [1-2], better morphology control (shape, size, distribution, bulk density etc.) [7-9], higher hydrogen response [9-11], adjustments in molecular weight (MW) and molecular weight distribution (MWD) [2-3, 7, 11-16], enhanced

comonomer incorporation efficiency, and more uniform chemical composition distribution (CCD) [17-18]. In order to achieve these targets, the choice of starting materials to obtain $MgCl_2$ carrier is one of the most substantial parameters [19]. In particular, spherical $Mg(OEt)_2$ precursor leads to catalysts featured with a high (but stable) activity as well as superior morphology [19-21]. One of the key steps to determine the performance of $Mg(OEt)_2$-based ZN catalysts is the chlorination step, an indispensable step to convert $Mg(OEt)_2$ into $MgCl_2$ [20-29], where a variety of chlorinating agents have been examined. For example, Derroitte *et al.* investigated various chlorination agents (HCl, $AlCl_3$, Cl_2, $SOCl_2$, NH_4Cl) to obtain $TiCl_4/MgCl_2$ catalysts and they found that the addition of HCl in the chlorinating step exhibited the highest yield in ethylene polymerization [24]. A research group in Idemitsu employed $SiCl_4$ as a chlorinating agent and revealed that the co-addition of a suitable amount of alcohol during the chlorination resulted in the highest activity in ethylene polymerization [22, 25]. While $SiCl_4$ is regarded as one of the most successful chlorinating agents, it also remains in final catalysts by generating allkoxysilane compound to affect the activity and polymer properties as a so-called third component [30]. Such "doped" ZN catalysts with other metal halides such as $ZnCl_2$ and $MnCl_2$ were studied by Fregonese *et al.* and Garofi *et al.*, respectively. It was found that the addition of a suitable amount of metal chlorides enhanced the activity of the resultant catalysts [31, 32].

The aim of the present paper is to investigate influences of various metal chlorides ($FeCl_2$, $MnCl_2$, and $ZnCl_2$) during the chlorination step using $SiCl_4$ on ethylene homo- and copolymerization activities of $Mg(OEt)_2$-based ZN catalysts and on properties of obtained polymers. It was found that a higher Ti/Mg atomic ratio on catalyst surfaces tended to give a higher ethylene homopolymerization activity, plausibly by alleviating mass transfer limitation. Among the three metal chlorides, the addition of $FeCl_2$ increased both the BET specific surface area and surface Ti/Mg ratio, leading to the highest activities in both ethylene homo- and copolymerization with 1-hexene. The addition of the metal halides improved the efficiency of comonomer incorporation, leading to the

formation of more branched polyethylene at a given condition.

EXPERIMENTAL

Raw materials

Ethylene of research grade (donated by Asahi Kasei Chemicals Corporation), $TiCl_4$ and $Mg(OEt)_2$ were used without further purification. Chlorinating agents ($SiCl_4$, $FeCl_2$, $ZnCl_2$, and $MnCl_2$) were purchased from Wako Pure Chemical Industries, Ltd. Triisobutylaluminum (TiBA) as an activator was supplied by Tosoh Fine Chem Corporation. *n*-Heptane and toluene were dehydrated by passing through a column with 4A molecular sieves and then bubbled with N_2 for 2 h. 1-Hexene as comonomer was similarly dehydrated in Schlenk tube containing 4A molecular sieves.

Catalyst preparation

A $TiCl_4/SiCl_4/MgCl_2$ catalyst (termed as ZN-Si) was synthesized according to the procedure in literature [22]. 10 g of $Mg(OEt)_2$ suspended in 150 ml of toluene was charged into 500 ml three-necked round bottom flask equipped with a mechanical stirrer under N_2 atmosphere. 2.55 ml of ethanol (the molar ratio of ethanol to $Mg(OEt)_2$ = 0.5) and 1.25 ml of $SiCl_4$ as the chlorinating agent (the molar ratio of $SiCl_4$ to $Mg(OEt)_2$ = 0.125) were subsequently added. The mixture was reacted at 80 ºC under stirring for 2 h. Thereafter, 25 ml (227 mmol) of $TiCl_4$ was dropwisely added to the mixture at 0 ºC over a period of 2 h, followed by slowly raising the temperature to 100 ºC. The mixture was allowed to react at this temperature for 2 h. Finally, the resultant solid was repetitively washed with hot toluene and *n*-heptane and kept as slurry in heptane.

A $TiCl_4/MgCl_2$ catalyst without other chlorinating agents beside $TiCl_4$ (termed as ZN-none) was prepared based on the procedure described above except the addition of EtOH and $SiCl_4$ as well as the heat treatment at 80 ºC. The catalysts with metal halide components (MCl_x, where M is Fe, Mn and Zn) were also prepared based on the same procedure as that of ZN-Si except that 0.063 mol/mol of $MCl_x/Mg(OEt)_2$ and 0.063 mol/mol of $SiCl_4/Mg(OEt)_2$ were added instead of 0.125 mol/mol of $SiCl_4/Mg(OEt)_2$ for ZN-Si. The resultant catalysts were termed as ZN-Fe,

ZN-Mn, and ZN-Zn for FeCl$_2$, MnCl$_2$, and ZnCl$_2$, respectively.

Catalyst characterization

The titanium content of the prepared catalysts was measured by a titration method [33]. N$_2$ adsorption experiments were performed on Belsorp-max at 77 K to determine the surface area of catalysts by the BET method. The catalyst samples were added in a tube under N$_2$ atmosphere and then degassed at 80 °C for 2 h prior to the measurement [34]. The catalyst morphologies were investigated with scanning electron microscope (SEM, Hitachi S-4100 Field Emission Electron Microscope). The samples were prepared in a glove bag under inert atmosphere, then transferred to a deposition device (Hitachi E-1030 Ion Sputter) for the Pt-Pd coating, and finally transferred to SEM chamber, during which the contact with air was minimized [35]. X-ray photoelectron spectroscopy (XPS) was acquired on Kratos Analytical Shimadzu spectrometer (Axis Ultra DMD model) with a monochromatic Al Kα source in order to investigate the composition of catalyst surface. Samples for XPS measurements were deposited on a carbon tape and fixed on a sample holder. The sample holder was put into transfer chamber under inert atmosphere. After evacuating, the holder was transferred to analysis chamber under operating pressure of 10^{-9} Torr. The measurements were carried out between 0-1000 eV at a resolution of pass energy 160 and step size 1 eV for a preliminary survey.

Homo- and copolymerization of ethylene

Slurry polymerization was performed in a 1 L stainless steel autoclave equipped with a mechanical stirrer. Heptane as solvent was introduced to the reactor under nitrogen and then saturated with ethylene at 50 °C. After that, a desired amount of TiBA was introduced to keep the concentration in the reactor at 10 mmol/L, followed by the catalyst injection with the concentration in the reactor kept at 10 mg/L. The polymerization was performed at 50 °C and constant pressure of 0.5 MPa. After 30 min, acidic ethanol was added to terminate the reaction. The obtained polymer was filtered, washed with methanol and dried in a vacuum oven at 60 °C for

Table 1. Characteristics of the different kinds of catalysts.

Catalyst	Ti content[a] (wt%)	BET surface area[b] (m^2/g)
ZN-none	10.4	220
ZN-Si	7.2	283
ZN-Fe	2.1	295
ZN-Mn	4.3	180
ZN-Zn	2.3	95

[a]Determined by titration.
[b]Determined by N$_2$ adsorption at 77K.

6 h. Copolymerization of ethylene with 1-hexene was performed under the same polymerization conditions and procedure, where the 1-hexene concentration in the reactor was 5.0 mol/L.

Characterization of polymer

The content of 1-hexene units in copolymers were measured by ^{13}C NMR using Bruker 400 MHz NMR spectrometer at 120 °C. 100 mg of a sample was dissolved in hexachloro-1,3-butadiene as a diluent and 1,1,2,2-tetrachloroethane-d$_2$ as an internal lock and internal chemical shift reference.

RESULTS AND DISCUSSION

Table 1 summarizes the Ti contents and the surface areas of prepared catalysts. It is interesting to note that when SiCl$_4$ was introduced in the chlorination step, the Ti content became lower than the catalyst prepared without the introduction of SiCl$_4$ (ZN-none), even if the surface area was rather enlarged. More interestingly, if SiCl$_4$ was added together with metal halides (FeCl$_2$, MnCl$_2$ or ZnCl$_2$), the Ti contents became much lower than that of ZN-None and ZN-Si. It could be considered that SiCl$_4$ and the metal halides could be adsorbed on Mg(OEt)$_2$ and react to form alkoxy-containing compounds on the surfaces [22], which might competitively block the adsorption of TiCl$_4$. Based on the N$_2$ adsorption measurement, it was found that ZN-Fe catalyst exhibited the highest surface area, while ZN-Zn catalyst exhibited the lowest surface area. The addition of the metal halides affected not only the chemical composition but also the physical

Table 2. Elemental analysis of catalysts by XPS measurements.

Catalyst	Chemical composition (atomic%)					Ti/Mg (atomic%/atomic%)
	Ti 2p	Cl 2p	Si 2s	Mg 2s	M[a]	
ZN-none	15.5	54.2	-	30.3	-	0.51
ZN-Si	10.5	25.4	50.3	13.8	-	0.77
ZN-Fe	18.0	30.2	35.0	16.5	0.3	1.09
ZN-Mn	13.9	21.7	22.7	41.4	0.1	0.34
ZN-Zn	9.8	28.2	39.5	22.7	n.d.	0.43

[a]Binding Energy of Metal 2p : Fe (721.5 eV), Mn (658.3 eV), and Zn (n.d.).

structures of the formed catalysts in a complicated manner.

The XPS measurement is recognized as one of the most powerful techniques for analyzing catalyst surfaces [36-41]. It was used to analyze the surface chemical composition of prepared catalysts, whose results are summarized in Table 2. It was found that the catalysts prepared in the presence of $SiCl_4$ exposed a significant amount of Si atoms on the surfaces. As a result, the atomic ratios of Mg and Cl atoms were obviously reduced. As will be described later, the Ti/Mg atomic ratio is important to infer how much Ti species are exposed on the outermost surfaces of the catalysts. The highest of Ti/Mg atomic ratio was obtained for ZN-Fe, while ZN-Mn and ZN-Zn decreased the Ti/Mg atomic ratio compared with ZN-Si.

SEM images were acquired in order to study the morphologies of the catalyst particles (Figure 1). Irrespective of different chlorinating steps, all of the catalysts exhibited similar morphologies: most of the catalyst particles replicated the spherical shape of the $Mg(OEt)_2$ precursor, while a few to several particles formed agglomerates probably during the $TiCl_4$ treatment [20, 21]. It is interesting to note that ZN-Mn and ZN-Zn with diminished surface areas also exhibited similar particle morphologies, suggesting that the modification with metal might exert influences in a more microscopic manner.

All the catalysts were subjected to ethylene homopolymerization and ethylene/1-hexene copolymerization. Table 3 shows the catalytic activities in both the g-PE/g-cat·h·atm and kg-PE/mol-Ti·h·atm units. For the ethylene homopolymerization, the co-addition of $FeCl_2$ and $SiCl_4$ in the chlorination step exhibited the highest activity per g-cat, which was three times greater than the catalyst prepared only with $SiCl_4$. On the contrary, the other metal chlorides ($MnCl_2$ and $ZnCl_2$) were less effective in boosting up the catalytic activity. It is interesting to note that the homopolymerization activities per Ti except for ZN-none were correlated with the Ti/Mg atomic ratio determined by XPS (Table 2), following the same order of ZN-Fe > ZN-Si > ZN-Zn > ZN-Mn. The exception of ZN-none, which gave the lowest activity, could be explained by the formation of inactive or less active titanium alkoxide species due to incomplete chlorination [21, 22]. Similar results on activity enhancements in ethylene homopolymerization were found by many researchers, mostly accompanied by a higher surface area and a larger Ti/Mg ratio of catalysts [42-45]. A higher homopolymerization activity accompanied by a greater exposure of Ti atoms on outer surfaces could be thought as a sign of easier mass transfer to the active center.

The introduction of 5.0 mol/L of 1-hexene remarkably enhanced the activities from 2 to 7 times compared with the homopolymerization activities for all the catalysts except for ZN-none. This phenomenon is generally understood as a consequence of physical factors [46]:

(i) Enhancement of monomer diffusion through the decreased crystalline polymer by the insertion of comonomer. This attributes to an increase in the monomer concentration at the active centers [46].

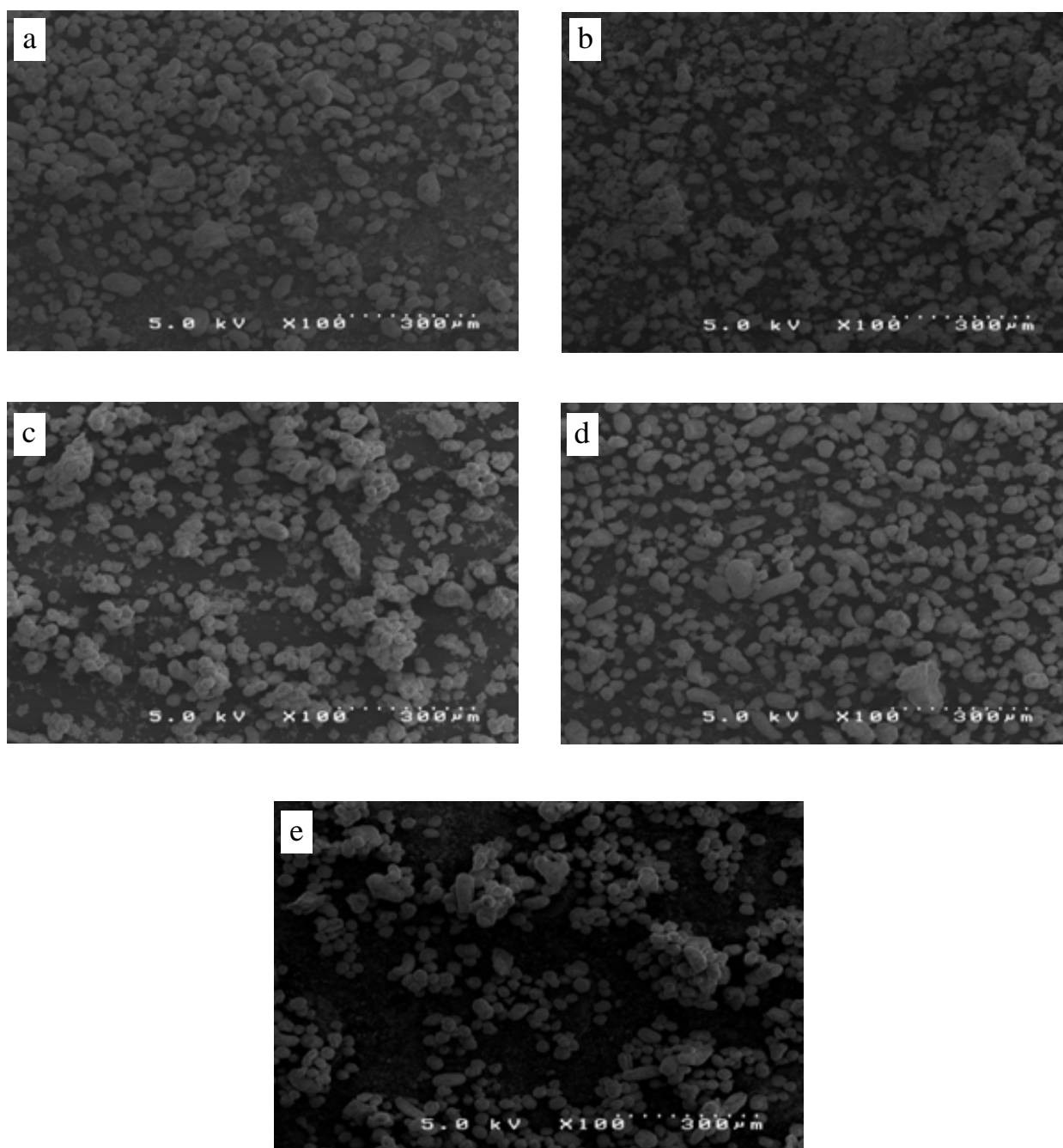(ii) The disintegration of catalyst particles during copolymerization thus exposing new potential

Figure 1. SEM images of catalyst particles for (a) ZN-none, (b) ZN-Si, (c) ZN-Fe, (d) ZN-Mn, and (e) ZN-Zn.

active centers, hence, increasing the diffusion of cocatalyst through copolymer [46].

The introduction of any MCl$_2$ (FeCl$_2$, MnCl$_2$, and ZnCl$_2$) markedly enhanced the insertion of comonomer (Table 3) as compared with the other two catalysts, independently of the Ti/Mg ratio

and the polymerization activities. It is generally known that the incorporation of Lewis acidic halides enhances comonomer incorporation due to an ability to attract higher olefin (1-hexene), which has higher electron density than ethylene [47]. Therefore, the introduction of Lewis acidic

Table 3. Ethylene homopolymerization and ethylene/1-hexene copolymerization results.

Metal chlorides	[1-hexene] (mol/L)	Activity[a,b]		1-Hexene content[c] (mol%)
		g-PE/g-cat·h·atm	kg-PE/mol-Ti·h·atm	
ZN-none	0	65	30	-
	5	24	11	5.3
ZN-Si	0	227	152	-
	5	751	502	5.9
ZN-Fe	0	182	421	-
	5	438	1012	8.4
ZN-Mn	0	84	94	-
	5	532	595	7.0
ZN-Zn	0	68	144	-
	5	467	989	7.7

[a]Homopolymerization conditions: Catalyst amount = 5.0 mg, [TIBA] = 10 mmol/L, heptane volume = 0.5 L, ethylene pressure = 5 atm, T = 50 ºC, t = 0.5 h.
[b]Copolymerization conditions: Catalyst amount = 2.0 mg, [TIBA] = 10 mmol/L, (heptane + 1-hexene) volume = 0.2 L with 5.0 mol/L of 1-hexene, ethylene pressure = 5 atm, T = 50 ºC, t = 0.5 h.
[c]Determined by ^{13}C-NMR.

halides is likely more important than the monomer diffusion for the comonomer incorporation.

CONCLUSION

In this study, influences of various metal chlorides ($FeCl_2$, $MnCl_2$ and $ZnCl_2$) were examined on the chlorination of $Mg(OEt)_2$ precursor with $SiCl_4$ to form $MgCl_2$-supported Ziegler-Natta catalysts for ethylene polymerization. It was found that the addition of these metal chlorides during preparation markedly affected the chemical composition and the ethylene polymerization performances of the resultant catalysts without affecting the particle morphologies. The ethylene homopolymerization activities of the catalysts were correlated with the surface Ti/Mg atomic ratio, which could be explained by the ease of monomer diffusion onto catalyst surfaces, and the $FeCl_2$-modified catalyst gave the best activity. On the other hand, the 1-hexene incorporation was enhanced by the addition of any metal chlorides plausibly due to enhanced coordination of 1-hexene at the Lewis acidic centers. Thus, we found that the co-addition of another metal halide in the preparation of $Mg(OEt)_2$-based Ziegler-Natta catalysts for ethylene polymerization is one

of the easiest approaches to improve the performances of the resultant catalysts.

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