Research Article

Impact of AlCl₃ and FeCl₂ Addition on Catalytic Behaviors of TiCl₄/MgCl₂/THF Catalysts for Ethylene Polymerization and Ethylene/1-Hexene Copolymerization

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Abstract

The present research focuses on elucidating of the impact of Lewis acids including AlCl₃ and FeCl₂ addition on catalytic behaviors during ethylene polymerization and ethylene/1-hexene copolymerization over the TiCl₄/MgCl₂/THF catalyst (Cat. A). In this study, the Cat. A with the absence and presence of Lewis acids was synthesized via the chemical route. Then, all catalyst samples were characterized and tested in the slurry polymerization. For ethylene polymerization, using the Cat. A with the presence of AlCl₃ apparently gave the highest activity among other catalysts. In addition, the activity of catalysts tended to increase with the presence of the Lewis acids. This can be attributed to an enhancement of active center distribution by the addition of Lewis acids leading to larger amounts of the isolated Ti species. Moreover, with the presence of Lewis acids, the effect of hydrogen on the decreased activity was also less pronounced. Considering ethylene/1-hexene copolymerization, it revealed that the catalyst with the presence of mixed Lewis acids (AlCl₃ + FeCl₂) exhibited the highest activity. It is suggested that the presence of mixed Lewis acids possibly caused a change in acidity of active sites, which is suitable for copolymerization. However, activities of all catalysts in ethylene/1-hexene copolymerization were lower than those in ethylene polymerization. The effect of hydrogen on the decreased activity for both polymerization and copolymerization system was found to be similar with the presence of Lewis acids. Based on this study, it is quite promising to enhance the catalytic activity by addition of proper Lewis acids, especially when the pressure of hydrogen increases. The characteristics of polymers obtained upon the presence of Lewis acids will be discussed further in more detail. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Ethylene/1-Hexene Copolymerization; Ziegler-Natta Catalysts; Lewis Acid; Linear Low-Density Polyethylene

1. Introduction

Polyethylene (PE) is the most widely used plastic in this world. As commodity plastic, its properties are varied upon the end use [1,2]. One of the most well-known PE is the linear low-density polyethylene (LLDPE). In fact, LLDPE consists of a small amount of short branches. It is commonly made by copolymerization of ethylene with longer α-olefins, such as: propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, etc. Addition of comonomer

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alters the polymer properties such as melting point, crystallinity and density [3]. Owing to their versatile and cost-effective of LLDPE resins, they are applied in a wide range of flexible film applications in both blown and cast film operations [4]. At present, more than 80 % of these copolymers in industrial production are synthesized by supported Ziegler-Natta catalysts (ZN) or metallocene catalysts [5]. However, LLDPE with narrow molecular weight distribution (MWD) and chemical composition distribution (CCD) is normally produced by metallocene catalysts due to their single site catalysts [5,6]. However, the narrow MWD leads to the difficulty in processability. Therefore, it is designed to achieve the broader MWD with narrow CCD of LLDPE to facilitate the processability and improve mechanical properties of polymer. To achieve this goal, the copolymerization using the ZN catalysts is one of the most powerful strategies. Unfortunately, in most cases, it revealed that ZN catalysts provide very low comonomer insertion compared with metallocene catalysts [4,5,7-10]. Thus, many researchers try to improve catalytic activity and comonomer incorporation in copolymer produced from ZN catalysts by modification of magnesium chloride ($MgCl_2$) supports in ZN catalysts [11-14], changing active species from $TiCl_4$ to VCl_4 or $VOCl_3$ [6] or changing cocatalyst [11,12]. Chen *et al.* [11] studied the effect of Lewis acid such as $AlCl_3$ and types of cocatalyst including triethylaluminum (TEA) and triisobuthylaluminum (TIBA) for ethylene/ 1-hexene copolymerization [11]. They found that $AlCl_3$ doped catalyst provided slightly higher efficiency and higher 1-hexene incorporation than catalyst without $AlCl_3$ doping. Besides, comonomer incorporation significantly increased when TEA was replaced by TIBA. Mulhaupt *et al.* [13] found that the addition of a sterically hindered phenol (2,6-di-tert-butyl-4-methylphenol) during the catalyst preparation led to the activity enhancement of a $MgCl_2$-supported ZN catalyst for ethylene and 1-olefin copolymerization [13]. Kong *et al.* [14] investigated effect of different structures of ligands (2-methyl-2-butanol and benzyl alcohol) to achieve high comonomer incorporation with heterogeneous ZN catalysts in ethylene/ 1-octene copolymerization as well [14]. They revealed that the modified catalysts exhibited higher activity and comonomer incorporation rate when compared with a simple $TiCl_4/MgCl_2$ catalyst without organo ligands. However, there were many ways, which tried to modify ZN catalysts that made worse in comonomer insertion such as adding some types of electron donor. Adding 2,6-diisopropylphenol as internal donor [12] or $Ph_2Si(OMe)_2$ as external donor [11] in the catalyst system caused the decrease in catalytic activity and 1-hexene insertion when compared to the catalyst without modification in ethylene/1-hexene copolymerization.

In this study, the $TiCl_4/MgCl_2/THF$ catalytic system was chosen because it is easy to prepare, low cost in production, good hydrogen response and comonomer insertion property [3,15]. Therefore, the $TiCl_4/MgCl_2/THF$-based catalyst (Cat. A) was prepared. The effects of single Lewis acid ($AlCl_3$ and $FeCl_2$) and their mixture were further investigated in order to improve the catalytic activity and comonomer incorporation. To investigate copolymer structure and to precede the reaction conditions closer to the industrial process, hydrogen was also added into the system to control the molecular weight of polymer. Moreover, all catalysts were tested to measure the catalytic activity for both ethylene polymerization and ethylene/1-hexene copolymerization. Effects of Lewis acid addition on the catalytic activity and properties of polymer will be elucidated and discussed further.

2. Materials and Method

2.1 Materials

All materials and operation steps were routinely conducted under nitrogen atmosphere using standard glove box and Schlenk technique. Polymerization grade of ethylene, hydrogen and nitrogen were purchased from Linde Co., Ltd. Tetrahydrofuran (THF), aluminum(III) chloride ($AlCl_3$) and iron(II) chloride ($FeCl_2$) were purchased from Sigma-Aldrich and used as Lewis acids without further purification. 1-hexene ($1\text{-}C_6H_{12}$) was supplied from Sigma-Aldrich and dehydrated with the 3Å molecular sieve. Titanium(IV) chloride ($TiCl_4$) was purchased from Merck. Anhydrous $MgCl_2$, *n*-hexane and triethylaluminum (TEA) were donated from Thai Polyethylene Co., Ltd.

2.2 Catalyst Preparation

2.2.1 $TiCl_4/MgCl_2/THF$ catalyst

The $TiCl_4/MgCl_2/THF$ catalyst (Cat. A) was synthesized according to the following steps. First, the slurry mixture of 1 g of anhydrous $MgCl_2$ (with the desired amount of single Lewis acid (the molar ratio of $AlCl_3$ or $FeCl_2/MgCl_2$ = 0.12) or mixed Lewis acids (the molar ratio of $AlCl_3$ and $FeCl_2/MgCl_2$ = 0.06 for each Lewis

acid), if any) and 150 mL of tetrahydrofuran (THF) was added into the 500 mL flask equipped with magnetic stirrer. Then, 1 mL of $TiCl_4$ was injected dropwise (the molar ratio of $TiCl_4/MgCl_2$ = 0.87). The catalyst slurry mixture was slowly heated up to 70 °C with the cooling system connecting to the condenser to prevent the loss of THF solvent and held at that temperature for 3 h. After that, this slurry was cooled down to 40 °C, following with the washing steps with *n*-hexane for seven times before obtain the final catalysts. After the preparation, there were four catalysts used for a comparative study including: $TiCl_4/MgCl_2/$ THF, $TiCl_4/AlCl_3/MgCl_2/THF$, $TiCl_4/FeCl_2/$ $MgCl_2/THF$, and $TiCl_4/AlCl_3/FeCl_2/MgCl_2/THF$. The nomenclature for each catalyst is denoted as Cat. A, Cat. A-Al, Cat. A-Fe, and Cat. A-Al-Fe, respectively.

2.3 Polymerization reaction

Both ethylene polymerization and ethylene/ 1-hexene copolymerization were performed in a 2-L autoclave reactor equipped with mechanical stirrer. First, the reactor and all feed lines were purified by evacuation of oxygen from the reactor, and then purging with nitrogen gas for several times at 70 °C. After that, it was conditioned with purging of nitrogen gas for 1 h, then cooled down to 30 °C, following by addition of 1 L of *n*-hexane into the reactor. To perform ethylene/1-hexene copolymerization, 20 mL of 1-hexene comonomer was also introduced into the reactor and stirred at 350 rpm for 5 min. Then, triethylaluminum and catalyst slurry (Al/Ti molar ratio = 140) were charged into the reactor, respectively. After that, 1 bar of nitrogen and the desired amount of hydrogen (0.5 and 1.5 bars) were filled into the reactor at 67 °C. To start polymerization, ethylene at total pressure of 8 bars was pressurized to initiate the polymerization at 75 °C. The polymerization was carried out for 1 h at 80 °C. Finally, the white powder of polymers was filtered and dried at room temperature overnight.

2.4 Characterization of Catalysts

2.4.1 Inductively Couple Plasma (ICP)

The catalyst composition (Ti, Mg, Al, and Fe) in bulk was determined by inductively couple plasma optical emission spectrometer (ICP-OES optima 2100 DV from Perkin Elmer). Prior to measurement, the catalyst sample was digested with hydrochloric acid and diluted with DI water.

2.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

The interaction between $TiCl_4$ and $MgCl_2$ support in the presence of THF was measured by Fourier transform infrared spectroscopy using Nicolet 6700 FT-IR spectrometer under transmittance mode. The catalyst powder was prepared as a thin film on NaCl disk and kept under argon atmosphere to prevent air and moisture during the analysis. The measurement was conducted in the range of wavenumber from 500 to 4000 cm^{-1} with scan frequency of 400 times.

2.4.3 X-Ray Diffraction (XRD)

The crystalline phases of the catalyst and $MgCl_2$ support were examined with XRD using Bruker of D8 Advance. Prior to measurement, the catalyst sample was prepared in a sample holder under argon atmosphere during the measurement. Diffraction patterns were analyzed with the scans from diffraction angle 2θ = 10° to 80° with scan speed of 0.3 s/step and a step size of 0.02.

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

The morphology and the elemental distribution of catalyst (Ti, Mg, Al, Fe, and Cl) were examined by SEM and EDX, respectively. The SEM of Hitachi mode S-3400N was applied, while the EDX was performed using Link Isis series 300 program.

2.5 Characterization of Polymers

2.5.1 [13]Carbon Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR)

^{13}C NMR is one of the most powerful techniques to determine the comonomer distribution. The ^{13}C NMR spectra of the copolymers were recorded using a high-resolution ^{13}C NMR Bruker DRX 500 spectrometer. The samples were measured at 125 °C in benzene-D6 with 90° of pulse angle and 12 s of pulse interval.

2.5.2 Differential Scanning Calorimetry (DSC)

Polymer melting point (T_m) and percentage of crystallinity (χ_c) were determined by DSC-TGA with TA Instruments SDT Q600 V8.1 Build 99. The DSC measurements were carried out with a heating rate of 10 ºC/min in the range of temperature from 30 ºC to 200 ºC. The crystallinity of polyethylene was calculated with the Equation (1).

$$X_c = \frac{\Delta H}{\Delta H^o} x 100 \qquad (1)$$

where; ΔH is the heat of fusion of polyethylene sample. ΔH^o is the heat of fusion of linear polyethylene, which equals to 290 J/g [16].

3. Results and Discussion

3.1 Characteristics of Catalysts

The elemental composition of catalysts in bulk measured by ICP is reported in Table 1. It shows that the Ti content in bulk of catalyst decreased with the addition of Lewis acid, especially for Cat. A-Al. Thus, Ti/Mg apparently decreased with Lewis acid addition. This can be attributed to Lewis acid addition reduced free-vacancies of $MgCl_2$ crystallization and Ti insertion [17] via adjustment of the active center distribution. Wang *et al.* [18] revealed that the addition of $AlCl_3$ promotes the destruction of $MgCl_2$ crystal lattice because $AlCl_3$ has the lower lattice energy than that of $MgCl_2$. Therefore, $AlCl_3$ lattice tends to form the lattice defects more than $MgCl_2$ lattice does. Then, the defects of $AlCl_3$ lattice may attract the Cl atoms of $MgCl_2$ lattice leading to the chlorine vacancies formation, and in turn, the attraction promotes the formation for the defects of $MgCl_2$ crystal lattice. As the result, $TiCl_4$ can disperse more uniformly and attach more tightly on the $MgCl_2$ support modified with $AlCl_3$ than that of the unmodified $MgCl_2$-supported catalyst [18]. Moreover, $AlCl_3$ was reported as an ineffective support for anchoring $TiCl_4$ [11]. Therefore, the

Cat. A-Al exhibited the lowest Ti content in bulk due to the reasons as mentioned previously.

Table 2 shows the results of elemental distribution on the catalyst surface measured by EDX technique. All catalysts show higher Ti contents measured by EDX technique than those measured by ICP technique (Table 1). It suggested that active sites were mainly located at the external surface of catalyst compared to the location within the catalyst pores. This is beneficial for polymerization to have higher amount of active surface Ti on ZN catalysts. Moreover, Lewis acid doped catalysts provided lower Ti/Mg ratio than none-doped Lewis acid catalyst.

To identify the interaction between $TiCl_4$ and $MgCl_2$ support, FTIR analysis was applied and it is displayed in Figure 1. Chu *et al.* [19] pointed that the pure THF has the symmetrical and asymmetrical C–O–C stretching IR bands at 912 cm⁻¹ and 1071 cm⁻¹, respectively [19]. In this work, the catalysts exhibit the symmetrical C–O–C stretching band at 878.8, 876.1, 874.6, and 864.5 cm⁻¹ for Cat. A, Cat. A-Al, Cat. A-Fe, and Cat. A-Al-Fe, respectively, whereas the asymmetrical C–O–C stretching vibration was also found and displayed at 1026.4, 1025.6, 1025.6, and 1016.8 cm⁻¹ for Cat. A, Cat. A-Al, Cat. A-Fe, and Cat. A-Al-Fe, respectively. It can be seen that the Lewis acid modified catalysts showed lower IR bands of C–O–C stretching band than those of Cat. A. This was because these catalysts formed titanium(III)-magnesium-THF complexes and the added Lewis acid or metal halides incorpora-

Table 1. Elemental composition in catalyst bulk measured by ICP technique

Catalyst	Element content (wt%)				Lewis acid/$MgCl_2$ (mol/mol)	Ti/Mg (mol/mol)
	Ti	Mg	Al	Fe		
Cat. A	4.78	7.61	-	-	-	0.32
Cat. A-Al	1.97	7.84	1.13	-	0.13	0.13
Cat. A-Fe	3.20	6.19	-	1.82	0.13	0.26
Cat. A-Al-Fe	3.35	5.74	0.31	0.83	0.11	0.30

Table 2. Elemental distribution on the catalyst surface measured by EDX technique

Catalyst	Elemental content on the surface of catalyst (wt%)					Lewis acid/$MgCl_2$ (mol/mol)	Ti/Mg (mol/mol)
	Ti	Mg	Cl	Al	Fe		
Cat. A	18.78	24.04	57.18	-	-	-	0.40
Cat. A-Al	8.12	23.20	65.00	3.68	-	0.14	0.18
Cat. A-Fe	10.22	19.79	62.82	-	7.17	0.16	0.26
Cat. A-Al-Fe	12.21	19.34	62.81	1.35	4.28	0.16	0.32

ting with the Ti-Mg-THF complex resulting in the lower vibrations of the C–O–C stretching bands of THF [19,20]. This causes a change in acidity of $MgCl_2$ compounds via an increase acidity of active sites. The C-H stretching band around 2984 to 2880 cm^{-1} was also found in these catalysts [21]. Furthermore, the O–H stretching band was observed in the range of 3361 to 3502 cm^{-1} suggesting the formation of alkoxide Ti [21] species via ring opening of THF. It indicated that the interaction between $MgCl_2$ support and THF changes the nature of Ti species through the formation of a transient cationic Ti mononuclear species, which finally generates a neutral alkoxide Ti species via the ring-opening of THF [22].

The XRD patterns of the catalysts are illustrated in Figure 2. As seen, the α-form of $MgCl_2$ support exhibits the characteristic peaks at 2θ = 14.7°, 30.0°, 34.8°, and 49.7°. In addition, the sharp peak at 2θ = 14.7° was assigned to the stacking of $MgCl_2$ triple layers along the crystallographic direction, while the other peaks at 2θ = 30.0°, 34.8°, and 49.7° were resulted from the stacking faults of $MgCl_2$ triple layers. The peak at 2θ = 34.8° was on (104) plane and the another peak at 2θ = 49.7° was on (110) plane [23]. However, it was hardly observed the characteristic peaks on the prepared catalysts, excepting for Cat. A-Fe. In fact, all catalysts reveal their characteristic peaks of the $MgCl_2$/THF complex around 2θ = 20.2° and 32.3° corresponding to the results reported by Chang *et al.* [24] and Phiwkliang *et al* [25]. Furthermore, the XRD peaks at 2θ = 11.8°,

17.8° and 18.0° were also detected and assigned to the formation of $TiCl_4$/THF, $TiCl_3$/THF and $TiCl_4$/$MgCl_2$/THF compound, respectively [26]. However, it is unable to detect the characteristic peak of Lewis acid because it completely overlaps with the peak of $TiCl_4$/$MgCl_2$/THF structure [10,27]. It should be noted that the addition of Lewis acid increases acidity of active sites; therefore, the adherent THF in the catalyst structure was eliminated efficiently and the $MgCl_2$/THF structure was destroyed [24]. This result is in agreement with that obtained from the FTIR measurement as shown in Figure 1, where the O–H stretching band in the catalysts was rarely observed. The morphology of catalysts is shown in Figure 3. All catalysts similarly exhibit the bar shape. Finally, the distribution of Lewis acid on the external surface of catalysts is shown in Figure 4. It can be seen that Lewis acid added is quite well-dispersed in the catalyst.

3.2 Catalytic Activity

3.2.1 Effect of Lewis acids and hydrogen pressures in ethylene polymerization

The results of catalytic activity for ethylene polymerization with addition of different Lewis acids are listed in Table 3. It revealed that the activity was in the following order: Cat. A-Al > Cat. A-Fe > Cat. A-Al-Fe > Cat. A. It indicated that addition of Lewis acids promoted the activity in ethylene polymerization. This is likely due to the efficient removal of THF [19,24]
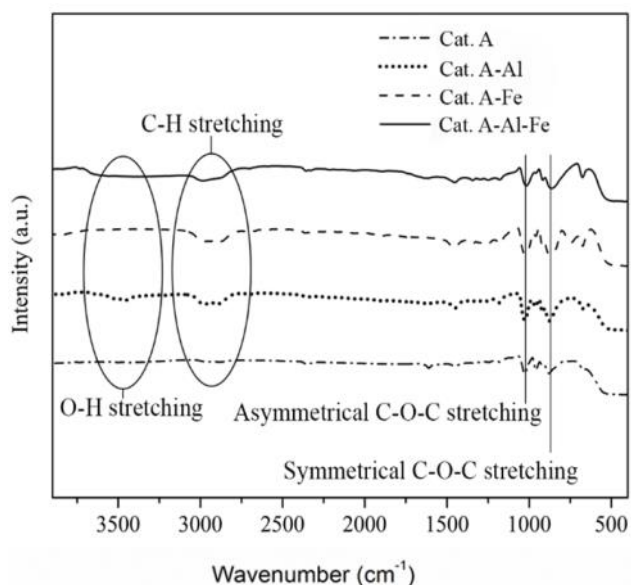

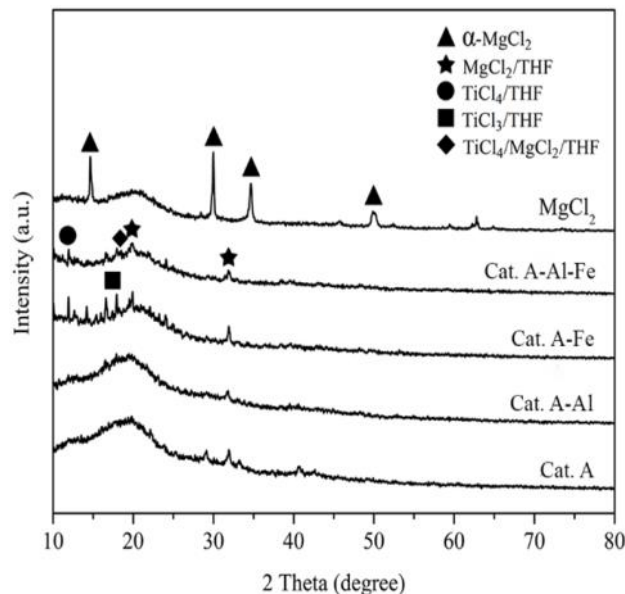**Figure 1.** FTIR spectra of all prepared catalysts

Figure 2. XRD patterns of all prepared catalysts

since THF remained can act as a catalyst poison [15,28]. It was found that Cat. A exhibited the lowest activity among other catalysts with Lewis acid addition, although it had the highest Ti/Mg ratio. Theoretically, a catalyst having high Ti/Mg ratio or Ti species on the catalyst surface should exhibit high polymerization activity. However, the aggregation of Ti species must be considered in this case since it results in a decrease of active site concentration [29]. Previously, Toshiaki *et al.* investigated the catalytic activity of two ZN catalysts, including isolated and clustered Ti species in ZN catalysts, for ethylene and propylene polymerization. They reported that the isolated Ti species (Ti located separately from each other) prevents the agglomeration of Ti species leading to high activity for both in ethylene and propylene polymerization [29]. It is presumable that a catalyst with high Ti/Mg ratio is likely to have the distribution of Ti in the clustered forms leading to decreased activity. Besides an enhancement of activity by Lewis acid addition from efficient THF removal, the addition of Lewis acid can also improve or adjust active center distribution (ACD) with the decrease of Ti/Mg ratio. The conceptual model for the Lewis acid roles can be proposed as seen in Scheme 1. On the other words, the Lewis acid addition can alter the Ti distribution into higher isolated form of Ti species. As the result, it can be observed that Cat. A-Al exhibited the highest activity due to the lowest Ti/Mg ratio at external catalyst surface presented on it. In addition, with single Lewis acid addition (Cat. A-Al and Cat. A-Fe), they rendered higher activity than Cat. A-Al-Fe (mixed Lewis acids). This is likely due to the relatively high surface Ti/Mg ratio of Cat. A-Al-Fe (as seen in Table 2) that results in more clustered Ti species. In summary, it is confirmed that one of the key factors to determine the catalytic activity is distribution of active Ti species at surface of catalyst.

In case of hydrogen addition during polymerization, effect of hydrogen on catalytic activity for ethylene polymerization behaviors is summarized as seen in Table 3. Activity of all catalysts decreased with hydrogen addition, which is common for ethylene polymerization with ZN catalysts [30,31]. In this study, Lewis acid doped catalysts exhibited higher activity than the one with the absence of Lewis acid (Cat. A). Kouzai *et al.* [32] claimed that chain transfer reaction by hydrogen can occur when polymerization sites locate in the instant surrounding of hydrogen dissociation sites [32]. Thus, it refers that the catalyst containing more clustered Ti species should have more hydrogen effect on catalytic activity than the one
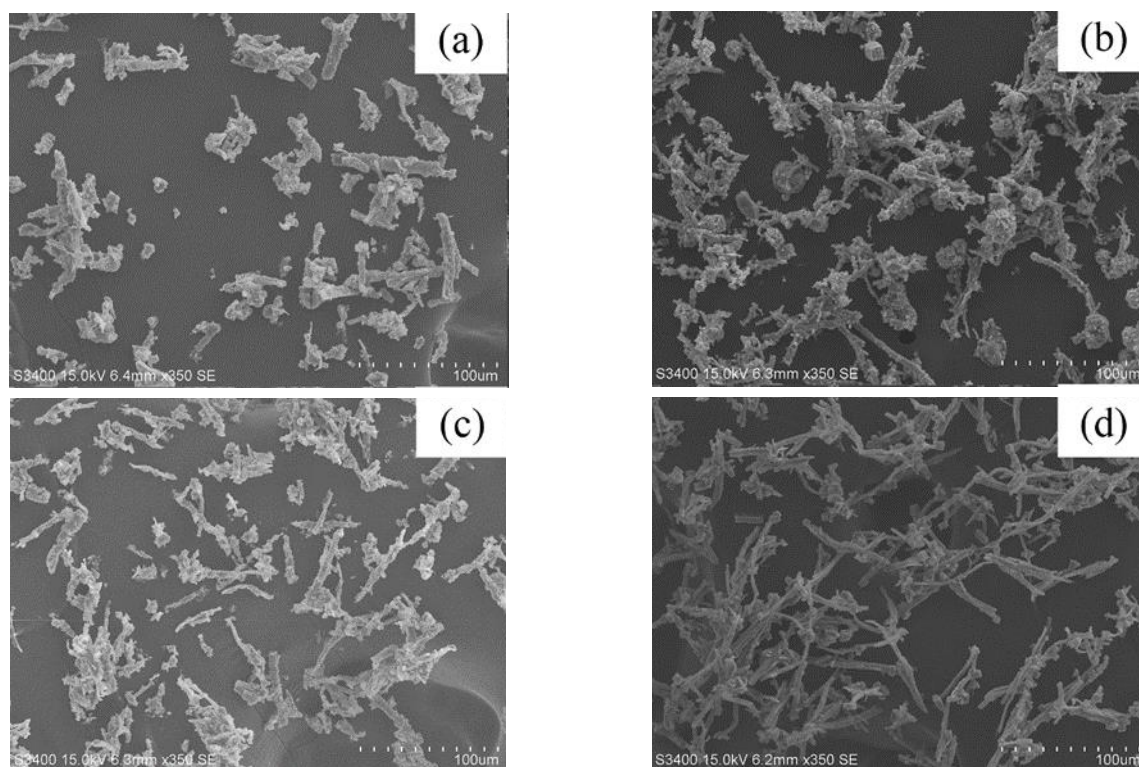

Figure 3. SEM images of all prepared catalysts: (a) Cat. A, (b) Cat. A-Al, (c) Cat. A-Fe, and (d) Cat. A-Al-Fe
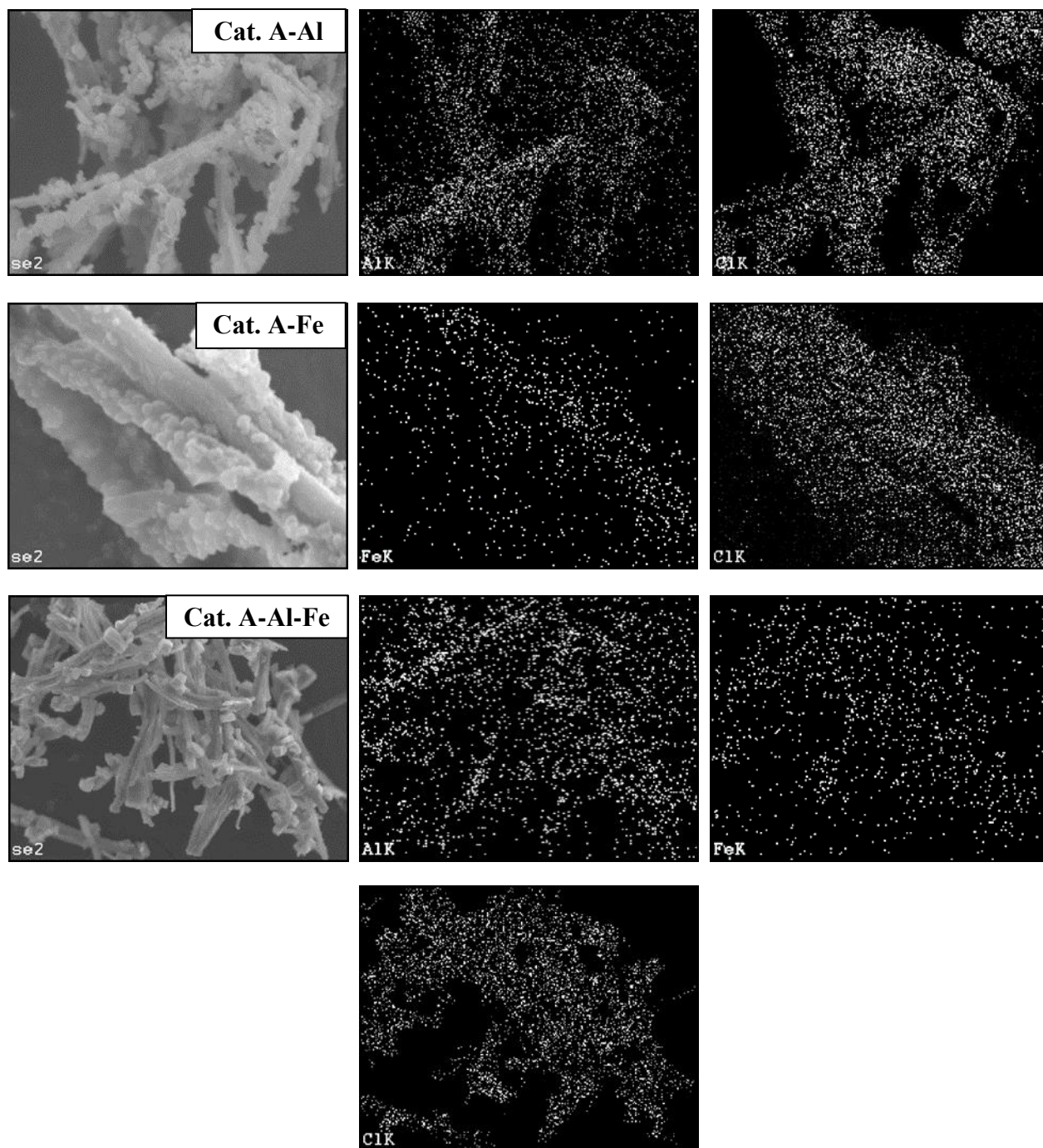
Figure 4. SEM/EDX mapping of Lewis acid doped catalysts

Table 3. Catalytic activity for ethylene polymerization[a] under different hydrogen pressures

Catalyst	Cat.A			Cat. A-Al			Cat.A-Fe			Cat.A-Al-Fe		
H₂ pressure (bar)	0	0.5	1.5	0	0.5	1.5	0	0.5	1.5	0	0.5	1.5
Activity (kg PE/gTi*h)	307	132	105	424	309	276	337	293	210	205	149	123

(a) Polymerization condition: 2-L autoclave reactor, [Ti] = 0.016 mmol, Al/Ti molar ratio = 140, co-catalyst = TEA, polymerization time = 1 h, reaction temperature = 80 °C, total pressure = 8 bars

having more isolated Ti species. It was found that activities of Cat. A decreased significantly (ca. 66 %) with increased hydrogen pressure of 1.5 bars, whereas for Cat. A-Al, Cat. A-Fe, and Cat. A-Al-Fe, it indicated decreasing in activity by only 35 %, 38 %, and 40 %, respectively when compared with its original one in the absence of hydrogen. Thus, it is worth noting that that Lewis acid addition is one of the most promising ways to suppress hydrogen effect on activity by regulation of the active center distribution. Furthermore, the use of single or mixed Lewis acid addition has no significant change in the decreased catalytic activity with hydrogen addition. This is likely because the hydrogen effect strongly depends on the distribution of Ti species.

3.2.2 Effect of Lewis acids and hydrogen pressure in ethylene/1-hexene copolymerization

Catalytic activity of ethylene/1-hexene copolymerization and 1-hexene insertion in copolymer are listed as seen in Table 4. It was found that with Lewis acid addition, all catalysts exhibited higher catalytic activity than Cat. A. The catalytic activity was in the following order: Cat. A-Al-Fe > Cat. A-Fe > Cat. A-Al > Cat. A. As seen, the Cat. A-Fe presented a slightly higher activity for copolymerization than the Cat. A-Al. This is attributed to $FeCl_2$ has higher electronegativity than $AlCl_3$ as seen from the FTIR result. Thus, the Cat. A-Fe exhibited slightly higher activity to react with monomer than Cat. A-Al. Furthermore, the mixed Lewis acid addition can generate the

Table 4. Catalytic activity of ethylene/1-hexene copolymerization[a] and 1-hexene insertion in copolymer measured by ^{13}C NMR technique

Catalyst	Cat. A		Cat. A-Al		Cat. A-Fe		Cat. A-Al-Fe	
H_2 pressure (bar)	0	1.5	0	1.5	0	1.5	0	1.5
Activity (kg PE/gTi*h)	207	89	240	127	261	136	274	189
1-hexene in copolymer (mol%)	0.12	0.16	0.21	0.21	0.13	0.19	0.16	0.20

(a) Polymerization condition: 2-L autoclave reactor, [Ti] = 0.016 mmol, 1-hexene feed = 0.16 M, Al/Ti molar ratio = 140, co-catalyst = TEA, polymerization time = 1 h, reaction temperature = 80 °C, total pressure = 8 bars
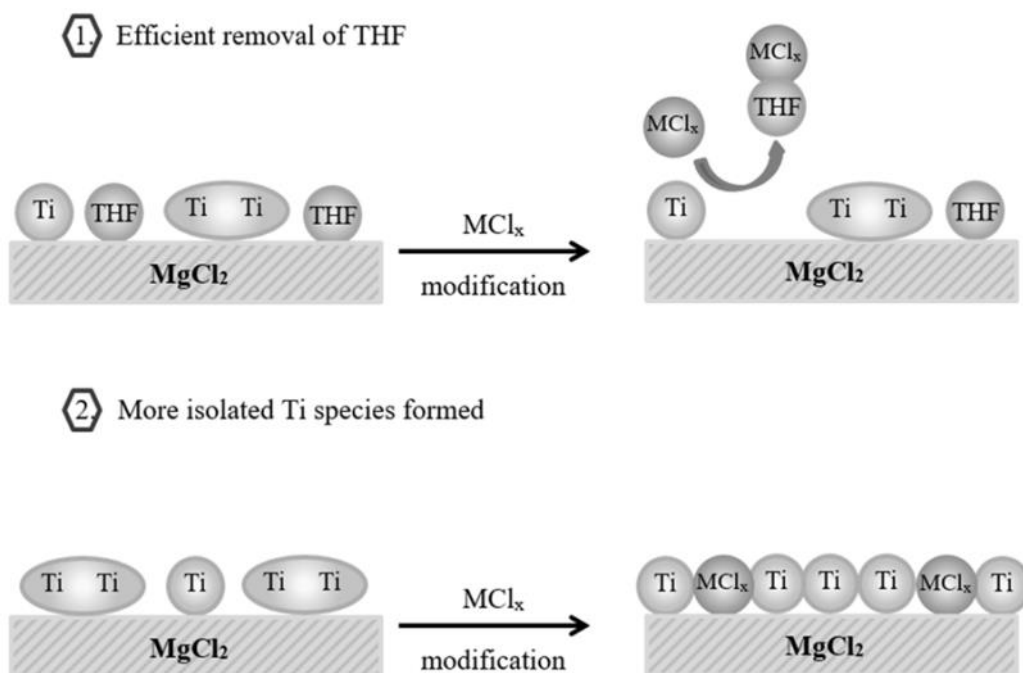
Scheme 1. A conceptual model for the Lewis acid roles

difference in acidity of active sites, which is more suitable for copolymerization than a single Lewis acid addition [3]. Therefore, the Cat. A-Al-Fe exhibited the highest catalytic activity. In addition, the catalysts with Lewis acid addition tended to gain higher 1-hexene insertion than Cat. A because they had better ACD on the catalysts surface than catalysts without Lewis acid addition as mentioned before. Thus, it facilitates the insertion of 1-hexene comonomer. Effect of hydrogen on ethylene/1-hexene copolymerization activities of all catalysts was investigated as well. As expected, all catalysts exhibited decreased catalytic activity with increasing hydrogen pressure because of chain transfer reaction by hydrogen [31,33]. Moreover, 1-hexene insertion tended to increase with increasing hydrogen concentration as well [31].

When compared, the catalytic activity between ethylene polymerization and ethylene/1-hexene copolymerization, it was found that catalytic activity was lower for the copolymerization system. This was because the concentration of ethylene at active sites decreased with the introduction of 1-hexene. Moreover, 1-hexene has more steric hindrance than ethylene causing more difficulty for insertion of 1-hexene to the backbone chain. Previously, Li *et al.* also ascribed that1-hexene is more difficult to reach the active sites compared to ethylene because 1-hexene has lower diffusivity than that of ethylene due to its larger molecular weight [34]. As summarized in Table 4, polymers obtained from all catalysts showed very low 1-hexene insertion (ca. 0.2 %) indicating that the polymer-chain structure is primarily linear, with pendant butyl branches created by incorporation of 1-hexene into the backbone. As a consequence, these butyl branches are mostly isolated due to the relatively low 1-hexene content [35].

3.3 Polymer Properties

3.3.1 Effect of Lewis acid and hydrogen on polymer properties

According to Table 5, the melting temperature and crystallinity of obtained polymers did not significantly change upon addition of Lewis acid. This is because these properties strongly depend on the amount of comonomer insertion, but not on the types of modifier or monomer [3].

When hydrogen was introduced into the system, the melting point of polymer decreased with increasing hydrogen concentration. This was because it occurred chain transfer reaction by hydrogen. As the result, the melting point was lower due to the decrease in molecular weight of polymer [31]. Furthermore, crystallinity tended to increase with hydrogen addition. This was because hydrogen blocked polymerization sites, then suppressed the polymerization rate resulting in an increase in crystallization rate [36].

3.3.2 Effect of 1-hexene on polymer properties

As reported previously, the polymer-chain structure is primarily linear with pendant butyl branches created by incorporation of 1-hexene into the backbone. As seen in Figure 5, it shows the typical ^{13}C NMR spectrum of ethylene-1-hexene copolymer using Cat. A-Al at H_2 pressure of 1.5 bars. From Table 5, the lower melting point and crystallinity of copolymer with the addition of 1-hexene were observed because the introduction of longer α-olefins to polyethylene chain leads to the decrease in chain regularity by producing the different sizes of crystallites and imperfections in the crystalline lattice [11,31,37].

4. Conclusion

In summary, the effect of Lewis acid addition in the ZN catalyst ($TiCl_4/MgCl_2/THF$) is elucidated for both ethylene polymerization and ethylene/1-hexene copolymerization. Based on results, it can be concluded that Lewis acid addition plays crucial roles in two ways; (i) efficient removal of THF (which is poison for this catalyst) and (ii) alter the active site distribution (more isolated Ti species formed). Those can result in increased activity for both systems with the absence and presence of hydrogen in polymerization. Considering, the ethylene polymerization system, addition of

Table 5. Polyethylene properties measured by DSC technique

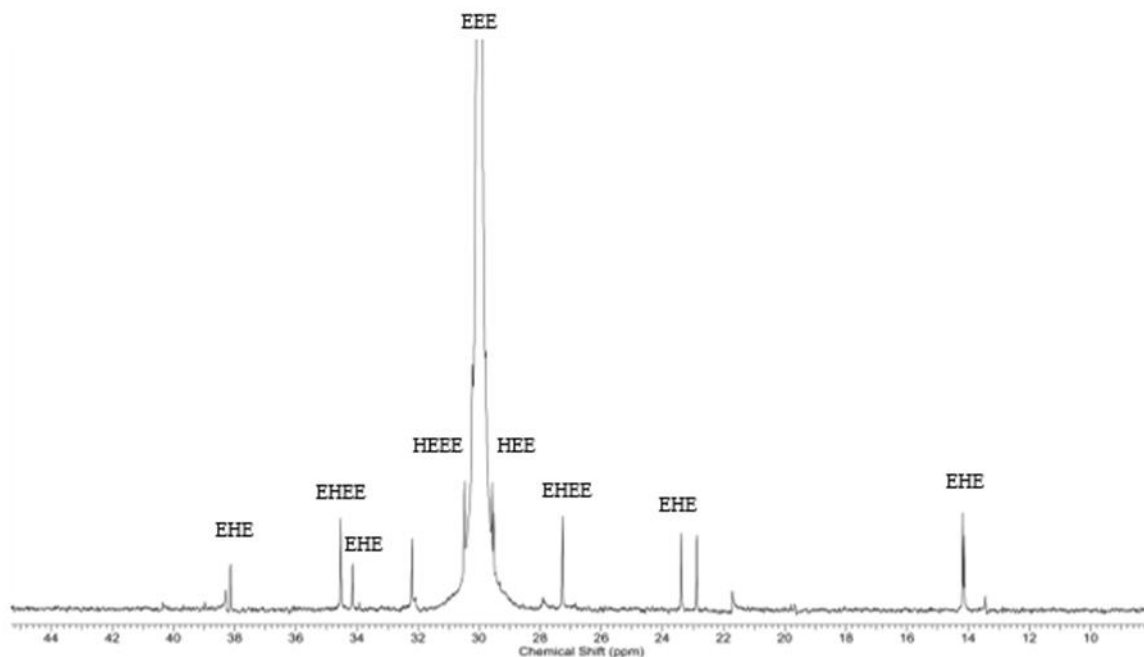| Catalyst	Cat. A			Cat. A-Al			Cat. A-Fe			Cat. A-Al-Fe		
H_2 pressure (bar)	0	0.5	1.5	0	0.5	1.5	0	0.5	1.5	0	0.5	1.5
T_m of polymer (°C)	132.4	130.8	128.7	132.8	130.5	128.9	133.2	131.4	129.4	132.2	130.1	128.7
T_m of copolymer (°C)	128.3	-	125.1	128.5	-	123.9	128.6	-	126.4	128.7	-	125.4
χ_c of polymer (%)	72.6	75.6	75.5	67.9	66.8	68.3	71.1	71.6	71.8	65.7	62.6	68.2
χ_c of copolymer (%)	59.8	-	63.5	59.9	-	59.6	60.2	-	61.3	56.7	-	64.7

Figure 5. Typical ^{13}C NMR spectrum of ethylene-1-hexene copolymer using Cat. A-Al at H$_2$ pressure of 1.5 bars

AlCl$_3$ in catalyst is the most promising, while for the copolymerization system, the addition of AlCl$_3$ and FeCl$_2$ is preferred. It should be noted that the incorporation of 1-hexene is very low, thus, properties of copolymer did not significantly change as much.

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