Research Article

A Comparative Study of AlCl$_3$ and FeCl$_2$-Modified TiCl$_4$/MgCl$_2$/THF Catalytic System in the Presence of Hydrogen for Ethylene Polymerization

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Ethylene homopolymerization over TiCl$_4$/MgCl$_2$/THF catalysts modified with different metal halide additives (AlCl$_3$ and FeCl$_2$) with and without hydrogen was investigated based on catalytic activity and polymer properties. Lewis acid modification can improve activity because it can remove the remaining THF in the final catalyst, which can poison the catalyst active sites via the ring-opening of THF that was confirmed by XRD measurements. Moreover, the activity enhancement was due to the formation of acidic sites by modifying the catalysts with Lewis acids. Thus, FeCl$_2$ doped catalyst (Fe-THF) exhibited the highest activity followed by AlCl$_3$ doped catalyst (Al-THF) and undoped catalyst (None-THF). In H$_2$/C$_2$H$_4$ molar ratio of 0.08, Fe-THF showed a better hydrogen response than Al-THF due to more titanium cluster distribution. Fe-THF is considered to have more clustered Ti species than Al-THF. As a consequence, it led us to obtain more possible chances to precede chain transfer reaction by hydrogen. The molecular weight, melting temperature, and crystallinity of obtained polymers were investigated by GPC and DSC measurement, respectively.

1. Introduction

The present generation of heterogeneous catalytic systems for polyolefin production based on TiCl$_4$/MgCl$_2$ supported catalyst is referred to Ziegler-Natta (ZN) catalyst. It is one of the most advanced industrial and academic applications of catalysis. One of the important steps to create the highly active ZN catalyst is the preparation method of the precatalyst prior to the activation with alkylaluminum [1]. Lewis base, normally an alcohol likes ethanol or an ether likes tetrahydrofuran (THF) [1–3], plays an important role in creating bimetallic complexes with magnesium dichloride [3, 4]. Even though ethanol is more preferable choice as Lewis base, there are still many researches employing THF in the process of catalyst preparation. This is due to its easiness to prepare, which leads to the lower in cost. It also provides good hydrogen response and the moderate activity and increases the molecular weight of polymer [4–6]. Besides, Sobota [7] revealed that THF is the most mature as a selectivity control agent

in ethylene polymerization. Therefore, THF complexes of MgCl$_2$ and TiCl$_x$ are frequently employed as the precursors. Another important factor that industries are concerned with is controlling of the molecular weight distribution of obtained polymers because it affects the final mechanical and processing properties of the polymer [8–11]. Polymer having short chains provides good processability, while polymer having high molecular weight fraction provides good mechanical properties. Hence, polymers having both short and long chains are required to produce polymers with a broad molecular weight distribution [12]. However, narrow or board molecular weight distribution depends on the desired application. As it is widely noticed, hydrogen is the key agent usually used to control molecular weight of polymer. Effect of hydrogen on activity is complicated to forecast because it depends on several factors such as type of catalyst system, monomer, donor systems, and polymerization conditions [13]. For example, hydrogen typically decreases activity in ethylene polymerization but increases in propylene

TABLE 1: Abbreviation of the prepared catalysts.

Catalyst abbreviation	Component
None-THF	$TiCl_4/MgCl_2/THF$
Al-THF	$TiCl_4/AlCl_3/MgCl_2/THF$
Fe-THF	$TiCl_4/FeCl_2/MgCl_2/THF$

polymerization for ZN catalyst [14]. Nevertheless, Hair and Hertl [15] revealed that the addition of a small amount of hydrogen can improve the activity in ethylene copolymerization. However, hydrogen effect on ZN catalyst systems is still ill-defined; however it is very significant. Thus, in this work, a comparative study of the $AlCl_3$ and $FeCl_2$ modified $TiCl_4$/ $MgCl_2$/THF catalytic system on the activity and polymer properties in the presence of hydrogen for ethylene polymerization was investigated.

2. Experimental

2.1. Materials. All materials and operation steps were conducted under nitrogen atmospheres using a standard glove box and Schlenk techniques. Polymerization grades of ethylene, hydrogen, and nitrogen were purchased from Linde Co., Ltd. Tetrahydrofuran (THF), aluminum trichloride ($AlCl_3$), and iron (II) chloride ($FeCl_2$) were purchased from Sigma-Aldrich and used without further purification. Titanium (IV) chloride ($TiCl_4$) was supplied from Merck. Anhydrous $MgCl_2$, n-hexane, and triethylaluminum (TEA) were donated by Thai Polyethylene Co., Ltd.

2.2. Catalyst Preparation Methods

2.2.1. $TiCl_4$/$MgCl_2$/THF Catalyst [2, 16]. A mixture of 2 g of anhydrous $MgCl_2$ (and Lewis acid if any) and 150 mL of tetrahydrofuran (THF) was added into the 500 mL three-necked round bottom flask equipped with magnetic stirrer. Then, 2 mL (0.87 mole) of $TiCl_4$ was injected dropwise. The reaction was heated up to 70°C and held for 3 h. After that, the reaction was cooled down to 40°C. The washing steps were carried out for 7 times with n-hexane prior to obtain the None-THF catalyst.

$TiCl_4$/$AlCl_3$/$MgCl_2$/THF and $TiCl_4$/$FeCl_2$/$MgCl_2$/THF were denoted as Al-THF and Fe-THF, respectively, as shown in Table 1. Lewis acid was directly added to $MgCl_2$ in THF solution. All modified catalysts were synthesized by the same procedure as used for the preparation of the unmodified catalyst (None-THF) excepting for adding anhydrous $AlCl_3$ for Al-THF and $FeCl_2$ for Fe-THF, with 0.07 mol/mol of Lewis acid/$MgCl_2$.

2.3. Polymerization Reaction

2.3.1. Effect of H_2/C_2H_4 Molar Ratio. Ethylene polymerization was performed in 2 L autoclave reactor connected with n-hexane liquid feed line and nitrogen, hydrogen, ethylene gas feed lines. Purification of reactor and all feed lines were conducted by evacuation and purging with nitrogen many times. After that, 1 L of n-hexane, triethylaluminum, and catalyst slurry (Al/Ti molar ratio = 140) were introduced into the reactor. Then the reaction was heated up to 67°C. At this temperature, 1 bar of nitrogen was filled and followed by the desired amount of hydrogen (H_2/C_2H_4 molar ratio = 0, 0.08, 0.20, and 0.30). Finally, the reactor was pressurized with the total pressure of 8 bars with ethylene at 75°C. The polymerization temperature and time were 80°C and 1 h, respectively. The obtained polymer was dried at room temperature overnight.

2.4. Characterizations

2.4.1. Catalyst

Inductively Coupled Plasma (ICP). Inductively coupled plasma optical emission spectrometer (ICP-OES optima 2100 DV from Perkin Elmer) was employed to determine element content in bulk. The catalyst sample was digested with 5 mL of hydrochloric acid and then diluted with DI water.

Fourier Transform Infrared Spectroscopy (FT-IR). The Fourier transforms infrared spectroscopy was applied with Nicolet 6700 FT-IR spectrometer with transmittance mode. The catalyst powder was prepared as a thin film on NaCl disk and kept under argon atmosphere during the analysis. The measurement was carried out in the range of scanning between 400 and 4000 cm^{-1} for 400 times.

X-Ray Diffraction (XRD). XRD was performed to identify phases and crystallinity of the catalyst and support samples using Bruker of D8 Advance. The sample was placed on holder under argon atmosphere to prevent air and moisture during the experiment. Diffraction patterns were recorded with the scanning speed of 0.3 second/step and step size 0.02 in the 2θ range of 10–80 degrees.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). SEM was used to identify the morphologies of catalyst, while EDX was applied to investigate the elemental distribution. The SEM of Hitachi mode S-3400N was employed. The EDX was performed using Link Isis series 300 program.

2.4.2. Polymer

Gel Permeation Chromatography (GPC). Molecular weight and molecular weight distributions of polymers were determined by using a high temperature GPC (Waters 150°C) equipped with a viscometric detector. The characterization was performed at 160°C and used 1,2,4-trichlorobenzene as a solvent.

Scanning Electron Microscopy (SEM). SEM was applied to determine the morphologies of the resultant polymers. The same equipment (as aforementioned) was carried out.

Differential Scanning Calorimetry (DSC). The melting temperature (T_m) and percentage of crystallinity (χ_c) of polyethylene were determined by DSC-TGA with TA Instruments

TABLE 2: The elemental composition of the prepared catalysts.

Catalyst	ICP measurement				EDX measurement			
	Element content (% wt)[a]			Ti/Mg (mol/mol)	Element content (% wt)[c]			Ti/Mg (mol/mol)
	Ti	Mg	M[b]		Ti	Mg	M[b]	
None-THF	4.07	6.87	—	0.30	6.52	24.32	—	0.14
Al-THF	2.96	6.51	0.97	0.23	9.56	24.50	2.65	0.20
Fe-THF	4.61	5.87	1.58	0.40	9.27	19.08	11.79	0.25

[a]Determined by ICP.
[b]M = Al or Fe.
[c]Determined by EDX.

SDT Q600 V8.1 Build 99. The characterization was performed at a heating rate of 10°C/min in the range of temperature = 30–600°C. The crystallinity of polymers was calculated by the following equation:

$$\chi_c = \left[\frac{\Delta H}{(\Delta H°)} \right] \times 100, \qquad (1)$$

where ΔH is heat of fusion of polyethylene sample.

$\Delta H°$ is that the heat of fusion of linear polyethylene equals to 290 J/g [16].

3. Results and Discussion

3.1. Catalyst Characterization. Table 2 reported the chemical compositions of all catalysts determined by ICP and EDX measurements. It was found that although the addition of TiCl$_4$ amount of all catalysts was fixed, the titanium contents in bulk, which were determined by ICP, were slightly changed compared with None-THF due to the presence of different Lewis acids on the support. This might be the fact that the Lewis acid modification can reduce free-vacancies of MgCl$_2$ crystallization and Ti insertion [17, 18]. Thus, the titanium content of Al-THF slightly decreased. According to this result, it is also in good agreement with the report by Coutinho and Xavier [19]. They observed that the addition of PCl$_3$ in TiCl$_4$/MgCl$_2$ via ball milling method decreased the Ti incorporation due to decrease of free-chloride crystal vacancies in the surface of milled MgCl$_2$ caused by the complexation of PCl$_3$. Furthermore, increasing of PCl$_3$ content can be attributed to the reduction of catalyst active sites resulting in drop in Ti incorporation. Nonetheless, Ti content in bulk of Fe-THF increased compared with None-THF. This is because the radius of iron (II) ions (Fe^{2+}) and the crystal compound structures (FeCl$_2$) were similar to Mg^{2+} and MgCl$_2$. Moreover, Tanase et al. [20] reported that the catalyst contained metal dichloride as a carrier material exhibited relatively high activity compared with MgCl$_2$. Therefore, FeCl$_2$ was considered as one of effective supports for anchoring TiCl$_4$ resulting in the improvement of Ti content. However, from the EDX result, it was found that all catalysts showed higher Ti content on catalyst surface than Ti content measured by ICP technique. This indicated that most Ti active sites were located on the surface of catalyst more than in the catalyst pores. In addition, the Lewis acid

contained catalysts showed a higher Ti/Mg ratio than that of unmodified catalyst. Fe-THF displays the highest Ti/Mg ratio. It indicated that a lot of Ti atoms can incorporate at MgCl$_2$ support.

3.1.1. FT-IR Spectroscopy of Catalysts. FT-IR spectroscopy was applied to define the interaction of TiCl$_4$ and MgCl$_2$ support as presented in Figure 1. Typically, IR spectra of the TiCl$_4$/MgCl$_2$ complex with THF were in the range of 1100–700 cm^{-1}, indicating the most sensitive to THF complexes with a metal center [21]. Many researchers reported that pure THF shows the symmetrical and asymmetrical C-O-C stretching bands around 913 cm^{-1} and 1071 cm^{-1}, respectively [21, 22]. However, TiCl$_4$/MgCl$_2$/THF catalysts modified with different Lewis acids (Al-THF and Fe-THF) exhibited a slight shift to the lower wavenumbers compared with None-THF. None-THF, Al-THF, and Fe-THF display the symmetrical C-O-C stretching bands at 883.4, 874.6, and 873.6, respectively, and its asymmetrical C-O-C stretching bands at 1032.6, 1025.1, and 1024.6, respectively. It indicated that metal halides incorporated with the Ti-Mg-THF bimetallic complex resulting in the lower frequencies of the C-O-C stretching bands of THF. Therefore, this result may cause an increase in the Lewis acidity of the active center [2, 3]. All catalysts also displayed C-H stretching band around 2885–2976 cm^{-1}. In addition, a neutral alkoxy Ti species, which are inactive, via the ring-opening of THF were also found [1]. These IR spectra were observed in the range of 3000–3600 cm^{-1}. These results are probably due to the fact that the interaction of MgCl$_2$ and THF can change the nature of Ti species through creating a transient cationic Ti mononuclear species, which finally leads to a neutral alkoxy Ti species via the ring-opening of THF [1].

3.1.2. XRD Measurement of Catalysts. XRD patterns of synthesized catalysts are reported in Figure 2. The peaks at $2\theta = 14.9°$, $30.2°$, $34.8°$, and $50.3°$ represent the high disorders of δ-form of MgCl$_2$ species, which are active for polymerization. The characteristic peaks of MgCl$_2$/THF complex were located at $2\theta = 20.4°$ and $32.0°$ [16, 17]. The XRD peak around $2\theta = 18.1°$ was also found and assigned as the creation of TiCl$_4$/MgCl$_2$/THF complex [23]. Moreover, the characteristic peaks of TiCl$_4$/THF complex and TiCl$_3$/THF complex were noticed at $2\theta = 11.1°$ and $17.8°$, respectively [16, 17, 23]. We did not observe the Lewis acid characteristic peak of Lewis acid
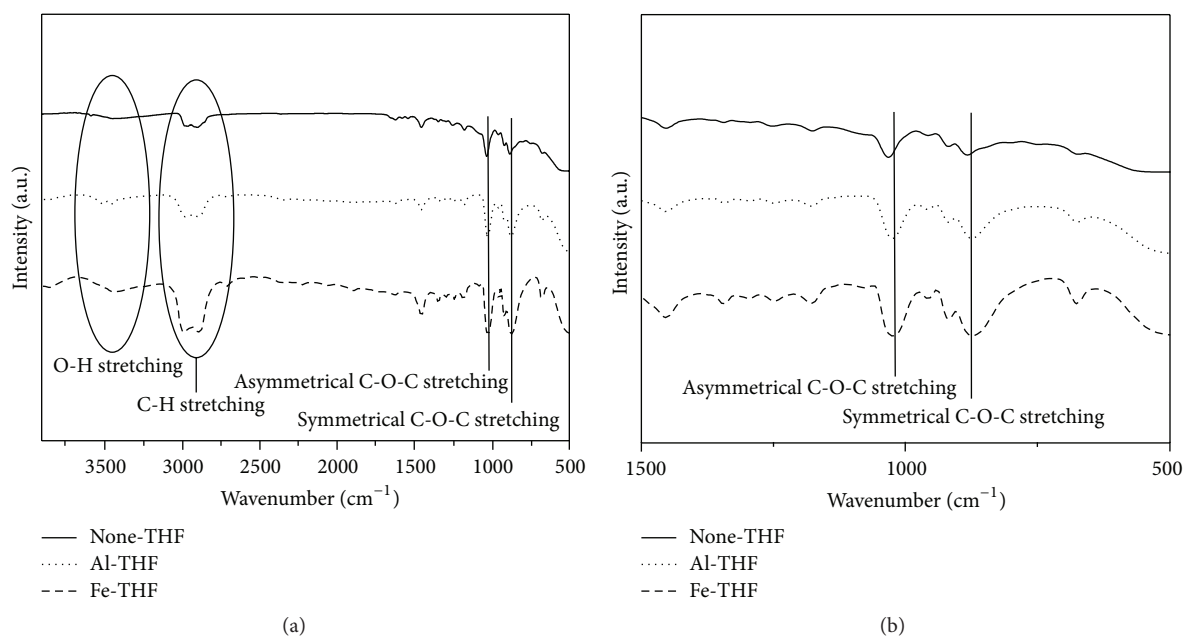
(a)

(b)

FIGURE 1: FT-IR spectra of catalysts: in the range of 500–3900 cm^{-1} (a), extend in the range of 500–1500 cm^{-1} (b).

modified catalysts because Lewis acid completely participated in TiCl$_4$/MgCl$_2$/THF structure [24, 25]. It can be suggested that the radius of Fe^{2+} (0.61 Å) is closer to Mg^{2+} (0.65 Å) than that of Al^{3+} (0.50 Å). Thus, the compatibility of FeCl$_2$ with MgCl$_2$ would be better than that of AlCl$_3$ with MgCl$_2$ [16, 26]. Due to the fact that Lewis acid can remove THF from MgCl$_2$/THF complex, therefore, Lewis acid presumably destroys the crystalline structure of MgCl$_2$/THF complex. This results in the lowering or loss in magnitude of XRD peaks at $2\theta = 20.4°$ and $32.0°$.

3.1.3. SEM Images of Catalysts.

Typical SEM images are shown in Figure 3. It can be seen that None-THF is in irregular shape while modified catalysts with Lewis acid (Al-THF and Fe-THF) are in shape of bar.

3.2. Catalytic Activity

3.2.1. Effect of Lewis Acids Modification on the Catalytic Activity in the Absence of Hydrogen.

According to Table 3, Lewis acid modification by adding AlCl$_3$ and FeCl$_2$ can improve the activity around 17% and 86% increase, respectively, compared with the activity of unmodified catalyst. This is because of the formation of acidic sites by modifying the catalysts with Lewis acids [2]. In addition, AlCl$_3$ and FeCl$_2$ could also remove THF in catalyst resulting in enhancement in the activity of ethylene polymerization. The remaining THF of MgCl$_2$·THF structure in the final catalyst leads to the reduction in catalytic activity because the remaining THF can poison the catalyst active sites [5]. THF occupies the coordination sites of Ti to make Ti a neutral alkoxy Ti species, which is an inactive center, via the ring-opening of THF [1]. Moreover, TEA can also coordinate with THF and remove some THF from the
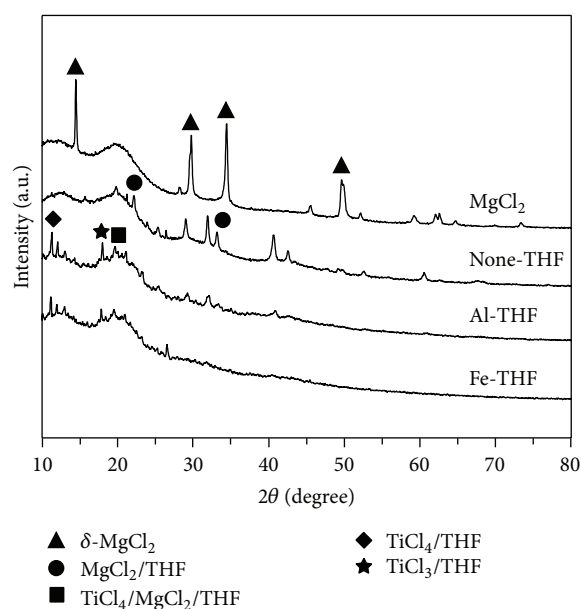

FIGURE 2: XRD patterns of prepared catalysts.

Ti center and then provide higher catalytic activity [5]. Chen and Fan [27] stated that the active center distribution of TiCl$_4$/MgCl$_2$ could change by doping AlCl$_3$, which can be observed by the polymer GPC curves through multiple Flory components. From the formation of more types of active center, Al-Mg-THF complex [28] leads to an improvement of catalyst performance. As mentioned earlier about the similar ionic radii of Fe and Mg, it could then be stated that FeCl$_2$ was more efficient to incorporate with MgCl$_2$ than AlCl$_3$. Therefore, Fe-THF gave higher activity than Al-THF.
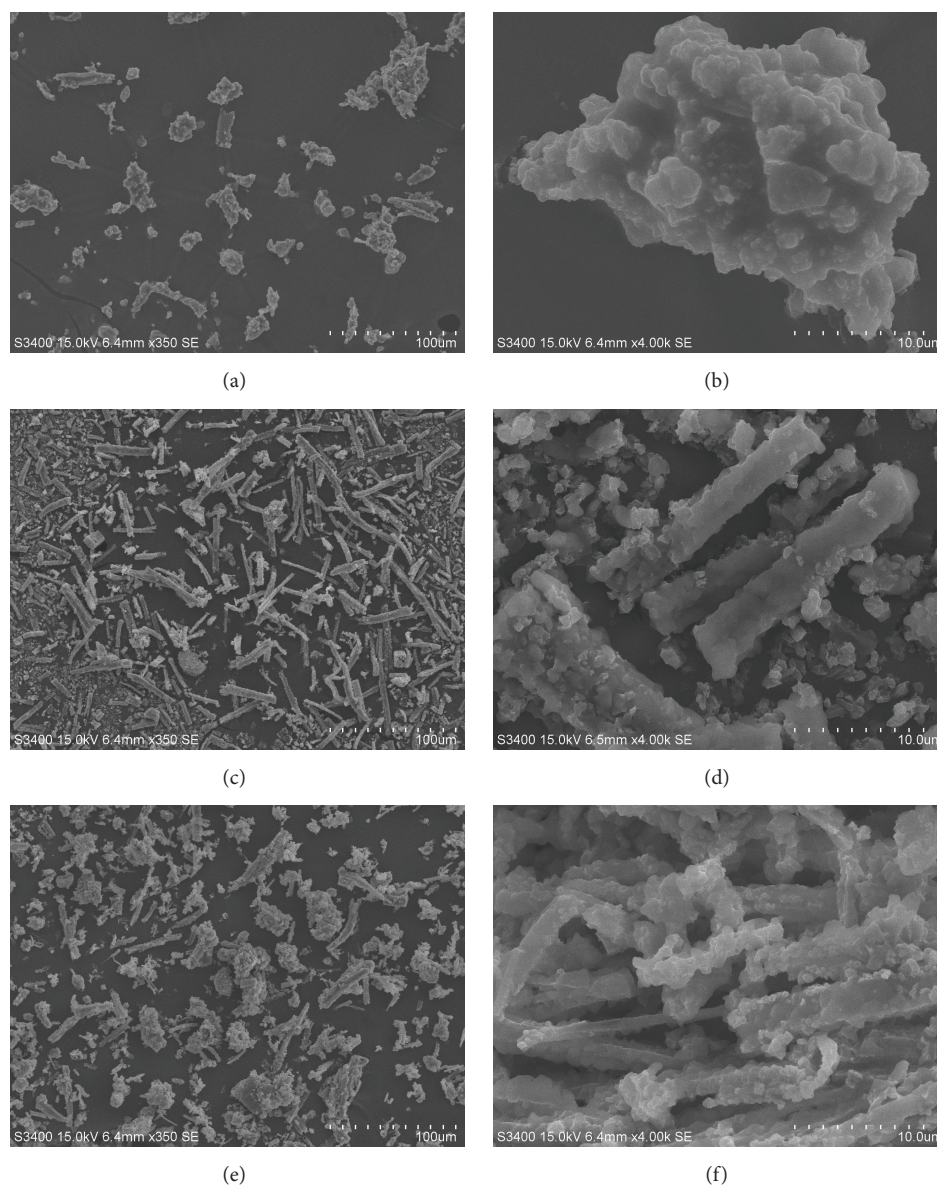
(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 3: SEM images of prepared catalysts: ((a), (b)) None-THF, ((c), (d)) Al-THF, and ((e), (f)) Fe-THF.

3.2.2. Effect of Lewis Acids Modification on Hydrogen Response for Ethylene Polymerization. $TiCl_4/MgCl_2/THF$ catalysts modified with Lewis acids ($AlCl_3$ and $FeCl_2$) were conducted in ethylene polymerization in the presence of various hydrogen pressures for comparative study on catalytic activities. The polymerization activities results of $TiCl_4/Lewis$ acid/$MgCl_2/THF$ catalysts are summarized in Table 3. Catalysts modified with Lewis acid presented the higher hydrogen response than unmodified catalyst, especially Fe-THF. Hydrogen response is high even in the system that has a small amount of hydrogen. Only small additional amount of hydrogen at H_2/C_2H_4 molar ratio of 0.08 results in 34% decrease in activity for Al-THF and 67% decrease in activity for Fe-THF. This indicates high hydrogen response for these catalysts in this H_2/C_2H_4 molar ratio period. From these results, this is probably due to increasing in acidic sites [2] by

doping Lewis acid. Therefore, addition of Lewis acid causes the formation of more clustered active center leading to obtaining more chances to proceed chain transfer reaction by hydrogen. This result is in good agreement with article reported by Kouzai et al. [29]. They revealed that chain transfer reactions by hydrogen will occur when hydrogen dissociation sites are located in the instant surrounding of polymerization sites. Thus, the more the clustered active species, the higher the hydrogen response. In part of higher hydrogen amount at H_2/C_2H_4 molar ratio of 0.2–0.3, the increment of hydrogen pressure in the system was conducted. Activity of all catalysts did not change much compared with its activity in the less-hydrogen system (H_2/C_2H_4 molar ratio of 0.08). It could be implied that most of active sites were deactivated by hydrogen. The reason is that the creation of titanium-hydride bond, which is less active, was higher.
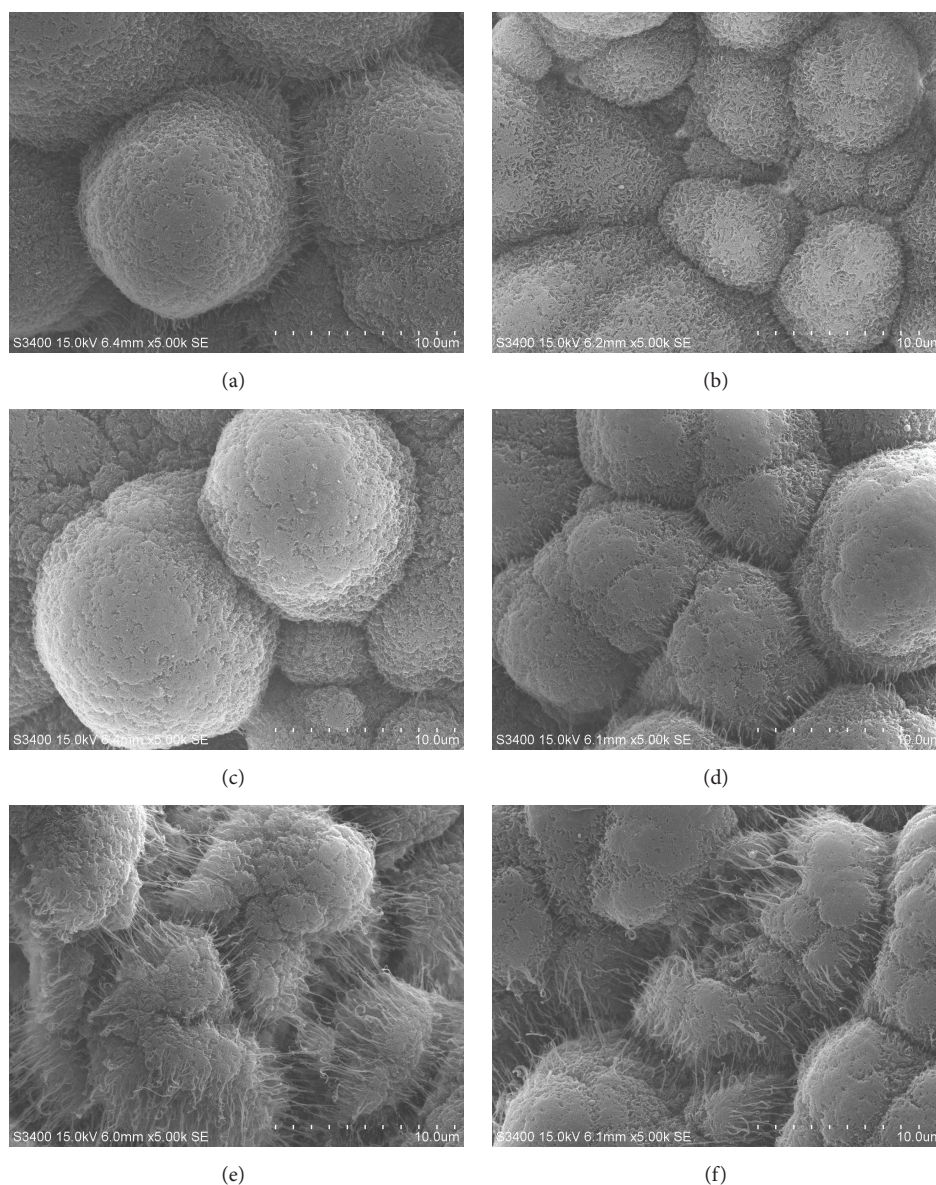
(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 4: SEM images of the polyethylene obtained by (a) None-THF, (c) Al-THF, and (e) Fe-THF in the absence of H_2 and (b) None-THF, (d) Al-THF, and (f) Fe-THF at H_2/C_2H_4 molar ratio = 0.30.

Moreover, only the uncoordinated Ti-C_2H_5 bond is capable of reaction with ethylene monomer to generate the chain growth reaction [30–32]. This results in the reduction in activity and lower hydrogen response. Fe-THF is considered as a more clustered catalyst than Al-THF because it has higher Ti content than Al-THF. Moreover, catalyst having less titanium content, Al-THF, exhibited a less deactivation effect than the catalyst having higher titanium content, Fe-THF, due to the less amount of surface active site being able to react with TEA. Therefore, Fe-THF indicated the higher hydrogen response which showed rapidly dropped activity than Al-THF. However, a higher Ti content has a higher stereospecificity than a lower Ti content forming an isolated Ti site [29, 33, 34]. As a consequence, one of the possible reasons was the aggregation of Ti species which caused the reduction of active

site concentration, resulting in remarkable depression of the monomer consumption [33] and finally decrease in activity. This result is in good agreement with the report of Taniike et al. [33]. They investigated the catalytic performance through the isolated and clustered Zeigler-Natta catalysts in ethylene and propylene homopolymerization. They also found that the isolated Ti species located on the $MgCl_2$ surface which acted as the loss of Ti-Ti interaction led to higher activity in both ethylene and propylene polymerization with $TiCl_3/MgCl_2$ model catalyst.

3.3. Polymer Characterization. The morphologies of obtained polyethylene are shown in Figure 4. It could be reported that all catalysts, including with and without Lewis acid modification, provided the similar morphology of polymer.

TABLE 3: Catalytic activity of different doped Lewis acid catalysts in ethylene polymerization.

Catalyst	H_2/C_2H_4 molar ratio	Activity[a] (kg PE/gTi ∗ h)	Activity ratio without H_2	Activity ratio with H_2
None-THF	0	732	1.00	1.00
	0.08	645	—	0.88
	0.20	362	—	0.49
	0.30	313	—	0.43
Al-THF	0	854	1.17	1.00
	0.08	560	—	0.66
	0.20	279	—	0.33
	0.30	246	—	0.29
Fe-THF	0	1364	1.86	1.00
	0.08	452	—	0.33
	0.20	330	—	0.24
	0.30	375	—	0.28

[a]Condition: polymerization was performed in 2 L autoclave, [Ti] = 0.008 mmol for all catalysts, Al/Ti molar ratio = 140, cocatalyst = TEA, polymerization time = 1 h, reaction temperature = 80°C, total pressure = 8 bars under 1 bar of nitrogen, and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.20, and 0.30.

TABLE 4: Influences of Lewis acids and hydrogen on polyethylene.

Catalyst	H_2/C_2H_4 molar ratio	Melting temperature[a] (T_m) in °C	Crystallinity[a] (χ_c) in %	Mw[b] (g/mol)	Mn[b] (g/mol)	Mw/Mn[b]
None-THF	0	132.9	55.4	—	—	—
	0.08	131.2	58.0	452,127	74,155	6.1
	0.20	129.8	59.7	249,214	40,292	6.2
	0.30	129.0	56.2	178,786	31,277	5.7
Al-THF	0	133.8	54.7	—	—	—
	0.08	131.2	60.7	335,552	53810	6.2
	0.20	130.0	60.1	204,614	35,852	5.7
	0.30	130.1	68.5	189,568	33,557	5.7
Fe-THF	0	134.2	52.8	—	—	—
	0.08	131.9	55.7	370,021	56,998	6.5
	0.20	130.0	66.8	230,272	35,756	6.4
	0.30	130.0	62.8	201,312	29,107	6.9

[a]Determined by DSC.
[b]Determined by GPC.
Condition: polymerization was performed in 2 L autoclave, [Ti] = 0.008 mmol for all catalysts, Al/Ti molar ratio = 140, cocatalyst = TEA, polymerization time = 1 h, reaction temperature = 80°C, total pressure = 8 bars under 1 bar of nitrogen, and desired amount of H_2/C_2H_4 molar ratio = 0, 0.08, 0.20, and 0.30.

Not only in the absence of hydrogen case, but also in the presence of hydrogen, the morphologies of resultant polymer were also similar.

3.3.1. Effect of Lewis Acids Modification on Polyethylene Properties.
According to Table 4, polymers producing from Al-THF and Fe-THF without additional hydrogen exhibited a slight increase in melting temperature, but Lewis acid modification (Al-THF and Fe-THF) decreases crystallinity when compared with None-THF. These are the results from utilizing of the different types of Lewis acids. All catalysts produce polymers having the similar Mw/Mn, which are quite narrow Mw/Mn. This is because the doped and undoped catalysts had basically the same types of active sites [26].

3.3.2. Effect of Hydrogen on Polyethylene Properties.
As presented in Table 4, the molecular weight of polymer decreased when hydrogen increased because chain termination reaction by hydrogen occurred. As a consequence, the melting temperature decreases due to the decrease in molecular weight of polyethylenes. In addition, the increase in hydrogen pressure tends to increase the crystallinity of all polymers [8]. This is because the polymerization rate is reduced by hydrogen resulting in increase in crystallization rate [8]. Mw/Mn of

all polymers did not change much at the different levels of hydrogen. This result is in agreement with that of Li Pi Shan et al. [13].

4. Conclusion

In conclusion, Lewis acid modification by using metal halide ($AlCl_3$ and $FeCl_2$) can improve activity due to the formation of acidic sites and the elimination of the remaining THF in the final catalyst as proven by XRD. In addition, $FeCl_2$ showed higher efficiency to remove the remaining THF in $MgCl_2$ structure than $AlCl_3$. Thus, the activity was in the order of Fe-THF > Al-THF > None-THF. In the presence of hydrogen, Fe-THF is considered to have more clustered Ti species than Al-THF. Therefore, Fe-THF showed a higher hydrogen response than Al-THF due to the titanium distribution. The increase in hydrogen results in the decrease in melting temperature, but it tends to increase the crystallinity of all polymers.

Additional Points

Research Highlights. (i) Active center distribution has a strong effect on $TiCl_4/MgCl_2/THF$ performances. (ii) The study on the active center distribution has not been yet clarified because of the limitation of characterization apparatus. (iii) Hydrogen response is considered to be one of the most effective ways to describe how the active sites dispersed in Ziegler-Natta catalysts. (iv) Lewis acid modification can improve activity due to the formation of acidic sites and removing the remaining THF in the catalyst. (v) Fe-THF is considered as a more clustered Ti species than Al-THF. (vi) $FeCl_2$-doped catalyst showed a higher hydrogen response than $AlCl_3$ doped catalyst due to its Ti distribution.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

Acknowledgments

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