

Effect of ZnCl₂- and SiCl₄-Doped TiCl₄/MgCl₂/THF Catalysts for Ethylene Polymerization

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ABSTRACT: In this research, ethylene polymerization was carried out in the presence of different additives (ZnCl₂, SiCl₄, and the combined ZnCl₂-SiCl₄) on TiCl₄/MgCl₂/THF catalytic system. The presence of ZnCl₂-SiCl₄ mixtures showed higher activity in ethylene polymerization when compared with the catalytic activity in the presence of single Lewis acids, ZnCl₂, or SiCl₄. The modified catalyst with ZnCl₂-SiCl₄ demonstrated the highest activity, which was more than three times the activity of the system without Lewis acid modification. The enhanced activity can be attributed to the reduction in the peak intensity of MgCl₂/THF complexes with Lewis acid compounds as proven by XRD. This was reasonable because of some THF removal from the structure of MgCl₂/THF by Lewis acid compounds. In addition to the effect of modification with additives on the partial elimination of THF, the catalytic activities could be increased due to the titanium atoms that have been locally concentrated on the surface as seen by energy dispersive X-ray spectroscopy measurement. On the basis of the *in situ* electron spin resonance measurement, the mixed metal chlorides (ZnCl₂-SiCl₄) addition could promote the amount of Ti³⁺ after reduction with triethylaluminum. It revealed that the modification of TiCl₄/MgCl₂/THF catalytic system with mixed metal chlorides (ZnCl₂-SiCl₄) is very useful for ethylene polymerization. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1588–1594, 2013

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INTRODUCTION

Titanium-based Ziegler–Natta catalytic systems for olefin polymerization have been widely utilized for over 50 years.^{1–3} Up to the present time, several researchers have devoted to improve the catalytic activities and polymer properties in both areas of academic and industrial researches. More than 50% of polyethylene (HDPE) and 90% of polypropylene (PP) of industrial production have been produced by Ziegler–Natta catalysts, which are the major processes to commercialize owing to their good catalytic activities and different polymer properties.^{1,4}

The Ziegler–Natta catalytic system consisting of titanium tetrachloride (TiCl₄), magnesium chloride (MgCl₂), and tetrahydrofuran (THF) as internal donors (TiCl₄/MgCl₂/THF) has been attractive for much attention as the promising ZN catalysts. The TiCl₄/MgCl₂/THF catalytic system has a good hydrogen response, providing moderate catalytic activity with low cost.^{5–8} However, this catalytic system still has a weak point, that is the catalyst could completely coordinate with THF leading to reduce its activity.^{8–10} Most researchers have reported that the treatment of catalysts with alkylaluminum compounds such as

diethylaluminum chloride (DEAC), triethylaluminum (TEA), and triisobutylaluminum (TIBA) before polymerization can improve the catalytic activity.^{8–10} The activity improvement in ethylene polymerization depends on the amounts of THF removed by DEAC as alkylaluminum compounds. However, the excess of THF removal by DEAC could lead to the reverse result.^{8,9} Nevertheless, it is generally accepted that the cocatalyst as strong Lewis acid is a highly hazardous organic compound and high cost. To improve the activity of catalyst and reduce the amounts of cocatalyst used in catalyst treatment step, the Lewis acid halides are a promising alternative way used to develop the performance of this catalytic system and resolve these drawbacks.

In general, Lewis acid halide additives added into MgCl₂ support have the ability to change surface properties of MgCl₂ crystalline, resulting in the modification of active center distribution of catalysts. It consequently leads to the improvement in catalytic performance and polymer properties.¹¹ The influences of ZnCl₂ doping on the catalytic performance for olefin polymerization were reported by Fregonese and Bresadola.¹² The catalyst doped with 0.73 wt. % of ZnCl₂ exhibited the highest activity, whereas the use of higher ZnCl₂ concentrations caused

lower activities. In addition, the introduction of ZnCl_2 into MgCl_2 support could promote the structural defects in the support indicating that the replacement of a partial Mg by Zn was occurred. This phenomenon is possibly occurred because their ionic radii are very similar ($\text{Zn}^{2+} = 0.88 \text{ \AA}$, $\text{Mg}^{2+} = 0.86 \text{ \AA}$). Besides, Lewis acid is also used to remove alcohol from recrystallization step of MgCl_2 ($\text{MgCl}_2 \cdot n\text{ROH}$ adduct). The catalyst obtained from SiCl_4 recrystallization was not only to provide the highest activity, but it also showed the highest isotacticity index in polymer.¹³

Therefore, this research focused on the improvement of catalytic performance and polymer properties by using the $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$ catalyst accompanied with Lewis acid compound additives (ZnCl_2 , SiCl_4 , and $\text{ZnCl}_2\text{-SiCl}_4$ mixtures). Up to now, there has not been any article reporting on the $\text{ZnCl}_2\text{-SiCl}_4$ mixtures as compared with single Lewis acid (ZnCl_2 , SiCl_4) for improving the $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$ catalytic system in ethylene polymerization. In particular, we have expected that the $\text{ZnCl}_2\text{-SiCl}_4$ modification should improve the activity of this catalytic system by more THF removal than that of single metal chloride.

EXPERIMENTAL

Material

All reagents and operations were performed under an inert argon atmosphere with standard Schlenk techniques and glove box. Argon was purified by passing through columns containing 3 Å molecular sieves and BASF catalyst, sodium hydroxide (NaOH), and phosphorus pentoxide (P_2O_5) to remove oxygen and moisture.¹⁴ Hexane and heptane were refluxed over sodium metal with benzophenone as an indicator and were distilled under argon before use. TiCl_4 , anhydrous MgCl_2 , ZnCl_2 , SiCl_4 , and tetrahydrofuran (THF) were used without further purification. Polymerization grade of ethylene was obtained from Thai Industrial Gas company and triethylaluminum (TEA) was donated by Tosoh Finechem, Japan.

Catalyst Preparation

The $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$ catalyst denoted as **Cat. A** was prepared by following the previously reported procedure.¹⁵ Under the argon atmosphere, 2 g of anhydrous MgCl_2 and 150 mL of tetrahydrofuran (THF) were added into a 500 mL four-necked round-bottom-flask equipped with mechanical stirrer and cooling system. Then, 2 mL of TiCl_4 was injected into the flask. The mixture was continuously stirred and the temperature was set at 68°C for 3 h. After cooling the solution to 40°C, the part of liquid was siphoned off and the solid part was washed several times with 100 mL of dry *n*-heptane. The catalyst was then dried under a vacuum at room temperature. The obtained catalyst powder was kept in glove box under argon atmosphere.

The catalysts modified by adding Lewis acid compound, $\text{TiCl}_4/\text{ZnCl}_2/\text{MgCl}_2/\text{THF}$ catalyst; $\text{TiCl}_4/\text{SiCl}_4/\text{MgCl}_2/\text{THF}$; and $\text{TiCl}_4/\text{SiCl}_4/\text{ZnCl}_2/\text{MgCl}_2/\text{THF}$ denoted as **Cat. B**, **Cat. C**, and **Cat. D**, respectively, were synthesized by the same procedure as mentioned in the preparation of **Cat. A**. However, each additive was doped along with MgCl_2 by 0.2 g of anhydrous ZnCl_2 for **Cat. B**, 0.2 mL of SiCl_4 for **Cat. C**, and 0.2 g of anhydrous ZnCl_2 mixed with 0.2 mL of SiCl_4 for **Cat. D**.

Table I. Abbreviation of the Prepared Catalysts

Catalyst abbreviation	Components
Cat. A	$\text{TiCl}_4/\text{MgCl}_2/\text{THF}$
Cat. B	$\text{TiCl}_4/\text{ZnCl}_2/\text{MgCl}_2/\text{THF}$
Cat. C	$\text{TiCl}_4/\text{SiCl}_4/\text{MgCl}_2/\text{THF}$
Cat. D	$\text{TiCl}_4/\text{ZnCl}_2/\text{SiCl}_4/\text{MgCl}_2/\text{THF}$

Catalyst Nomenclature

The abbreviation of the modified catalysts with the different additives (ZnCl_2 , SiCl_4 , and the combined $\text{ZnCl}_2\text{-SiCl}_4$) is shown in Table I.

Ethylene Polymerization Test

The polymerization of ethylene was conducted in a 100 mL semibatch stainless steel autoclave reactor equipped with magnetic stirrer. The desired amounts of hexane (total volume of 30 mL) and TEA as cocatalyst were injected into the reactor. Then, 10 mg of catalyst powder was added into autoclave. After that, the reactor was dipped in liquid nitrogen to stop reaction. After evacuating the remaining argon, the reactor was heated up to 80°C. The reaction was started by continuous feeding ethylene gas until the consumption of 0.018 mol of ethylene was reached and the reaction time was recorded for calculating the activity of catalysts. The reaction was then terminated by adding acidic methanol.¹⁴ The obtained polymer was washed with methanol, filtered, and finally dried under vacuum oven at 60°C for 6 h.

Catalyst Characterization

Elemental Analysis of Catalysts.

The content of Ti, Si, Zn, and Mg in the catalysts was measured with ICP (Perkin Elmer 20 model PLASMA-1000). The amount of THF in the catalysts was determined by gas chromatography (GC), using a SHIMADZU GC-14B equipped with a flame ionization detector (FID) and N_2 as carrier. The composition of all catalysts is shown in Table II.

Surface Area Measurement

The specific surface area was determined by nitrogen physisorption method. The single point specific surface area of the catalysts was performed on Micromeritics Chemisorb 2750 at 77 K. Prior to the measurement, the catalyst sample was added into a tube under N_2 atmosphere.

X-ray Diffraction (XRD) Analysis

XRD was performed to determine the bulk crystalline phases of samples. It was carried out using a Bruker D8 Advance diffractometer at 40 kV, 40 mA with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Diffraction patterns were recorded in the reflection mode at room temperature with the scans from diffraction angle $2\theta = 10^\circ\text{--}60^\circ$ with scan speed of 0.3 s/step and a step size of 0.02. All powder samples were prepared in glove box under argon atmosphere and loaded into a holder covered with a Mylar film to prevent air and moisture during the experiment.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

SEM and EDX were used to determine the morphologies and elemental distribution throughout the catalyst samples,

Table II. Elemental Composition of All Prepared Catalysts in This Work

Catalysts	Ti (wt. %) ^a	Si (wt. %) ^a	Zn (wt. %) ^a	Mg (wt. %) ^a	Mg/Ti (mol/mol) ^a	THF (wt. %) ^b
Cat. A	5.5	-	-	6.5	2.33	32.7
Cat. B	5.0	-	4.9	6.2	2.44	30.6
Cat. C	5.4	4.9	-	6.5	2.37	26.5
Cat. D	3.9	1.1	5.5	6.2	3.13	21.6

^aDetermined by ICP. ^bMeasured by GC.

respectively. The SEM was performed with a JEOL mode JSM-6400. The EDX of Link Isis series 300 program was applied. The catalyst samples were conducted with argon overflow to protect air and moisture during the experiment.

Electron Spin Resonance (ESR)

ESR was used to measure Ti oxidation states with activated catalysts. The samples were activated with TEA under inert argon atmosphere. The ESR of Jeol mode JES-RE2X was operated at room temperature (25°C). The *g*-values of ESR were calculated by diphenylpicrylhydrazyl (DPPH) as the reference.

Polymer Characterization

Scanning Electron Microscopy (SEM)

SEM was used to determine the morphologies of polymers obtained. The same equipment (as aforementioned) was applied.

Differential Scanning Calorimeter (DSC)

The DSC of Perkin Elmer Pyris Diamond was used to investigate the melting temperature (T_m) and the percentage of crystallinity (χ_c) of polymers. A standard heating and cooling were operated at 20°C/min in the temperature range of 50–200°C under nitrogen flow. T_m was determined in the second scan. From the endothermic curve, the result was referred to the heat of fusion (H). The percentages of crystallinity of the polymers were determined with the following equation.

$$\% \text{Crystallinity } (\chi_c) = (\Delta H / \Delta H^\circ) \times 100 \quad (1)$$

where $\Delta H^\circ = 290 \text{ J/g}$ is the heat of fusion of linear PE as reported in Carlini et al.¹⁶

The Molecular Weight of Polymers

The molecular weights of polymers obtained in this study were determined by solution viscosity. Samples were dissolved in 1,2,4-trichlorobenzene and measured at 150°C with a capillary viscometer. The efflux time was recorded. The data were used for viscosity calculations and converted to the viscosity average molecular weight (M_v).

RESULTS AND DISCUSSION

Characterization of the Catalysts

Table II presents the chemical compositions of all catalysts determined by ICP. It was found that the titanium contents and the ratios of Mg/Ti of **Cat. A**, **Cat. B**, and **Cat. C** were similar. However, the titanium content of **Cat. D** ($\text{ZnCl}_2\text{-SiCl}_4$ mixture in $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$ system) decreased by 29%, while its Mg/Ti ratio increased by 34%, when compared to **Cat. A**. It is

interesting to note that the addition of $\text{ZnCl}_2\text{-SiCl}_4$ mixture in this catalyst might reduce free-vacancies of MgCl_2 crystallization and Ti insertion, which is corresponding to the result of Coutinho and Xavier.⁸ They disclosed that the addition of PCl_3 in $\text{TiCl}_4/\text{MgCl}_2$ via ball milling method decreased the incorporation of Ti on this catalyst system. In addition, the content of THF decreased with the Lewis acid modification, suggesting that the Lewis acids could remove some THF in the catalyst structure. According to the information in Table II, the $\text{ZnCl}_2\text{-SiCl}_4$ mixture showed the highest amount of THF removal from the catalyst structure. It was also observed that the amount of Zn was higher than that of Si in **Cat. D**, even though their amounts were added equally in the catalyst preparation step (Lewis acid/ MgCl_2 of 0.063). Owing to higher acidity of SiCl_4 than ZnCl_2 , more removal ability of THF from MgCl_2 was achieved. Moreover, a portion of SiCl_4 content could possibly remove THF as well. In accordance with the similar ionic radii of Zn and Mg,¹² ZnCl_2 was more efficient to incorporate with MgCl_2 support than SiCl_4 . Therefore, it was reasonable to obtain higher content of Zn in **Cat. D**.

The XRD patterns of all catalysts are shown in Figure 1. The broad peak around $2\theta = 26^\circ$ was assigned to a Mylar film used for prevention of air and moisture. The precursor, anhydrous MgCl_2 , exhibited the strongest reflections at 2θ of about 15.1° , 30.3° , 35° , and 50.5° . The characteristic peaks of MgCl_2/THF complex were presented at $2\theta = 10.4^\circ$, 20.2° , and 32.3° .⁸

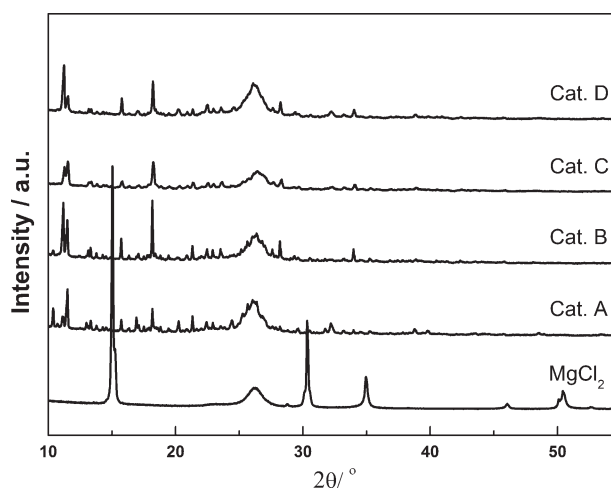


Figure 1. X-ray diffraction patterns of $\alpha\text{-MgCl}_2$, **Cat. A**, **Cat. B**, **Cat. C**, and **Cat. D**.

Table III. The Surface Area of Catalysts Measured by the N₂ Physisorption

Catalysts	Surface area (m ² /g)
Cat. A	4.4
Cat. B	6.5
Cat. C	7.6
Cat. D	11.3

All catalysts showed the XRD patterns around $2\theta = 11.5^\circ$ and 18.3° indicating the formation of the TiCl₄/MgCl₂/THF complex.¹⁷ Moreover, all catalysts exhibited the peaks around 11.1° and 13.2° indicating the TiCl₄/THF complex and the TiCl₃/THF complex showed XRD peaks at 16.7° .^{8,17} The disappearance of Lewis acid spectra was occurred when ZnCl₂ and SiCl₄ were incorporated in TiCl₄/MgCl₂/THF system because of its well-dispersed form. It can be explained that the crystallite sizes of ZnCl₂ and SiCl₄ are smaller than 3 nm, which are restricted by means of XRD technique.¹⁸ Nevertheless, it was found that the introduction of Lewis acid compounds probably broke the crystalline structure of MgCl₂/THF complex, attributing to the reduction or disappearance of the intensity of XRD patterns at $2\theta = 10.4^\circ$, 20.2° , and 32.3° . The ZnCl₂-SiCl₄ mixture (**Cat. D**) had high efficiency to decrease the peak intensity of MgCl₂/THF complexes when compared to that with single metal chloride modification (**Cat. B and Cat. C**).

The single point specific surface area of the catalysts was determined using the nitrogen physisorption method as shown in Table III. The modified catalysts with Lewis acids had a higher surface area than that of the unmodified catalyst. This indicated that the addition of Lewis acid possibly broke the crystal growth or prevented the aggregation of MgCl₂/THF support leading to increased surface area. This result was similar to Kang et al.,¹⁹ who reported that Lewis acids could extract EB in the support to make the high surface area of catalyst as well. Moreover, the result of catalyst surface area is in good agreement with XRD results as mentioned earlier.

To investigate the surface of catalysts, especially the Ti content on catalyst surface, EDX technique was used. Table IV displays the Ti content of catalysts doped and undoped with the Lewis acid. It can be seen that the Ti concentration in each catalyst was varied upon different electronic environment of catalyst. This results indicated that **Cat. D** exhibited the highest amount of Ti on surface, suggesting that the concentration of Ti on surface can be increased by the addition of double metal chlorides (ZnCl₂-SiCl₄). Moreover, the tendency of Ti content on the surface of each catalyst was in the range of **Cat. D** > **Cat. C** > **Cat. B** > **Cat. A**. However, when compared with ICP result, it can be observed that titanium atoms at surface were higher than that in the bulk because the addition of Lewis acids could remove THF from the structure of MgCl₂/THF (as shown in Table II).

In addition, the distribution of elements on catalyst surface should be considered. The EDX mapping for all catalysts was used for this objective as shown in Figure 2. It can be clearly

seen that the dispersion of Ti modified with Lewis acids was better especially for the modification of mixed metal chlorides (**Cat. D**) on the catalyst granule than the one without Lewis acid modification. Then, the different catalysts doped and undoped with Lewis acid modification were evaluated for ethylene polymerization.

To investigate the effect of Lewis acid on active sites, the ESR analysis was performed. ESR has been widely used to examine the oxidation state of Ti³⁺.^{20,21} It is well known that the different characteristics in Ziegler–Natta catalysts depend on the oxidation state of titanium during polymerization. The titanium valences including Ti⁴⁺, Ti³⁺, and Ti²⁺ are produced by reacting TiCl₄ with activator such as AlR₃. The Ti³⁺ species are active species for the polymerization of both ethylene and propylene, while the Ti²⁺ which is the over-reduction of Ti³⁺ is only active for ethylene polymerization.^{22,23} The *in situ* ESR measurement of prepared catalysts was recorded at room temperature with [Al]/[Ti] mole ratio of 100. The spectra of ESR, the area and the relative area of the catalysts with various additives are shown in Figure 3 and Table V, respectively. For all catalysts, two main signals with *g*-values of 1.97 and 1.94 were observed. However, the different *g*-values are assigned to the different kinds of the Ti³⁺ coordination. The *g*-value of 1.97 is referred to the tetrahedral coordination of Ti³⁺ and the *g*-value of 1.94 is assigned to the six-coordinated Ti³⁺ dissolved in MgCl₂,²⁴ or a single octahedral coordinated Ti³⁺.²⁵ However, it should be noted that the amount of Ti³⁺ species can be obtained from double integration of each ESR spectrum of catalyst.²¹ In Table IV, the trend of relative area was in the order of **Cat. D** > **Cat. B** > **Cat. A** > **Cat. C**. It showed that the addition of Lewis acids in catalyst tended to increase the amounts of Ti³⁺ species. However, the addition of SiCl₄ (strong Lewis acid) resulted in only slight change of Ti³⁺ amounts because of the over-reduction of TEA from Ti⁴⁺ to Ti³⁺ and Ti³⁺ to Ti²⁺. This phenomenon is similar to the catalyst modified with AlCl₃, which has low activity of ethylene/1-hexene copolymerization with TEA as cocatalyst. Chen and Fan²⁶ proposed that high Lewis acidity of active sites modified with AlCl₃ was easily reduced to Ti²⁺ with TEA having a strong reducing power.

Effect of Various Lewis Acids on the Catalytic Activity for Ethylene Polymerization

The ethylene polymerization was carried out in the presence of different additives (ZnCl₂, SiCl₄, and the combined ZnCl₂-SiCl₄) on TiCl₄/MgCl₂/THF catalysts for comparative study on catalytic activities influenced by different catalysts. The polymerization activities of TiCl₄/MgCl₂/THF catalysts modified with Lewis acid are summarized in Table VI. The trend of catalytic

Table IV. Ti Content of All Catalysts Measured by the EDX Analysis

Catalysts	Ti (wt %)
Cat. A	7.86
Cat. B	10.28
Cat. C	10.72
Cat. D	12.70

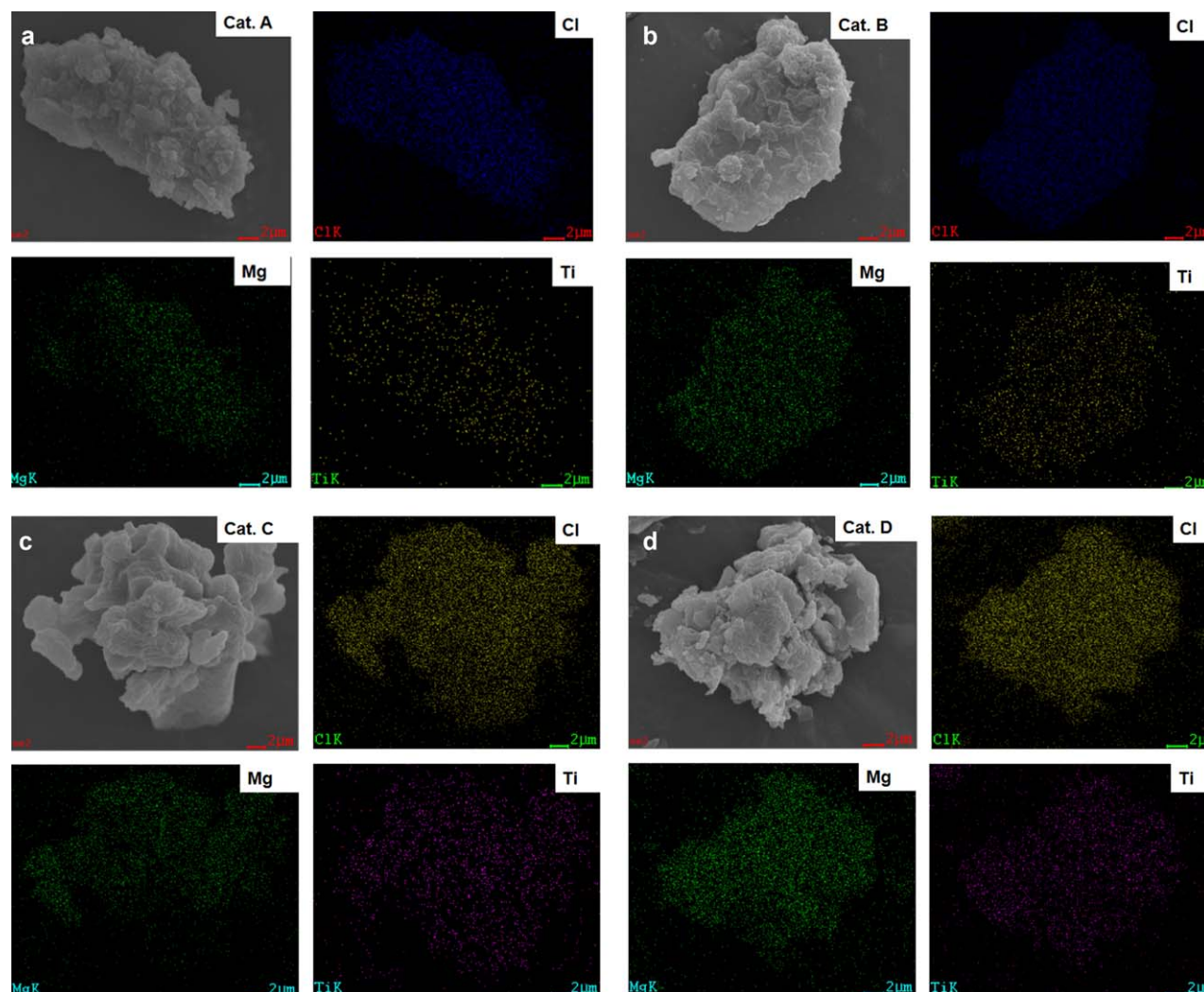


Figure 2. SEM/EDX mapping of (a) Cat. A, (b) Cat. B, (c) Cat. C, and (d) Cat. D. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

activities was in the order of **Cat. D > Cat. C > Cat. B > Cat. A**. The $\text{ZnCl}_2\text{-SiCl}_4$ was the most effective modifier for $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$ system because the Lewis acid compound probably

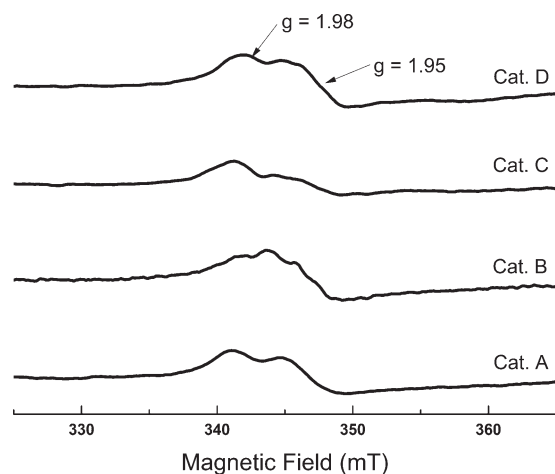


Figure 3. ESR spectra of the catalysts: Cat. A, Cat. B, Cat. C, and Cat. D.

increases the chain propagation rate constant^{8,27} owing to an increase in the Ti concentration on catalyst surface. Moreover, the activity of catalysts increased with decreasing the intensity of XRD patterns of MgCl_2/THF complexes since the addition of Lewis acid compounds could remove the THF from the catalyst, especially for the $\text{ZnCl}_2\text{-SiCl}_4$ system as seen in the XRD results in Figure 1. This was in a good agreement with the result reported by Chang et al.⁸ with the introduction of DEAC into

Table V. ESR Data on Ti^{3+} Species After Modification with ZnCl_2 and SiCl_4 onto $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$ Catalysts

Catalysts	Area $\times 10^{-3}$ (a.u.) ^a	Relative area ^b
Cat. A	147.90	1.00
Cat. B	179.13	1.21
Cat. C	104.00	0.70
Cat. D	208.56	1.41

^aThe amount of Ti^{3+} species. ^bRelative area = $\text{Area}_{(\text{Cat. B or Cat. C or Cat. D})} / \text{Area}_{(\text{Cat. A})}$.

Table VI. The Activity of Different Catalysts in Ethylene Polymerization^b

Catalysts	Activity (kg PE/mol Ti.h) ^a	Activity ratio ^b
Cat. A	405.6	1.00
Cat. B	517.7	1.28
Cat. C	529.8	1.31
Cat. D	1053.3	2.60

^aEthylene polymerization conditions: Wt. of cat. = 10 mg, a ratio of Al/Ti = 100, *n*-hexane = 30 mL, [ethylene] = 0.018 mol, T = 80°C. ^bActivity ratio = Activity_(Cat. B or Cat. C or Cat. D)/Activity_(Cat. A).

the MgCl₂-THF complex. It was also found that the yields of ethylene polymerization were enhanced by adding DEAC into the catalysts due to some of THF removal.

To confirm the effect of Lewis acid-modification in catalysts on the activity upon ESR measurement, the area of ESR signal was used to assess, and the results was in the order of **Cat. D** > **Cat. B** > **Cat. A** > **Cat. C**, while the activity of catalysts was increased in the order of **Cat. D** > **Cat. C** > **Cat. B** > **Cat. A**. From this result, the catalyst modified with SiCl₄ showed higher activity than the unmodified catalyst. However, it revealed only small amount of Ti³⁺ present because higher amount of Ti²⁺ species was formed after activation with TEA, leading to more active for ethylene polymerization. Therefore, the addition of SiCl₄ resulted in higher activity than that with the ZnCl₂

doped- and undoped catalysts. In addition, it is suggested that the influence of Lewis acid nature on the oxidation states of Ti may lead to an increase or decrease of polymerization activity. However, it should be noted that the addition of mixed metal chlorides-modification catalyst can result in increased ethylene polymerization activity, which can be attributed to increased Ti³⁺ species.

Effect of Different Lewis Acids on the Properties of Polyethylene

The obtained polyethylenes were further characterized by SEM, DSC, and the viscosity method. The morphologies of the obtained polyethylene are shown in Figure 4. The morphology of all polymers generating from different additives were similar. Table VII shows the influence of Lewis acids on the properties of polyethylene synthesized by TiCl₄/MgCl₂/THF catalytic system. This result showed that *T_m*, *T_c* and crystallinity of all polymers were similar to the unmodified catalyst as proven by DSC analysis. In addition, the viscosity average molecular weight (*M_v*) of the synthesized polyethylene was measured by the viscosity method. It was found that the presence of the Lewis acid in catalyst showed a trend to give a slight increase in the *M_v* of polyethylene, excepting for **Cat. C**. This was similar to result of Pinyocheep et al., who found that the molecular weight of PE increased by increasing the amounts of Ti³⁺ species.²¹ Increased Ti³⁺ species of the catalysts modified with Lewis acid (as seen from the ESR results) could also increase the *M_v* of PE due to decrease in polymer chain termination reactions.

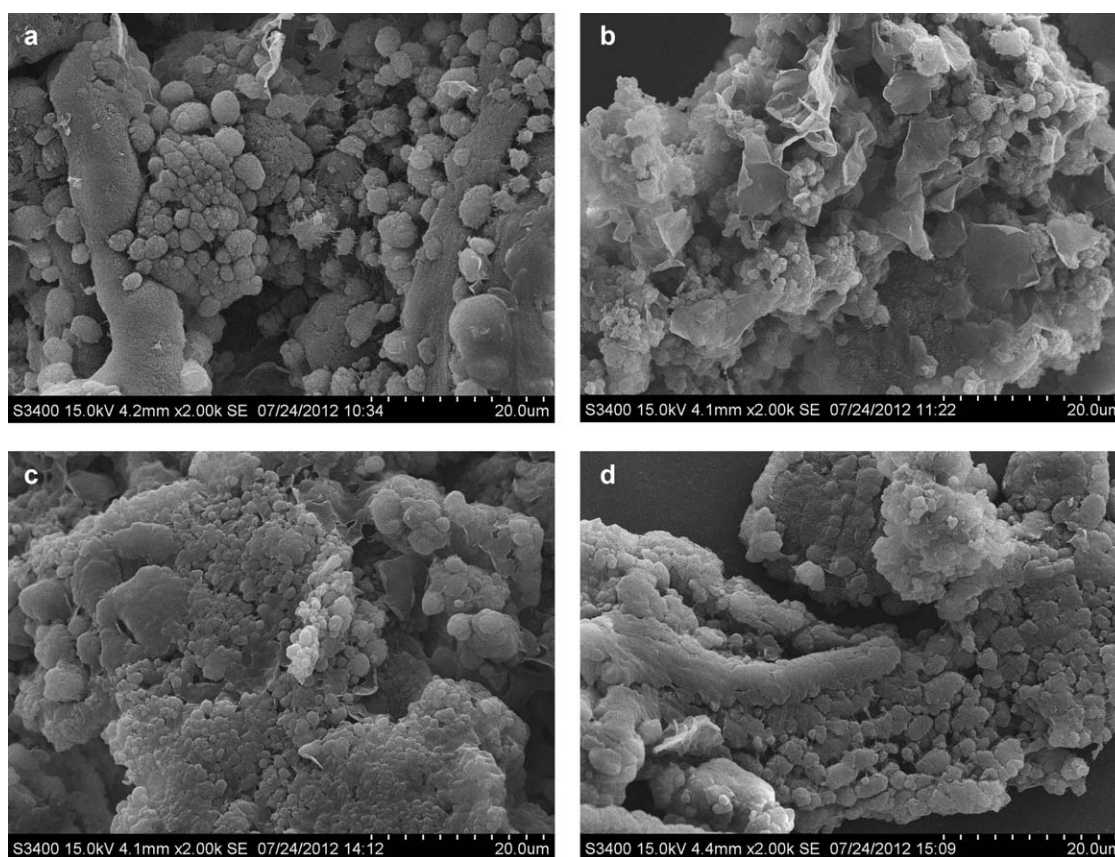


Figure 4. SEM micrographs of polyethylene obtained by (a) Cat. A, (b) Cat. B, (c) Cat. C, and (d) Cat. D.

Table VII. The Influence of Lewis Acids on the Properties of Ethylene Polymerization

Catalysts	Melting temperature (T_m) in °C ^a	Crystallization temperature (T_c) in °C ^a	Crystallinity (X_c) in % ^a	Viscosity average molecular weight (M_v) in g/mol ^b
Cat. A	134.28	111.64	52.56	383,936
Cat. B	133.84	112.12	54.30	392,555
Cat. C	133.81	112.07	49.88	372,199
Cat. D	132.56	113.63	53.21	423,086

^aDetermined by DSC. ^bMeasured by the viscosity method.

CONCLUSIONS

The $TiCl_4$ catalysts on $MgCl_2/THF$ support modified with Lewis acid halides such as $ZnCl_2$, $SiCl_4$, and $ZnCl_2-SiCl_4$ mixtures were investigated for ethylene polymerization. The influence of Lewis acid halides was found to increase the catalytic activity in ethylene polymerization in the sequence of **Cat. D** > **Cat. C** > **Cat. B** > **Cat. A**. The addition of mixed metal chlorides ($ZnCl_2-SiCl_4$) remarkably enhanced polymerization activity (almost three times) because some THF removal from the catalyst leading to an increase in the amounts of titanium on the surface. According to ESR results, the amounts of Ti^{3+} species were increased with the mixed metal chlorides modified catalyst, resulting higher the viscosity average molecular weight of polymers. However, the Lewis acid modifications did not affect on the properties of resulting polymers.

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