

CHAPTER V

RESULTS AND DISCUSSIONS

5.1 Ethylene Polymerization on the Prepared Catalyst

5.1.1 The Effect of Al_(TMA)/Zr Mole Ratio on Catalytic Activity

The effect of Al_(TMA)/Zr mole ratio was studied with SiO₂/Cl₂Si(CH₃)₂/MAO-Cp₂ZrCl₂ catalyst. Trimethylaluminum (TMA) was used as cocatalyst when the molar ratio of Al_(TMA)/Zr was varied in the range of 500 to 5000. The polymerizations were carried out in toluene solvent at 40°C for 30 min. using 80 psi of ethylene, 100 mg of catalyst precursor and zirconium concentration of 6.6667x10⁻⁵ M with total solution volume of 15 ml. The results of the influence of Al_(TMA)/Zr mole ratio on the catalytic activity are shown in Table 5.1 and Figure 5.1.

Table 5.1 Catalytic activity at different Al_(TMA)/Zr mole ratios^a

Al _(TMA) /Zr Mole Ratio	Yield (g)	Catalytic Activity (kg PE/mol Zr.h)
500	0.7015	1403
1000	0.8300	1660
2000	1.1560	2312
3000	1.9050	3810
4000	1.7355	3471
5000	1.6495	3299

^a polymerization conditions: [Zr] = 6.6667x10⁻⁵ M, precursor = 100 mg, 40°C, 30 min, 80 psi, total volume = 15 ml

(The data of yield and catalytic activity are the average values of two times for each experiment.)

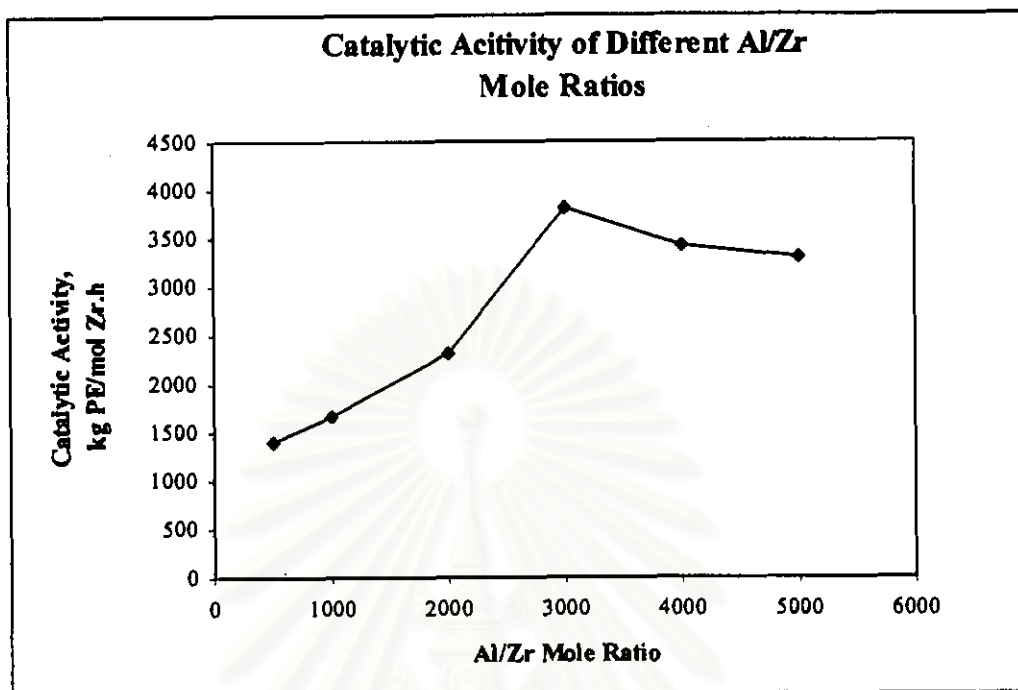


Figure 5.1 Catalytic activity at different $[Al]_{TMA}/[Zr]$ mole ratios

From Figure 5.1, the activity shows a tendency to increase with increasing $Al_{(TMA)}/Zr$ mole ratio. The maximum activity is achieved at $Al_{(TMA)}/Zr$ as 3000 and then the activity gradually decreases at higher mole ratios. It is interesting to attribute that TMA is the activator, which alkylates zirconocene complex and improves the catalytic activity in the ethylene polymerization [109].

The decreasing activity at higher $Al_{(TMA)}/Zr$ mole ratios may concern with the appropriate oxidation state of catalytic species for the polymerization. It has been suggested that the active species for ethylene polymerization is Zr^{4+} [150-151]. Based on this consideration, a higher concentration of TMA, which is a strong reducing agent in the catalytic system, favors the reduction of Zr^{4+} to inactive Zr^{3+} species in the ethylene polymerization [152].

As describe above, it can be noted that the concentration of TMA in catalytic system affects to the activity in ethylene polymerization. If the amount of TMA is insufficient or excess, the catalytic activity decreases. Therefore, it has to use

the optimum concentration of TMA in the catalytic system to achieve the maximum catalytic activity for ethylene polymerization.

5.1.2 The Effect of Catalyst Concentration on Catalytic Activity

The effect of catalyst concentration was investigated with $\text{SiO}_2/\text{Cl}_2\text{Si}(\text{CH}_3)_2/\text{MAO-Cp}_2\text{ZrCl}_2$ catalyst. The catalyst concentration was tested in the range of 3.3333×10^{-5} M to 1×10^{-4} M. The polymerizations were performed in toluene at 40°C for 30 min. using 80 psi of ethylene, 100 mg of catalyst precursor with $\text{Al}_{(\text{TMA})}/\text{Zr}$ mole ratio of 3000, and total solution volume of 15 ml. The results for the effect of catalyst concentration on the catalytic activity are shown in Table 5.2 and Figure 5.2.

Table 5.2 Catalytic activity of different catalyst concentrations^b

Catalyst Concentration, [Zr] ($\times 10^5$ M)	Mole of Zr ($\times 10^7$ mole)	Yield (g)	Catalytic Activity (kg PE/mol Zr.h)
3.3333	5.0	0.9160	3664
5.0000	7.5	1.7149	4573
6.6667	10.0	1.9050	3810
8.3333	12.5	1.8225	2916
10.0000	15.0	1.8052	2407

^b polymerization conditions: $\text{Al}_{(\text{TMA})}/\text{Zr} = 3000$, precursor = 100 mg, 40°C , 30 min, 80 psi, total volume = 15 ml

(The data of yield and catalytic activity are the average values of two times for each experiment.)

From the results given in Table 5.2 and Figure 5.2, the catalytic activity increases markedly with an increase in the amount of catalyst and the activity is shown the highest at the catalyst concentration of 5.0×10^{-5} M. Then, the activity at its higher catalyst concentration decreases drastically with raising the catalyst concentration.

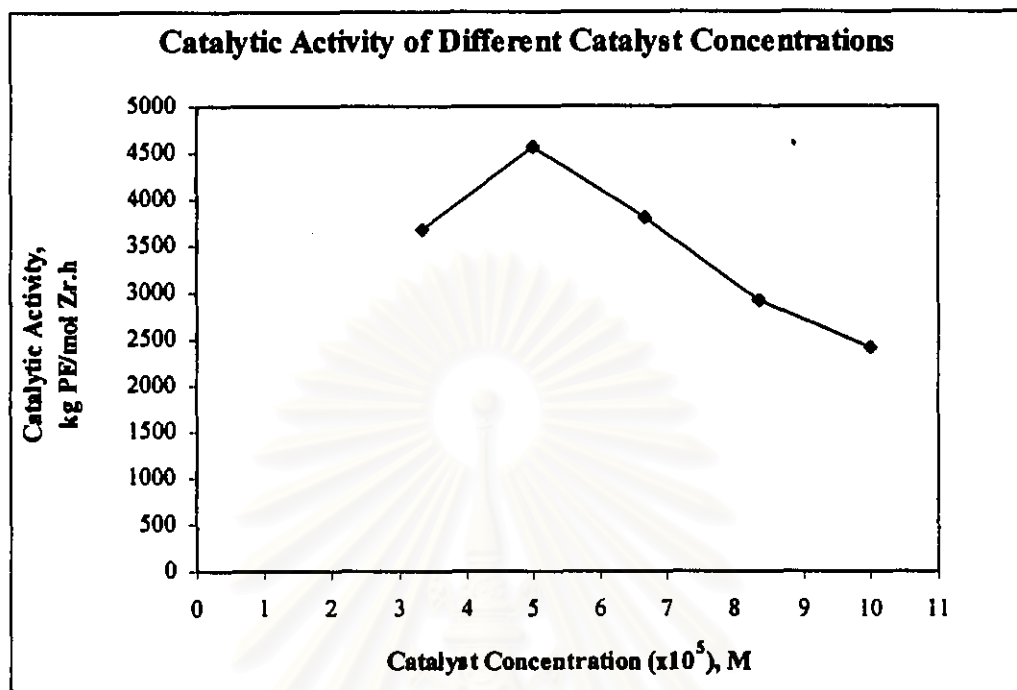
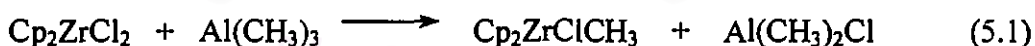
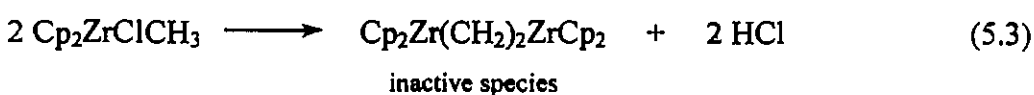
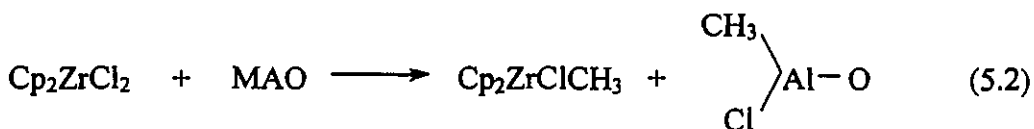


Figure 5.2 Catalytic activity of different catalyst concentrations

The general mechanism proposed by Giannini *et al.* is that Cp_2ZrCl_2 is monoalkylated by trimethylaluminum (TMA) to give Cp_2ZrClMe as shown in equation 5.1 [116].



However, at high catalyst concentration, a complexation of two $\text{Cp}_2\text{ZrClCH}_3$ is formed to the inactive species suggested by the mechanism for $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ which is illustrated in equations 5.2 and 5.3 [29, 100]. It is important that the inactive species which undergoes reaction in equation 5.3 causes the intermediate deactivation.



The mechanism of formation of active species probably comprises with the following reactions presented in Figure 5.3. The calcined SiO_2 is reacted with $\text{Cl}_2\text{Si}(\text{CH}_3)_2$ followed by treatment with aqueous sodium hydrogen carbonate to obtain the modified SiO_2 . Its surface structure is well defined and it is quite to control precisely the content of Si-OH groups. It may be due to the capability of silane compound to distribute the hydroxyl group on SiO_2 surface.

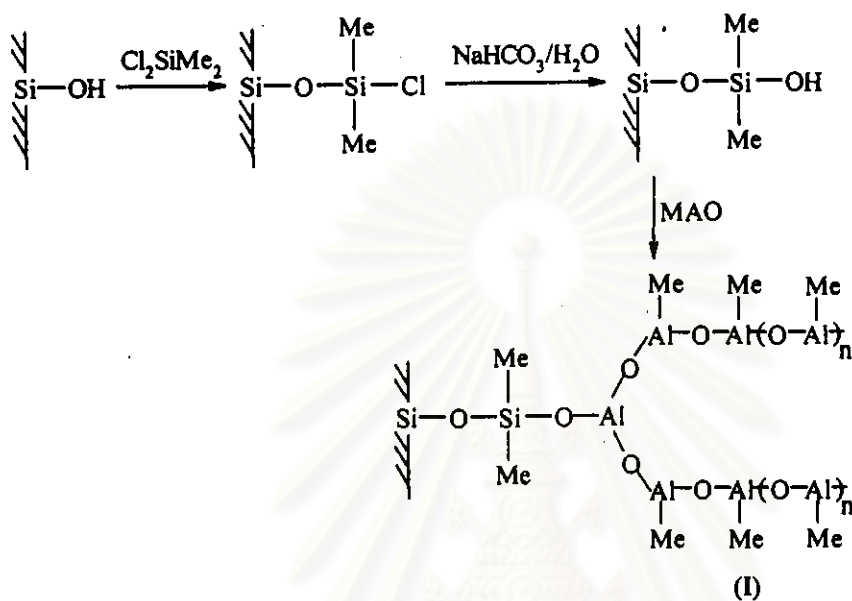
Next, the modified SiO_2 is brought into contact with MAO to yield the catalyst precursor. MAO would react with the surface hydroxyls in the modified silica surface to form the stable Si-O-Al bond. [29]

For the preactivation of Cp_2ZrCl_2 and TMA, possibly Cp_2ZrCl_2 first is monoalkylated by TMA to form Cp_2ZrClMe . And then it interacts with the MAO fixed on the modified SiO_2 surface. The surface MAO removes a Cl^- ion from Cp_2ZrClMe and produces the cationic. Zirconocene methyl species floats over the solid surface, much like in solution. Both ionic species are postulated to be trapped and stabilized as multi-coordinated "crown" aluminoxane complexes. These complex would be quite stable against dissociation. [11, 110]

From this consideration, it may be announced that the increasing catalytic activity with the raise of catalyst concentration is ascribed to the building up of $\text{Cp}_2\text{ZrClCH}_3$ which results in the active species. Catalyst concentration above 5.0×10^{-5} M causes the decrease in activity. This is generally elucidated to the formation of $\text{Cp}_2\text{Zr}(\text{CH}_2)_2\text{ZrCp}_2$ inactive species.

Mechanism of Formation of Active Species

The catalyst precursor formation



Preactivation of Cp_2ZrCl_2 and TMA



The active species formation

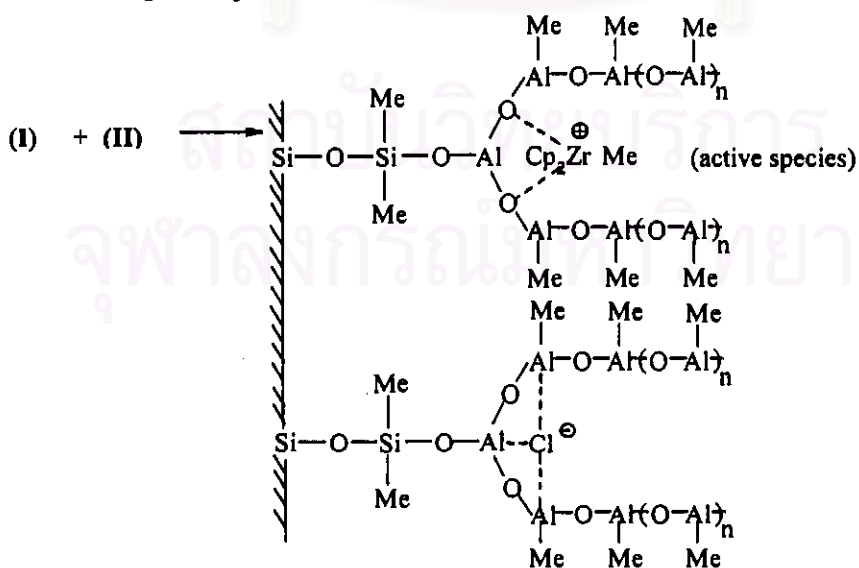


Figure 5.3 Mechanism of formation of active species [11,18,110]

5.1.3 The Effect of Polymerization Temperature on Catalytic Activity

The influence of the polymerization temperatures (T_p) was investigated with different polymerization temperature viz., 30, 40, 50, 60, and 80°C. The other parameters such as $Al_{(TMA)}/Zr$ mole ratio, Zr concentration and polymerization time were fixed at 3000, 5.0×10^{-5} M and 30 minutes, respectively and using 100 mg of catalyst precursor. Table 5.3 and Figure 5.4 illustrate the results for the influence of temperature on catalytic activity.

Table 5.3 Catalytic activity of different polymerization temperatures^c

Polymerization temperature (°C)	Yield (g)	Catalytic Activity (kg PE/mol Zr.h)
30	1.0398	2773
40	1.7149	4573
50	1.9155	5108
60	2.1935	5849
80	1.9841	5291

^c polymerization conditions: $[Zr] = 5 \times 10^{-5}$ M, $Al_{(TMA)}/Zr = 3000$, precursor = 100 mg,
30 min, 80 psi, total volume = 15 ml

(The data of yield and catalytic activity are the average values of two times for each experiment.)

The results reported in Figure 5.4 indicates that the activity is enhanced with increasing polymerization temperature. Maximum catalytic activity is reached at 60°C and slowly decreases with a further increase of temperature.

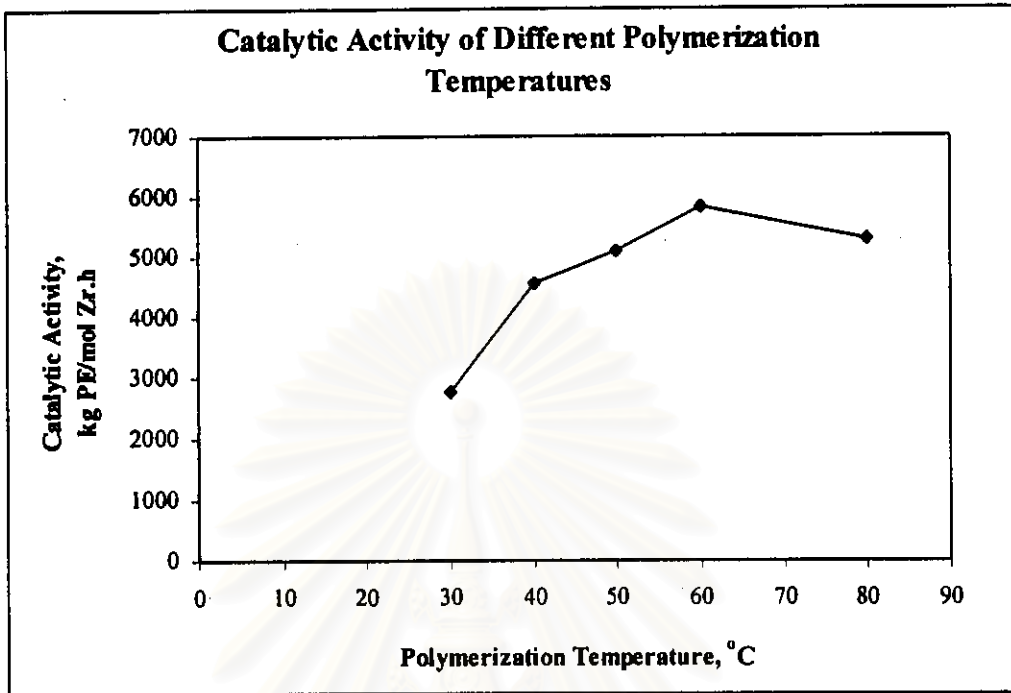
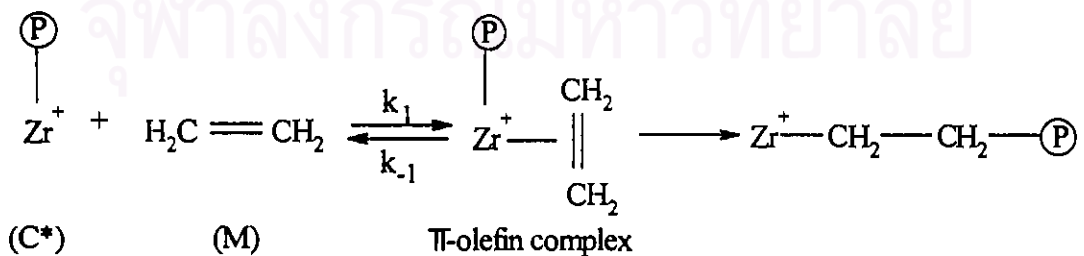


Figure 5.4 Catalytic activity of different polymerization temperatures

The above results can be explained by a widely accepted mechanism of propagation in Ziegler-Natta catalysis which involves the initial formation of a π -complex of an olefin with the catalyst metal, followed by chain migratory insertion [129].

Using the same mechanism, the propagation process in zirconocene system for olefin polymerization can be written as ,



when C^* = active site

M = monomer

$\textcircled{\text{P}}$ = polymer chain

In the low polymerization temperature range, the π -olefin complex is more stable which is associated to the process of activated insertion. This affects to the increase of activity with the increasing polymerization temperature (T_p). On the other hand, the decline in activity with further rising T_p probably involves the readily dissociation of the complex causing the low propagation rate. In other words, reduced catalytic activity may be attributed to the deactivation of the catalytic species [67,153].

5.1.4 The Effect of Ethylene Pressures on Catalytic Activity

Ethylene polymerization was conducted using parameters at polymerization temperature 60°C , $\text{Al}_{(\text{TMA})}/\text{Zr}$ mole ratio of 3000, zirconium concentration of 5.0×10^{-5} M and polymerization time of 30 minutes. The various ethylene pressures were examined at 10, 30, 50, 70 and 80 psi. The results are summarized in Table 5.4 and the graphical plot of catalytic activity versus ethylene pressure is presented in Figure 5.5.

Table 5.4 Catalytic activity of different ethylene pressures^d

Ethylene Pressure (psi)	Yield (g)	Catalytic Activity (kg PE/mol Zr.h)
10	0.8240	2197
30	1.2585	3356
50	1.6358	4362
70	2.0783	5542
80	2.1935	5849

^d polymerization conditions: $[\text{Zr}] = 5 \times 10^{-5}$ M, $\text{Al}_{(\text{TMA})}/\text{Zr} = 3000$, precursor = 100 mg, 60°C , 30 min, total volume = 15 ml

(The data of yield and catalytic activity are the average values of two times for each experiment.)

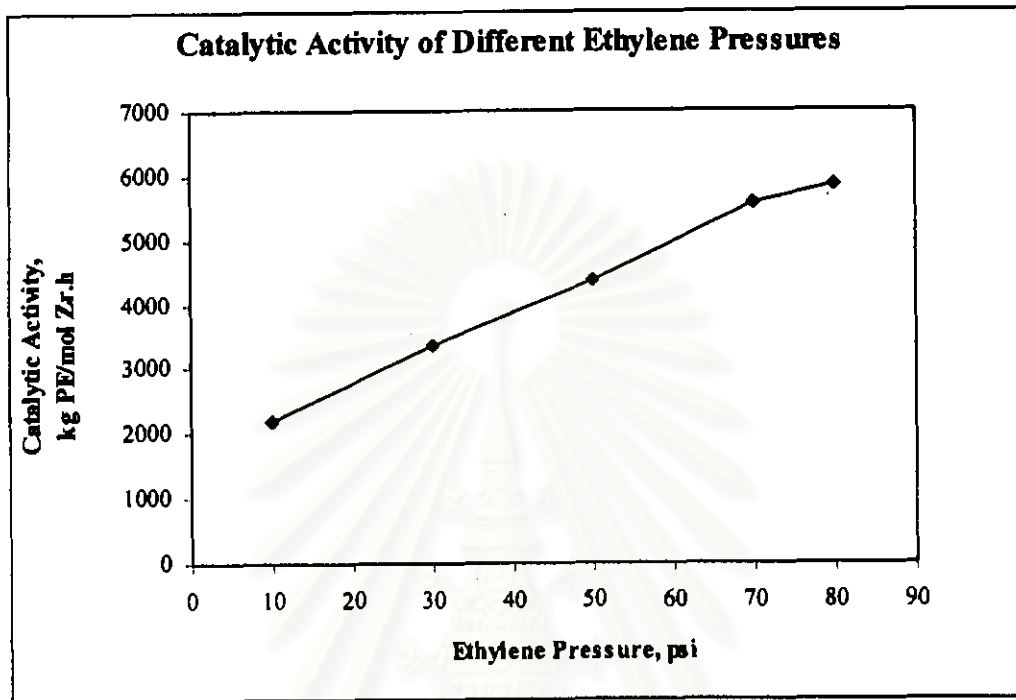


Figure 5.5 Catalytic activity of different ethylene pressures

As shown in Figure 5.5, the activity increases nearly linearly with the increase of ethylene pressure. In slurry polymerization, increasing of monomer pressure promotes the reaction rate due to the increasing monomer concentration. According to a kinetic model proposed by Chien, it is shown as following [53].

$$R_p = k_p[C^*][M]$$

When R_p = rate of polymerization

k_p = the propagation rate constant

$[C^*]$ = concentration of active species

$[M]$ = concentration of monomer

It is reasonable to note that the productivity depends on the monomer concentration. Chien also found that increasing the ethylene pressure increases the

concentration of ethylene diffused into the media, subsequently, it leads to the rise of the catalytic activity. Thus catalytic activity increases as the ethylene pressure is increased.

5.1.5 The Effect of Various Silane Compounds on Catalytic Activity

Ethylene polymerization was performed keeping other parameters unchanged at polymerization temperature 60°C, zirconium concentration $5.0 \times 10^{-5} \text{ M}$, $\text{Al}_{(\text{TMA})}/\text{Zr}$ mole ratio at 3000, ethylene pressure of 80 psi and polymerization time 30 of minutes. Several kinds of silane compounds; ClSiMe_3 , Cl_2SiMe_2 , Cl_3SiMe , and SiCl_4 , were used to obtain the modified silica. The typical results of ethylene polymerization are shown in Table 5.5 and Figure 5.6.

Table 5.5 Catalytic activity of various silane compounds^c

Type of Silane Compounds	Yield (g)	Catalytic Activity (kg PE/mol Zr.h)
No silane	0.4808	1282
ClSiMe_3	0.6511	1736
Cl_2SiMe_2	2.1935	5849
Cl_3SiMe	2.3523	6273
SiCl_4	2.6120	6965

^c polymerization conditions: $[\text{Zr}] = 5 \times 10^{-5} \text{ M}$, $\text{Al}_{(\text{TMA})}/\text{Zr} = 3000$, precursor = 100 mg, 60°C, 80 psi, 30 min, total volume = 15 ml

(The data of yield and catalytic activity are the average values of two times for each experiment.)

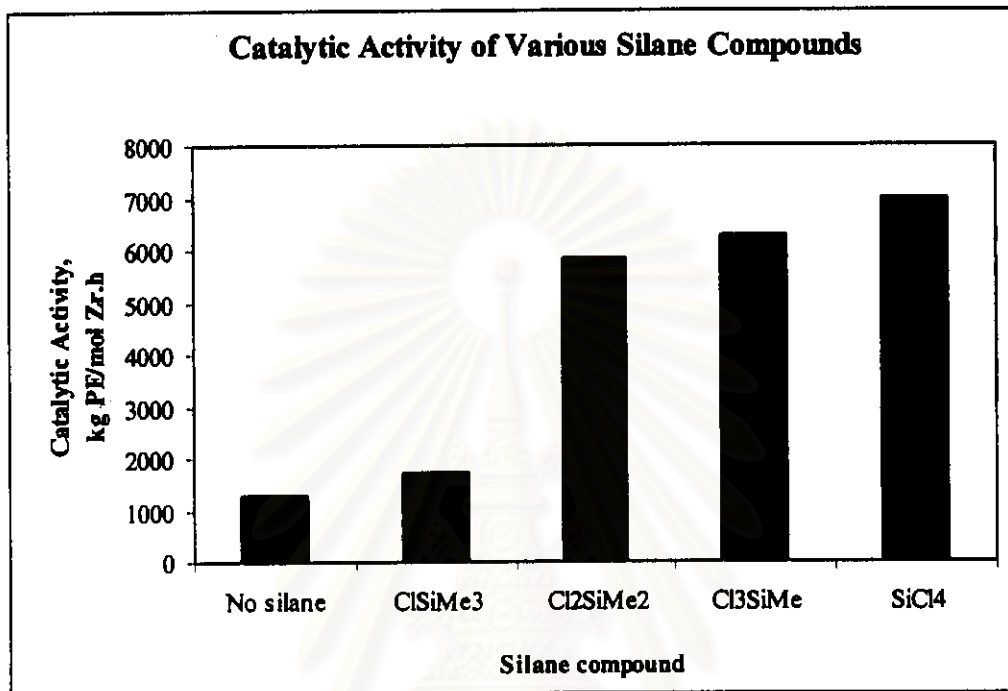


Figure 5.6 Catalytic activity of different silane compounds

It is instantaneously obvious from Table 5.5 and Figure 5.6 that SiCl₄ shows the highest activity among the silane compounds used in this study and we can observe an increase of activity that parallels the increase of number of chlorine atom of the silane compound, following the order SiCl₄ > Cl₃SiMe > Cl₂SiMe₂ > ClSiMe₃ > no silane. A plausible explanation is that the chlorine atom(s) of silane compound being on the silica surface can be exchanged to hydroxyl group(s) by reacting with aqueous solution of sodium hydrogen carbonate to obtain the modified silica. The increase of number of the hydroxyl group(s) probably leads the increasing attached MAO on the modified silica that enhances the catalytic activity. However, the activity has not been tripled and doubled corresponding to the number of hydroxyl group(s) in case of the modified silica treated with SiCl₄ and Cl₃SiMe, respectively. This can be considered that MAO can react with some of hydroxyl group(s) whereas the others still remain because of the bulkiness of reacted MAO which can block the vicinal hydroxyl group(s) thus makes it more difficult for other MAO to attach.

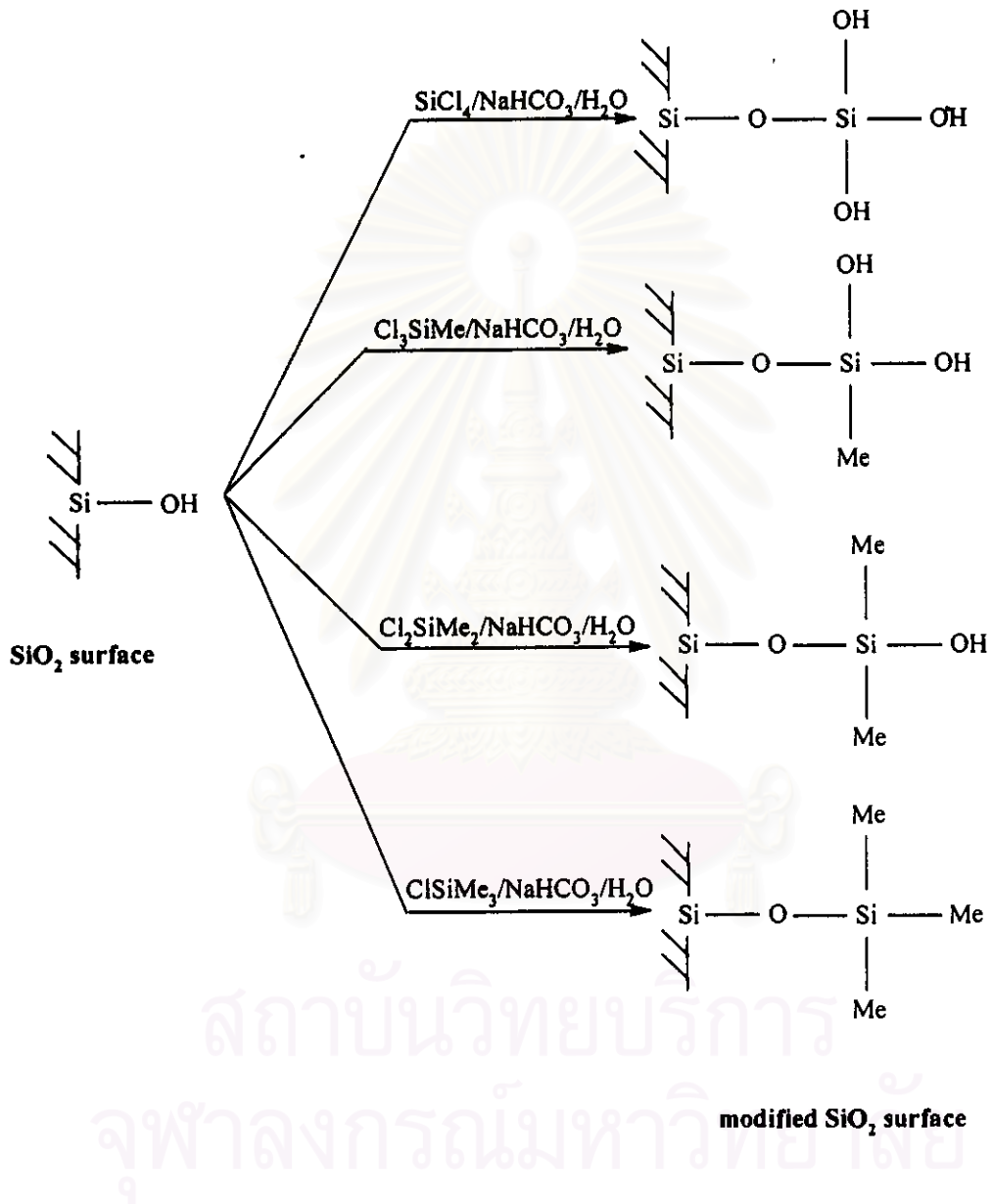


Figure 5.7 Proposed model of hydroxyl groups on the modified SiO₂ surface

5.2 Characterization of Catalyst Precursor

5.2.1 Morphology

Morphology of prepared catalyst precursor using Scanning Electron Microscope (SEM) is presented in Figure 5.8 whereas Figure 5.9 shows the SEM picture of silica. It is found that most of the catalyst precursors are globulelike which replicate the shape of the silica particles.

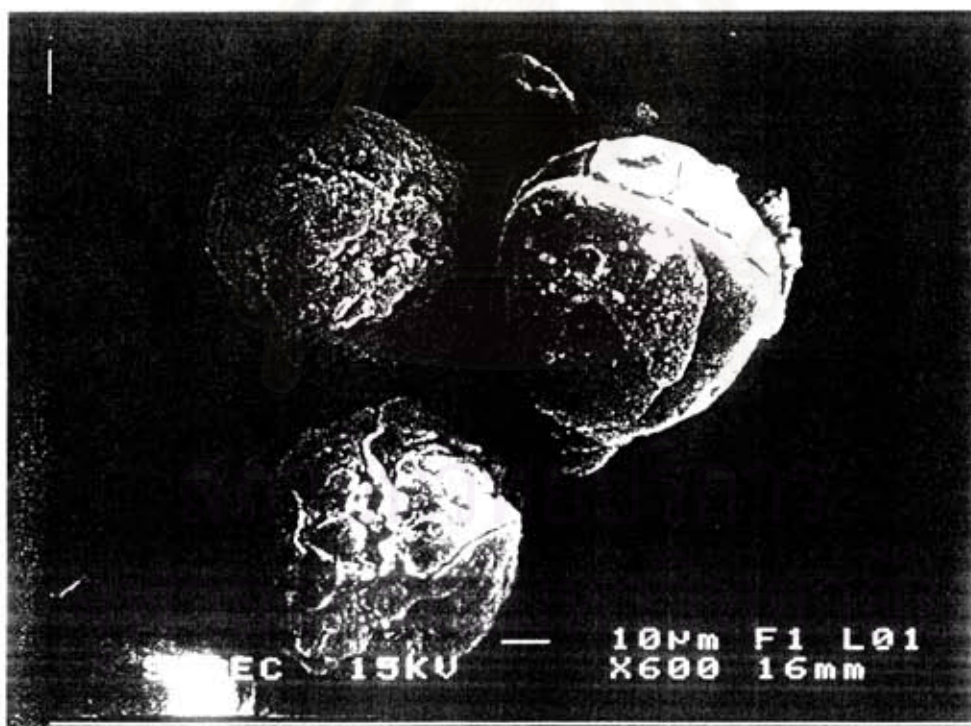


Figure 5.8 Scanning electron microscope image of prepared catalyst precursor

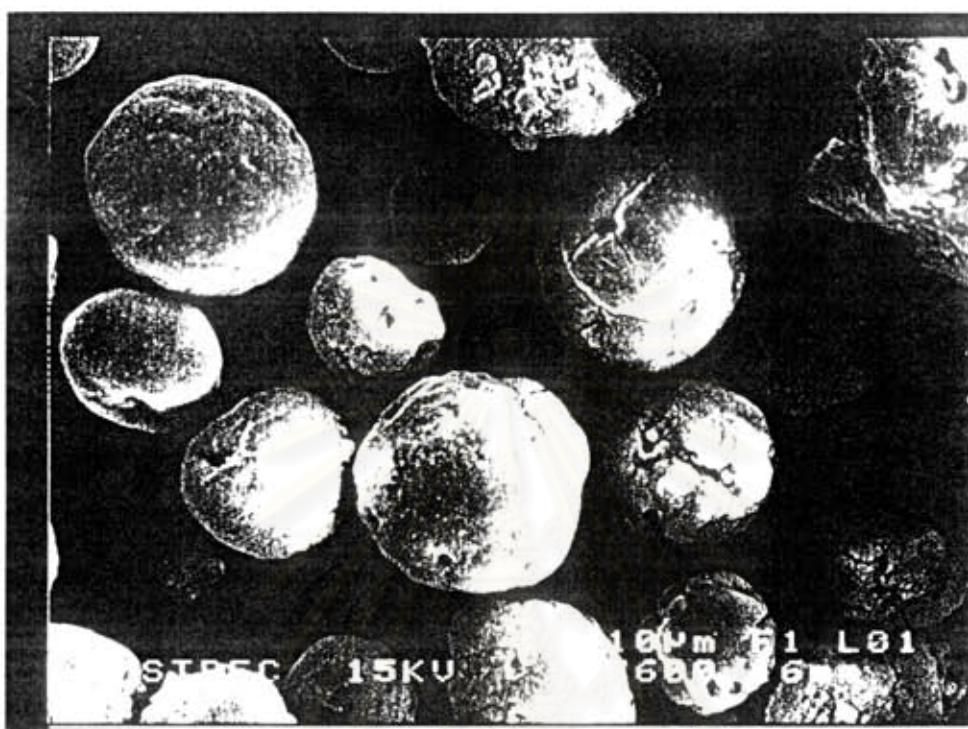


Figure 5.9 Scanning electron microscope image of silica

5.3 Characterization of the Polyethylene

5.3.1 Chemical Structure Determination

5.3.1.1 Infrared Spectroscopy (IR)

The infrared spectrum of polyethylene produced from supported metallocene catalyst is presented in Figure 5.10. In this study, it is found that all of the experimental polyethylenes determined in each effect exhibit the similar IR pattern. The infrared identification of polyethylene is assigned to the organic groups as summarized in Table 5.6.

Table 5.6 The assignment of infrared identification of polyethylene

Wave Number (cm ⁻¹)	Assignment
720	C-H bending
1470	-CH ₂ bending
2850-2920	-CH ₂ - , CH ₃ - stretching

From the above results, it is observed that produced polyethylene and standard polyethylene peaks in the FT-IR library software are alike as shown in Figure 5.11. For this reason, it can be confirmed that the products obtained from these polymerizations are all polyethylene



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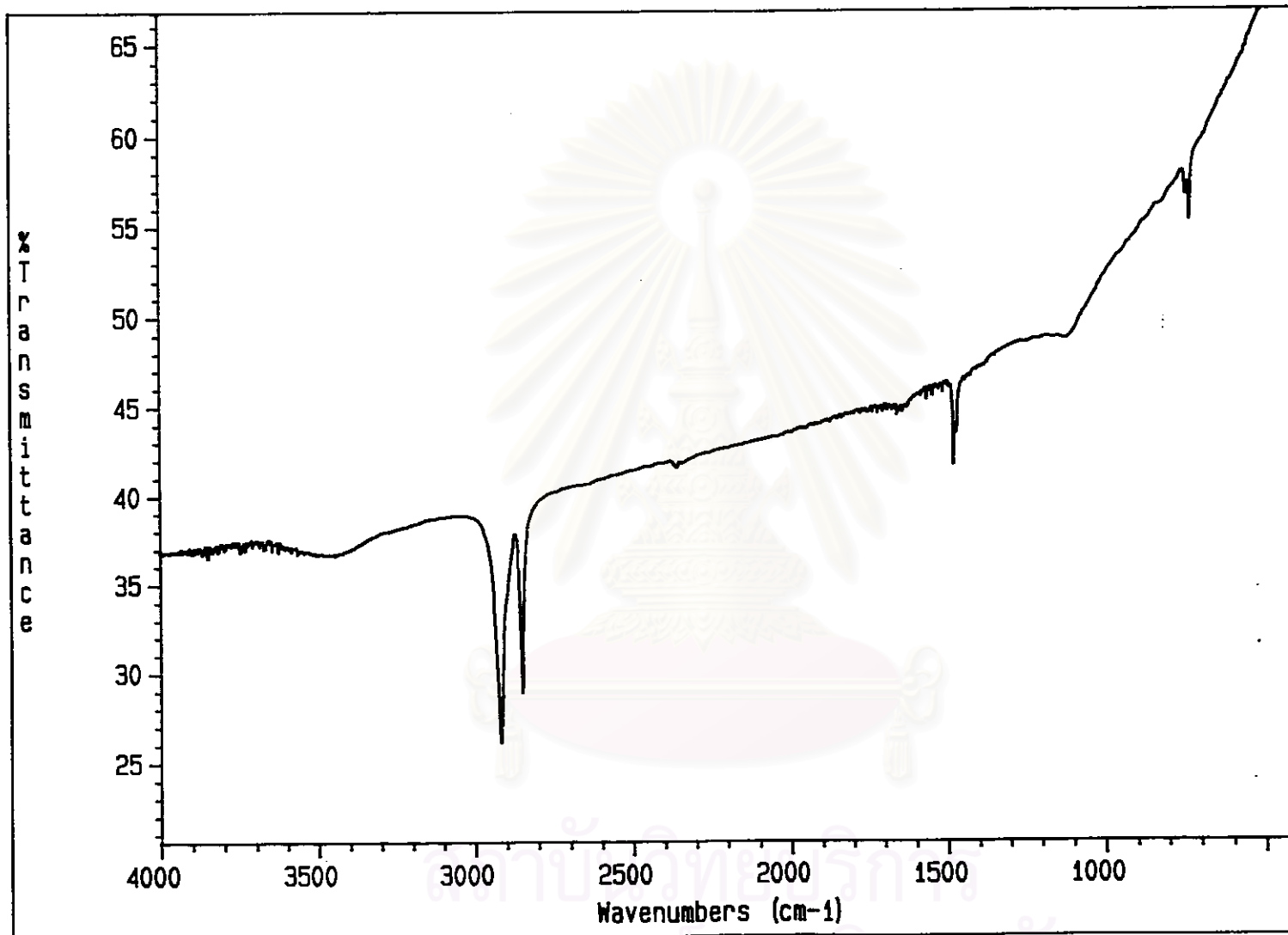


Figure 5.10 Infrared spectrum of polyethylene in this study

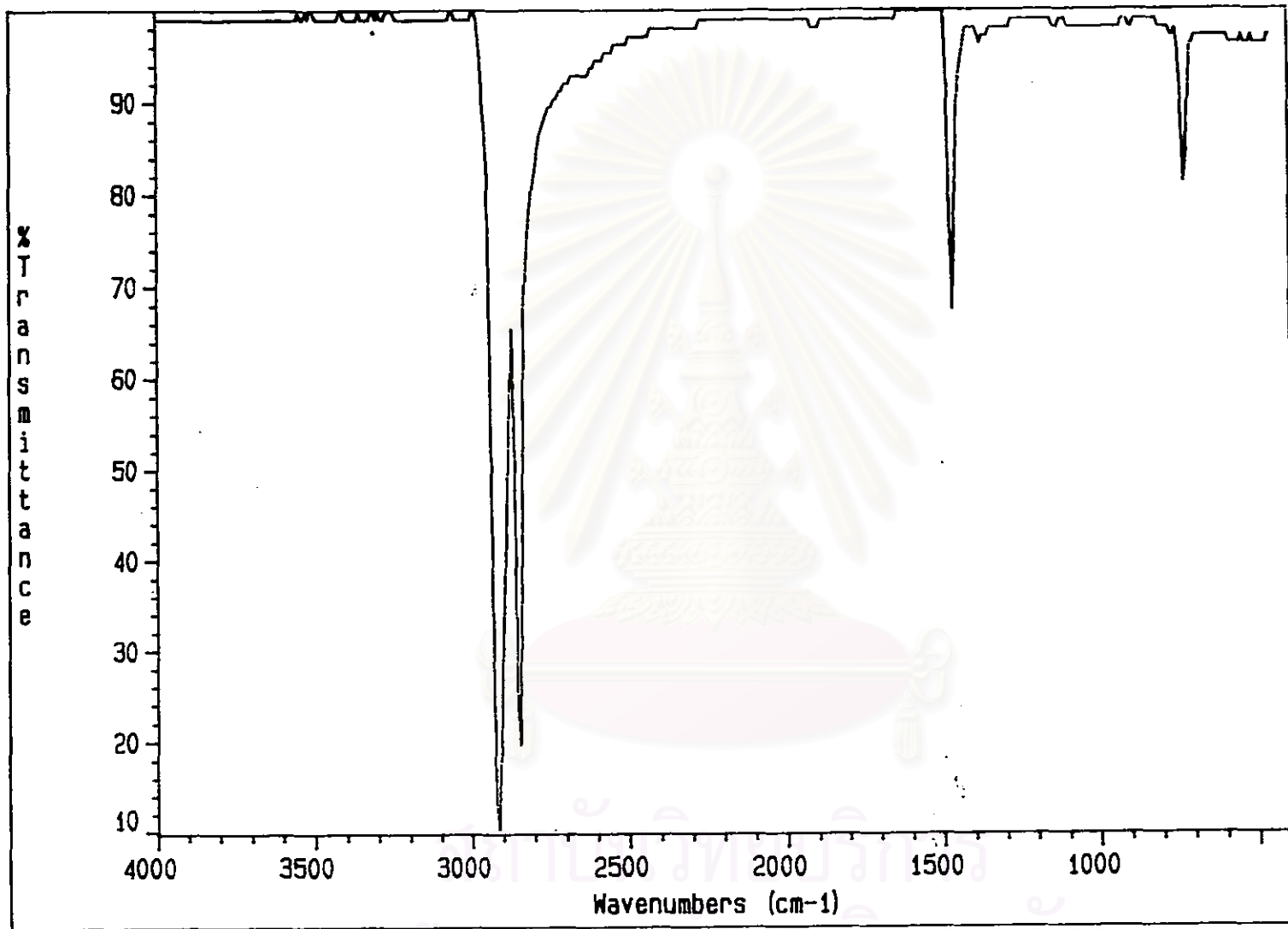


Figure 5.11 Infrared spectrum of standard polyethylene in the FT-IR library software

5.3.2 Morphology

The obtained polyethylene in this study was observed by scanning electron microscopy technique to determine its morphology as shown in Figure 5.12. The polyethylene consists of uniform polymer particles of a spherical shape replicating that of the catalyst precursor particles. Besides, all morphologies of polyethylene product show no significant differences. This finding implies that each polymer particle results from the polymerization of an individual support of catalyst system.

In addition, the SEM image of polyethylene produced with the $\text{SiO}_2/\text{silane}/\text{NaHCO}_3/\text{MAO}$ and $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system was compared to that with the homogeneous catalyst system as shown in Figure 5.13. This can be considered that the shape of polyethylene with the heterogeneous system is spherical fiber, while on the contrary the polyethylene with the homogeneous system looks non-uniform fiber. Therefore, it can be reported that the heterogeneous catalyst improves the morphology of polyethylene.



Figure 5.12 Scanning electron microscope image of polyethylene produced with the heterogeneous metallocene catalyst system



Figure 5.13 Scanning electron microscope image of polyethylene produced with the homogeneous metallocene catalyst system

5.3.3 Melting Temperature (T_m)

The melting temperatures of polyethylene obtained with the supported metallocene catalysts were evaluated by Differential Scanning Calorimeter. The results of various effects, such as Al/Zr molar ratio, catalyst concentration, polymerization temperature, ethylene pressure, and silane compound on T_m of produced polymer are demonstrated in Table 5.7-5.11, respectively. The DSC curves of these polyethylenes are also shown in Appendix A.

Table 5.7 Melting temperature of polyethylene with various Al/Zr mole ratios

Al/Zr Mole Ratio	Catalytic Activity (kgPE/mol Zr.h)	T_m (°C)
500	1403	132.31
1000	1660	132.15
2000	2312	-
3000	3810	134.56
4000	3471	132.45
5000	3299	132.91

Table 5.8 Melting temperature of polyethylene with various catalyst concentrations

Catalyst Concentration, [Zr] ($\times 10^5$ M)	Catalytic Activity (kgPE/mol Zr.h)	T_m (°C)
3.3333	3664	132.33
5.0000	4573	134.03
6.6667	3810	134.56
8.3333	2916	134.60
10.0000	2407	-

Table 5.9 Melting temperature of polyethylene with various polymerization temperatures

Polymerization Temperature (°C)	Catalytic Activity (kgPE/mol Zr.h)	T _m (°C)
30	2773	132.69
40	4573	132.73
50	5108	133.79
60	5849	132.45
80	5291	132.90

Table 5.10 Melting temperature of polyethylene with various ethylene pressures

Ethylene Pressure (psi)	Catalytic Activity (kgPE/mol Zr.h)	T _m (°C)
10	2197	-
30	3356	134.32
50	4362	132.60
70	5542	-
80	5849	132.45

Table 5.11 Melting temperature of polyethylene with various silane compounds

Type of Silane Compounds	Catalytic Activity (kgPE/mol Zr.h)	T _m (°C)
ClSiMe ₃	1736	132.64
Cl ₂ SiMe ₂	5849	132.45
Cl ₃ SiMe	6273	131.67
SiCl ₄	6965	132.53

From the above Tables, melting temperatures of obtained polyethylene are observed in the range of 131.67 to 134.60. It indicates that all produced polymers are typical of high-density polyethylenes.

5.3.4 Crystallinity

The crystallinities of polyethylene were determined by Differential Scanning Calorimeter. % Crystallinity of the polymers is defined in equation 5.4 [154].

$$\chi (\%) = (\Delta H_m / \Delta H_m^\circ) \times 100 \quad (5.4)$$

where $\chi (\%) =$ % crystallinity

$\Delta H_m =$ the heat of fusion of sample

$\Delta H_m^\circ =$ the heat of fusion of perfectly crystalline polyethylene,
286 J/g [155]

The crystallinities of obtained polyethylenes with different effects are summarized in Tables 5.12-5.16.

Table 5.12 Crystallinity of polyethylenes with various Al/Zr mole ratios

Al/Zr Mole Ratio	Catalytic Activity (kgPE/mol Zr.h)	ΔH_m (J/g)	χ (%)
500	1403	101.70	35.56
1000	1660	92.84	32.40
2000	2312	-	-
3000	3810	128.41	44.90
4000	3471	133.12	46.54
5000	3299	121.55	42.50

Table 5.13 Crystallinity of polyethylenes with various catalyst concentrations

Catalyst Concentration, [Zr] ($\times 10^5$ M)	Catalytic Activity (kgPE/mol Zr.h)	ΔH_m (J/g)	χ (%)
3.3333	3664	99.75	34.88
5.0000	4573	114.72	40.11
6.6667	3810	-	-
8.3333	2916	128.41	44.90
10.0000	2407	118.27	41.35

Table 5.14 Crystallinity of polyethylenes with various polymerization temperatures

Polymerization Temperature ($^{\circ}$ C)	Catalytic Activity (kgPE/mol Zr.h)	ΔH_m (J/g)	χ (%)
30	2773	133.31	46.61
40	4573	137.88	48.21
50	5108	143.71	50.25
60	5849	133.92	46.83
80	5291	130.14	45.50

Table 5.15 Crystallinity of polyethylenes with various ethylene pressures

Ethylene Pressure (psi)	Catalytic Activity (kgPE/mol Zr.h)	ΔH_m (J/g)	χ (%)
10	2197	-	-
30	3356	123.87	43.31
50	4362	135.66	47.43
70	5542	-	-
80	5849	133.92	46.83

Table 5.16 Crystallinity of polyethylenes with various silane compounds

Type of Silane Compounds	Catalytic Activity (kgPE/mol Zr.h)	ΔH_m (J/g)	χ (%)
ClSiMe ₃	1736	146.31	51.16
Cl ₂ SiMe ₂	5849	133.92	46.83
Cl ₃ SiMe	6273	119.58	41.81
SiCl ₄	6965	147.79	51.68

According to the data in Tables 5.12-5.16, the polyethylenes produced with the supported catalyst system present the range of % crystallinity between 32.40 and 51.68.

5.3.5 Average Molecular Weight and Molecular Weight Distribution

The molecular weight and molecular weight distribution of polymer produced at different conditions were presented in Tables 5.17-5.21 and GPC curves were also shown in Appendix B.

Table 5.17 Mw and MWD of the obtained polyethylene at various Al_{(TMA)/Zr} mole ratios

Al _{(TMA)/Zr} mole ratio	Mw	Mn	Mw/Mn
500	-	-	-
1000	867,014	594,114	1.46
2000	-	-	-
3000	824,824	585,376	1.41
4000	809,310	526,672	1.54
5000	-	-	-

As reported by the data in Table 5.17, it indicates the decreasing molecular weight (Mw) with increasing Al/Zr molar ratio, but no direct relation between the molar ratio and polydispersity (MWD) is appeared. Concerning polydispersity of polymer product, all polymers show the narrow distributions (Mw/Mn = 1.41-1.54).

Table 5.18 Mw and MWD of the obtained polyethylene at various catalyst concentrations

Catalyst Concentration, [Zr] ($\times 10^5$ M)	Mw	Mn	Mw/Mn
3.3333	-	-	-
5.0000	839,398	577,300	1.45
6.6667	824,8024	585,376	1.41
8.3333	775,770	487,180	1.59
10.0000	-	-	-

Besides, the relationship mentioned above can be observed in case of the obtained polyethylene at various catalyst concentrations, and polydispersity exhibits in the range of 1.41 – 1.59 as presented in Table 5.18.

Table 5.19 Mw and MWD of the obtained polyethylene at various polymerization temperatures

Polymerization Temperature (°C)	Mw	Mn	Mw/Mn
30	-	-	-
40	845,693	596,932	1.42
50	-	-	-
60	793,904	533,072	1.49
80	714,167	502,581	1.42

In Table 5.19, properties of polymers produced at different polymerization temperatures are shown. These data indicate an inverse relationship between polymerization temperature and Mw. Higher temperatures should cause the deactivation of the π -complex species, leading to lower molecular weight polyethylene. Besides, it may be due to the chain transfer reaction, especially the β -H elimination [4]. Reducing T_p can be efficiently suppress the chain transfer reaction since it has higher activation energy than the propagation reaction, thus increasing Mw. With increasing T_p , activation energy of chain transfer reaction becomes available, leading to a decrease in polymer molecular weight [153]. In contrast, molecular weight distribution (MWD) did not appear to be related to the polymerization temperature. The polymer polydispersity remains low ($M_w/M_n = 1.42-1.49$).

Table 5.20 Mw and MWD of the obtained polyethylene at various ethylene pressures

Ethylene Pressure (psi)	Mw	Mn	Mw/Mn
10	-	-	-
30	789,850	482,573	1.64
50	-	-	-
70	648,650	386,538	1.68
80	793,904	533,072	1.49

According to the data in Table 5.20, no direct relation between the ethylene pressure and molecular weight of the obtained polyethylene as well as polydispersity. The polydispersity shows in the range of 1.49-1.68.

Table 5.21 Mw and MWD of the obtained polyethylene at various silane compounds

Type of Silane Compounds	Mw	Mn	Mw/Mn
ClSiMe ₃	784,348	490,154	1.60
Cl ₂ SiMe ₂	793,904	533,072	1.49
Cl ₃ SiMe	878,576	599,464	1.47
SiCl ₄	806,402	505,565	1.60

As shown in Table 5.21, all polymers show the narrow distributions (Mw/Mn = 1.47-1.60)

5.3.6 The Comparison of Commercial Ziegler-Natta Catalyst and SiO₂/Silane/MAO-Cp₂ZrCl₂/TMA Catalyst Systems

The catalytic activity of SiO₂/SiCl₄/MAO-Cp₂ZrCl₂/TMA catalyst system was compared to that of the commercial Ziegler-Natta catalyst system. Besides the activity, polymers produced with both of these systems were also considered. The comparison of commercial Ziegler-Natta catalyst and SiO₂/SiCl₄/MAO-Cp₂ZrCl₂/TMA catalyst systems in catalytic activity and obtained polymers were summarized in Table 5.20.

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Table 5.22 The comparison of commercial Ziegler-Natta and $\text{SiO}_2/\text{SiCl}_4/\text{MAO}-\text{Cp}_2\text{ZrCl}_2/\text{TMA}$ catalyst systems

	Commercial Ziegler-Natta Catalyst[#]	$\text{SiO}_2/\text{SiCl}_4/\text{MAO}-\text{Cp}_2\text{ZrCl}_2/\text{TMA}$ Catalyst
1. Catalytic Activity (kgPE/mol Metal.hr)	13,167	6,965
2. Polymer Property		
- T_m (°C)	129	132.5
- %Crystallinity	-	51.68
- M_w	3.2×10^5	8.1×10^5
- M_w/M_n	2.65	1.60

[#] catalyst system: $\text{MgCl}_2/\text{TiCl}_4/\text{DIBP}/\text{TEA}$

Source of data: Bangkok Polyethylene Co., Ltd.

As shown in Table 5.20, it can be suggested that the properties of polymer obtained with $\text{SiO}_2/\text{silane}/\text{MAO}-\text{Cp}_2\text{ZrCl}_2/\text{TMA}$ catalyst system were better and more suitable to use in plastic industries than those with the commercial Ziegler-Natta catalyst with the higher melting temperature and molecular weight and the narrow molecular weight distribution. However, the catalytic activity of $\text{SiO}_2/\text{silane}/\text{MAO}-\text{Cp}_2\text{ZrCl}_2/\text{TMA}$ catalyst system (6,965 kgPE/mol Zr.hr) was still lower than that of the commercial Ziegler-Natta catalyst (13,167 kgPE/mol Ti.hr). Thus, the improvement in the catalytic activity of $\text{SiO}_2/\text{silane}/\text{MAO}-\text{Cp}_2\text{ZrCl}_2/\text{TMA}$ catalyst system should be attempted.

In addition, morphology of polyethylene produced with the $\text{SiO}_2/\text{silane}/\text{MAO}-\text{Cp}_2\text{ZrCl}_2/\text{TMA}$ and commercial Ziegler-Natta catalyst systems was compared. The SEM image of the polyethylene produced with the $\text{SiO}_2/\text{silane}/\text{MAO}-\text{Cp}_2\text{ZrCl}_2/\text{TMA}$ catalyst system is shown in Figure 5.12 whereas Figure 5.14 presents the SEM image of the polyethylene produced with the commercial Ziegler-Natta catalyst system. It is found that the shape of polyethylene with the commercial Ziegler-Natta catalyst

system is similar to that with the SiO_2 /silane/MAO- Cp_2ZrCl_2 /TMA catalyst system which is the spherical shape.

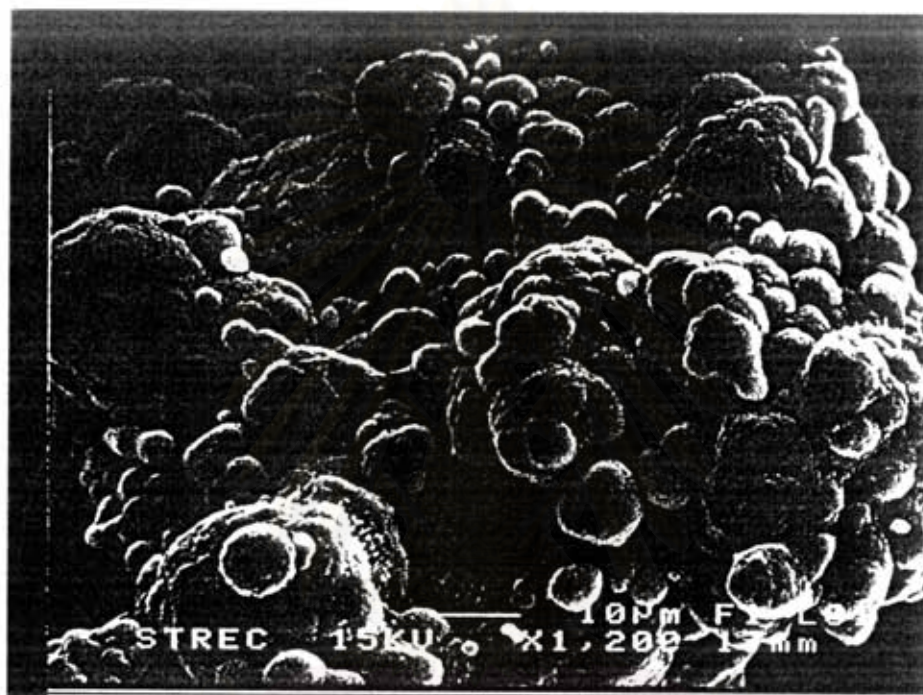


Figure 5.14 Scanning electron microscope image of polyethylene produced with the commercial Ziegler-Natta catalyst system