

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Preliminary Study of Catalyst Support Preparation

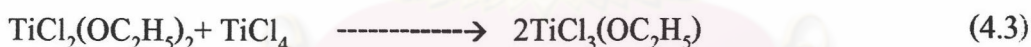
For ethylene slurry polymerization by using Z/N catalyst, the good supported catalyst should be fine particle and can disperse easily. In this research, the supported catalyst was prepared according to U.S. patent number 5,648,903.<sup>[4]</sup> There are many parameters that have effect on catalyst support morphology such as reaction temperature, stirring rate and addition rate of  $\text{TiCl}_4$ .

In general, commercial  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  has average particle size around 500 microns and the most suitable catalyst particle size is around 10 microns. Particle size of catalyst support is very important for catalyst preparation, its analysis and polymerization. In catalyst preparation procedure, catalyst support and supported catalyst particle should not be too fine because it can cause long time washing and thus high cost for production. The large particle size of catalyst support or supported catalyst will enable the difficulty of total titanium, Ti(III), Mg, Cl and activity analysis. Therefore, accuracy cannot be obtained due to the error from sampling. Furthermore, the big or heavy particles would lead to blocking of transferring pipe in production line and very fine particles would result in fine polyethylene which would affect on drying efficiency.

#### 4.1.1 Effect of Temperature on Reaction of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ with $\text{TiCl}_4$

The high activity Z/N catalysts were prepared according to U.S. Patent number 5,648,903.<sup>[4]</sup> Catalyst support was firstly prepared by reaction of  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  with  $\text{TiCl}_4$ . After addition of dropwise  $\text{TiCl}_4$  to suspension of  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  at 85 °C with stirring rate at 350 rpm, milky white fine particle was resulted in the first hour. Further addition, particles slightly turned to yellow. Catalyst support was then washed titanium content in supernatant less than 10 mmol/L. Catalyst support was analyzed as total titanium, magnesium and chloride concentration. After reacting with TEA at Ti/TEA mole ratio of two, supported catalyst had turned from dark brown to black color were ready for ethylene slurry polymerization.

It has been known that the reaction temperature has strong effect on rate of  $\text{MgCl}_2$  formation<sup>[16]</sup> and its morphology. Equations 4.1 to 4.3 show the reaction between  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  and  $\text{TiCl}_4$ .



The first step, Equation 4.1, has exothermic characteristic.<sup>[19]</sup> In this study, temperature of this reaction was varied as shown in Table 4.1. At 80 °C and 350 rpm, coarse particles were obtained which could not be used for ethylene slurry polymerization. These probably due to the incomplete reaction caused by too low reaction temperature (Entry No. 1, Table 4.1).

**Table 4.1** Conditions of catalyst support preparation and their characteristic

Entry No.	Reaction temperature (°C)	Stirring rate (rpm)	Catalyst support
1	80	350	Coarse
2 <sup>a</sup>	85	350	Very fine
3	90	350	Fine and heavy
4	85	100	Coarse
5 <sup>b</sup>	85	350	Fine, heavy and coarse
6	85	450	Too fine

<sup>a</sup> Dropwise of TiCl<sub>4</sub>

<sup>b</sup> One portion addition of TiCl<sub>4</sub>

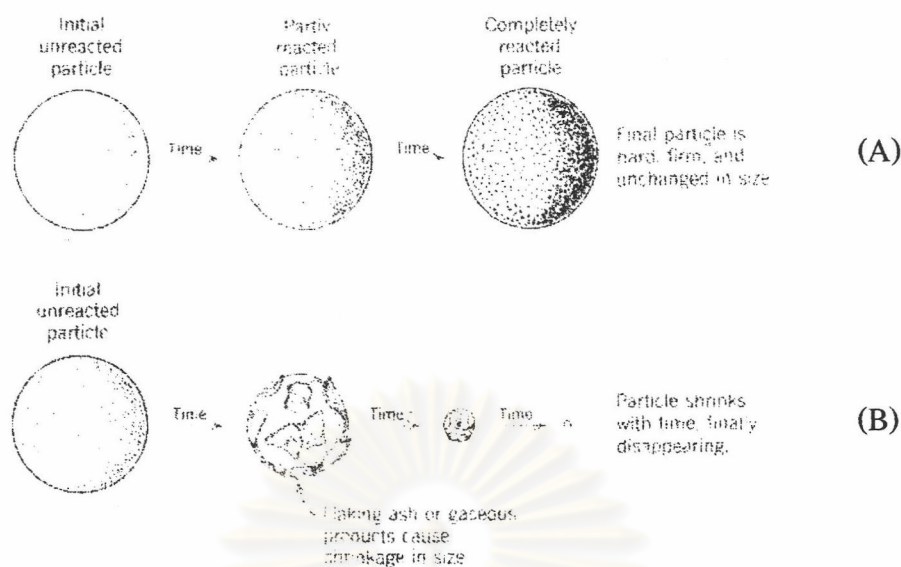
At 85 °C and 350 rpm, fine catalyst supports were formed. It was found that this catalyst support was dispersed very well in the solvent. Therefore it could be suitable for ethylene slurry polymerization (Entry No. 2, Table 4.1). At 90 °C and 350 rpm, the mixture of fine and heavy particles were formed. This probably was caused by the rapid reaction between Mg(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and TiCl<sub>4</sub>. It was difficult to deal with because they easily precipitated. These heavy particles from the reaction of TiCl<sub>4</sub> with ethanol that inherent in Mg(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> catalyzed by HCl as shown in equations 4.4, 4.5 and 4.6.



Mild condition should be done because equation 4.4 is simple to happen while  $\text{TiCl}_4$  is alcohol or moisture sensitive. The by-product of this reaction is HCl that accelerates the reaction in equation 4.5 and generates  $\text{C}_2\text{H}_5\text{OH}$ . High concentration of HCl in reactor will enhance both reactions. Therefore, more  $\text{H}_2\text{TiCl}_6$  complex that is inactive for ethylene slurry polymerization will be formed (Entry No 3, Table 4.1). Accordingly, hydrochloric acid is must be suppressed. Consequently, the suitable temperature for Z/N catalyst support preparation was 85 °C.

#### 4.1.2 Effect of Stirring Rate on Reaction of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ with $\text{TiCl}_4$

Generally, in heterogeneous system, the appearance of catalyst support was effected by the dispersion of  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  during the reaction. Well dispersion will lead to the formation of fine particles. Variation of stirring rate was thus applied in this study. At stirring rate of 100 rpm (Entry No. 4, Table 4.1), catalyst support was coarse because of the incomplete reaction between  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  and  $\text{TiCl}_4$ . The remaining  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  was also observed. Such particles could not be analyzed and used for ethylene polymerization as discussed in Section 4.1. At stirring rate of 350 rpm (Entry No. 2, Table 4.1), catalyst support particles were fine and easily analyzed and used for ethylene slurry polymerization. At stirring rate of 450 (Entry No. 6, Table 4.1), the particle were too fine and difficult to settle down during washing and separation steps. This could be explained by the fluid-solid reaction models<sup>[17]</sup>, the progress-conversion model and the unreacted core model as shown in Figure 4.1.



**Figure 4.1** The fluid-solid reaction models; the progress-conversion model (A) and the unreacted core model (B)

The progressive-conversion model explains that solid is converted continuously and progressively throughout the particle. Solid particles remain unchanged in size. On the contrary, in the unreacted core model reaction occurs first at the outer skin of the particle. The zone of reaction moves into the solid and may leave behind completely converted material and inert solid. This means that at low stirring rate of 100 rpm, unreacted core model could not be completely happened and unreacted  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  remained, while it occurred completely of high stirring rate. Consequently, the suitable stirring rate for catalyst support preparation was 350 rpm.

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### 4.1.3 Effect of Addition Rate of $\text{TiCl}_4$

High sensitive characteristic of  $\text{TiCl}_4$  leads to complexity of reaction.<sup>[19]</sup> Normally, fine particle precipitates if the rate of reaction is slow. As discussed in Section 4.1.1,  $\text{TiCl}_4$  concentration in the reaction must be considered which can be controlled by rate of addition. Addition of  $\text{TiCl}_4$  is attempted by either adding in one portion or dropwise. Fine, heavy and coarse particles were resulted when one portion addition of  $\text{TiCl}_4$  was performed (Entry No. 5, Table 4.1). These particles were derived from many reactions, Equations 4.4 to 4.6. However, fine particles were obtained when  $\text{TiCl}_4$  was added dropwise to the dispersed  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  mixture until complete addition in 5 hours (Entry No. 2, Table 4.1).  $\text{HCl}$  from the reaction between  $\text{TiCl}_4$  and  $\text{C}_2\text{H}_5\text{OH}$  was formed faster than it was used in Equation 4.5. This is the reason why the rapid addition of  $\text{TiCl}_4$  can cause the formation of  $\text{H}_2\text{TiCl}_6$ . Consequently, dropwise addition of  $\text{TiCl}_4$  was suitable for this catalyst support preparation.

### 4.1.4 Activity of Supported Catalyst

Only Entries No. 2, 3 and 6 were taken for analysis as described in Section 3.4.2. After reacting with TEA, Z/N catalyst was obtained. Then the catalyst was used for ethylene slurry polymerization. The weight of polyethylene from each polymerization was measured and compared. The results showed that supported catalyst, Entry No. 3, Table 4.1 had activity less than  $20 \text{ kg PE} \times \text{g}^{-1} \text{ Ti} \times \text{h}^{-1}$ . It should be noticed that the heavy aggregates could block piping and tubing devices for the scale-up production. Therefore, such condition was not appropriate. For Entries No. 2 and 6, both exhibited higher activity than  $35 \text{ kg PE} \times \text{g}^{-1} \text{ Ti} \times \text{h}^{-1}$ . However, polyethylene Entry No. 6 was too fine particle and could create problem in drying step during production. Accordingly, most suitable catalyst support preparation condition was Entry No. 2.

## 4.2 Z/N Catalyst for Low Molecular Weight HDPE

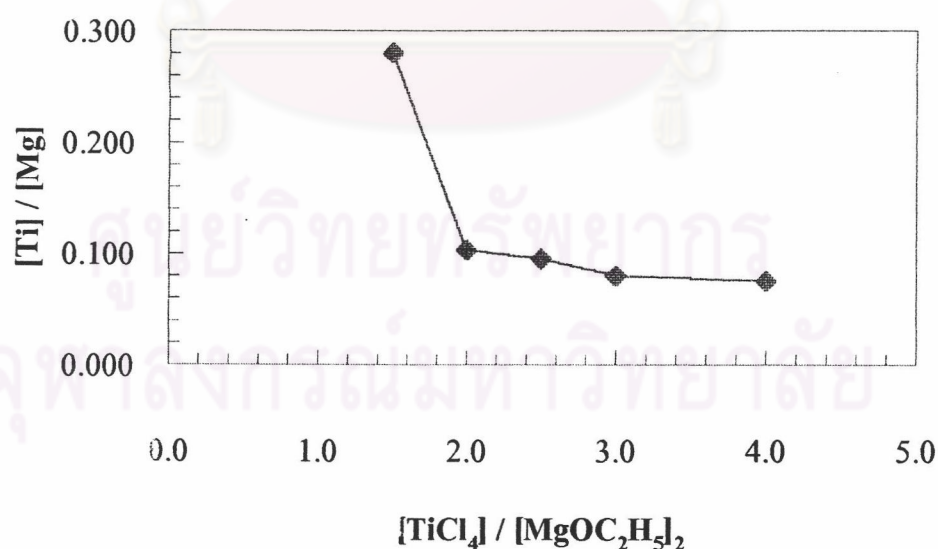
### 4.2.1 Variation of $\text{TiCl}_4$ and $\text{Mg}(\text{OC}_2\text{H}_5)_2$ ratio

Knowing that only a few percentage of the titanium atoms taking part of the catalyst composition are effectively active sites, a reduction in the amount of titanium might not lead to a drastic number of active sites.<sup>[18]</sup> On the other hand, the decreasing of titanium compound on support discloses high activity active sites. Titanium content of catalyst could be decreased by using excess  $\text{TiCl}_4$  as shown in Equations 4.1, 4.2 and 4.3. In theory, the complete reaction need  $\text{TiCl}_4$  1.33 time of  $\text{Mg}(\text{OC}_2\text{H}_5)_2$ . The ethoxy titanium chloride compound on catalyst support would be converted to  $\text{TiCl}_3(\text{OC}_2\text{H}_5)$  and which was removed by dissolving in hot aliphatic hydrocarbon.<sup>[19]</sup> The reaction of  $\text{TiCl}_4$  and  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  were carried out at the condition of Entry No. 2, Table 4.1. The  $\text{TiCl}_4$  treatment produces the catalysts (R1, R2, R3, R4 and R5). Different titanium content on catalyst supports,  $[\text{Ti}]/[\text{Mg}]$  were resulted as exhibited in Table 4.2. When  $\text{TiCl}_4$  increased, less titanium content on catalyst support was obtained.

**Table 4.2** The influence of  $\text{TiCl}_4/\text{Mg}(\text{OC}_2\text{H}_5)_2$  and properties of resulted HDPE

Catalyst	$[\text{TiCl}_4]/[\text{Mg}(\text{OC}_2\text{H}_5)_2]$	$[\text{Ti}]/[\text{Mg}]$	Average activity on polymerization ( $\text{kg PE} \times \text{g}^{-1}\text{Ti} \times \text{h}^{-1}$ )	$\text{MFI}_5$ ( $\text{g}/10 \text{ min}$ )
R1	1.5	0.280	$61.2 \pm 8.3$	20.3
R2	2.0	0.103	$246.8 \pm 16.3$	19.7
R3	2.5	0.095	$356.9 \pm 24.4$	19.0
R4	3.0	0.080	$537.1 \pm 120.9$	18.9
R5	4.0	0.075	$676.0 \pm 199.2$	15.0

It should be noted that titanium content on catalyst support was rapidly decreased when  $[\text{TiCl}_4]/[\text{Mg}(\text{OC}_2\text{H}_5)_2]$  increased from 1.5, R1 to 2.0, R2 as shown in Table 4.2. This is attributed to the impregnation of the most chloroethoxytitanium compound on outer surface of catalyst support. However, the increase in  $\text{TiCl}_4$  did not strongly affect on titanium content on catalyst support, R3, R4 and R5. Figure 4.2 showed this phenomenon.



**Figure 4.2** Variation of  $\text{TiCl}_4$  concentration effected on titanium content on catalyst support



However, the most appropriate catalyst support for producing low molecular weight HDPE, activity on polymerization and melt flow index of HDPE should be considered.

#### 4.2.2 Influence of Catalyst Composition on Catalyst Activity

R1, R2, R3, R4 and R5 were individually reacted with TEA and then they used for ethylene polymerization. Activity of catalyst was monitored and the individual catalyst composition ( $[Ti]/[Mg]$ ) was determined. As revealed by Bosowska, K., and Nowakowska, M., catalyst activity was improved when titanium content on catalyst support was reduced.<sup>[12]</sup> Table 4.2 shows that activity of catalyst was increased from 61.2 to 676.0  $\text{kg PE} \times \text{g}^{-1} \text{Ti} \times \text{h}^{-1}$  while  $[Ti]/[Mg]$  of supported catalyst was reduced from 0.280 to 0.075 when the ratio of  $[TiCl_4]/[Mg(OC_2H_5)_2]$  increased. That means excess  $TiCl_4$  reacts with all titanium complex in a consequence as shown in Equation 4.1 to 4.3 to the final  $TiCl_3(O(C_2H_5))$  which was removed from catalyst by washing with hot aliphatic hydrocarbon. This effect led to the elimination of less activity active site catalyst. Figure 4.2 demonstrated the effect of titanium content of catalyst support on their activity.

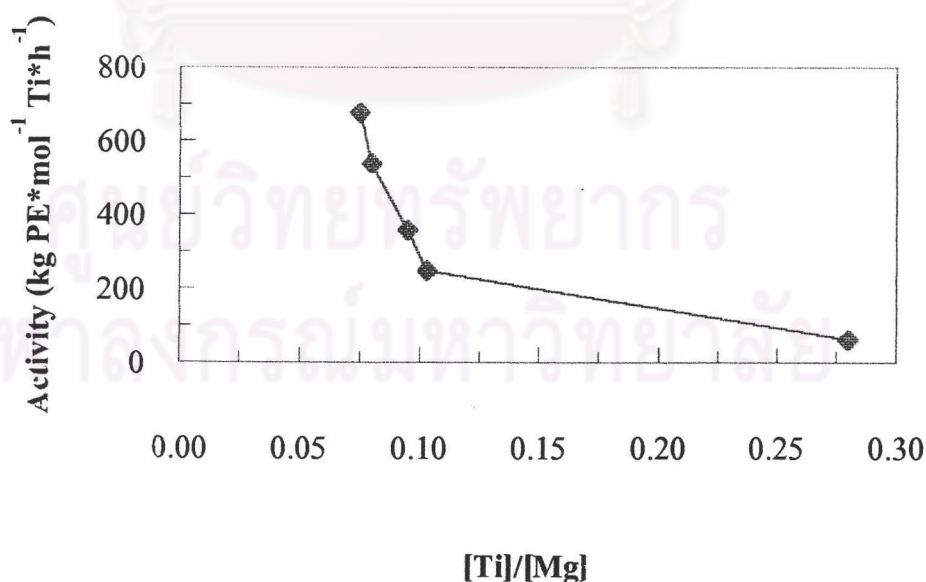


Figure 4.3 Effect of titanium content of catalyst support on its activity

These results indicated that chloroethoxytitanium eliminated from catalyst support has low activity while other titanium compound on catalyst support show high activity. However, their high activity R4 and R5 (Table C1, Appendix C) induced the fluctuated results because it could easily react with hydrogen or impurity present in the reaction. Therefore, R3 gave high and reasonable activity.

#### 4.2.3 Melt Flow Index of HDPE

Most consideration in physical properties of HDPE is  $MFI_5$  value, which correlates to its molecular weight and rheology. In Section 4.2.2, HDPE from ethylene slurry polymerization is powder like.  $MFI_5$  of HDPE resulted from R1 to R3 catalysts were in the range of 19.0 to 20.3 g/10 min indicating the low molecular weight of HDPE. As described in Section 2.8, the supported catalyst with low titanium content should have different polymerization kinetic comparing to the one with high titanium content. Thus, initials time of polymerization and then reaches constant. Consequently, these catalyst preparation conditions were suitable for producing low molecular weight HDPE. However, HDPE resulted from using R1, R2 and R3 catalysts showed the similar  $MFI_5$  and could be used anyone.

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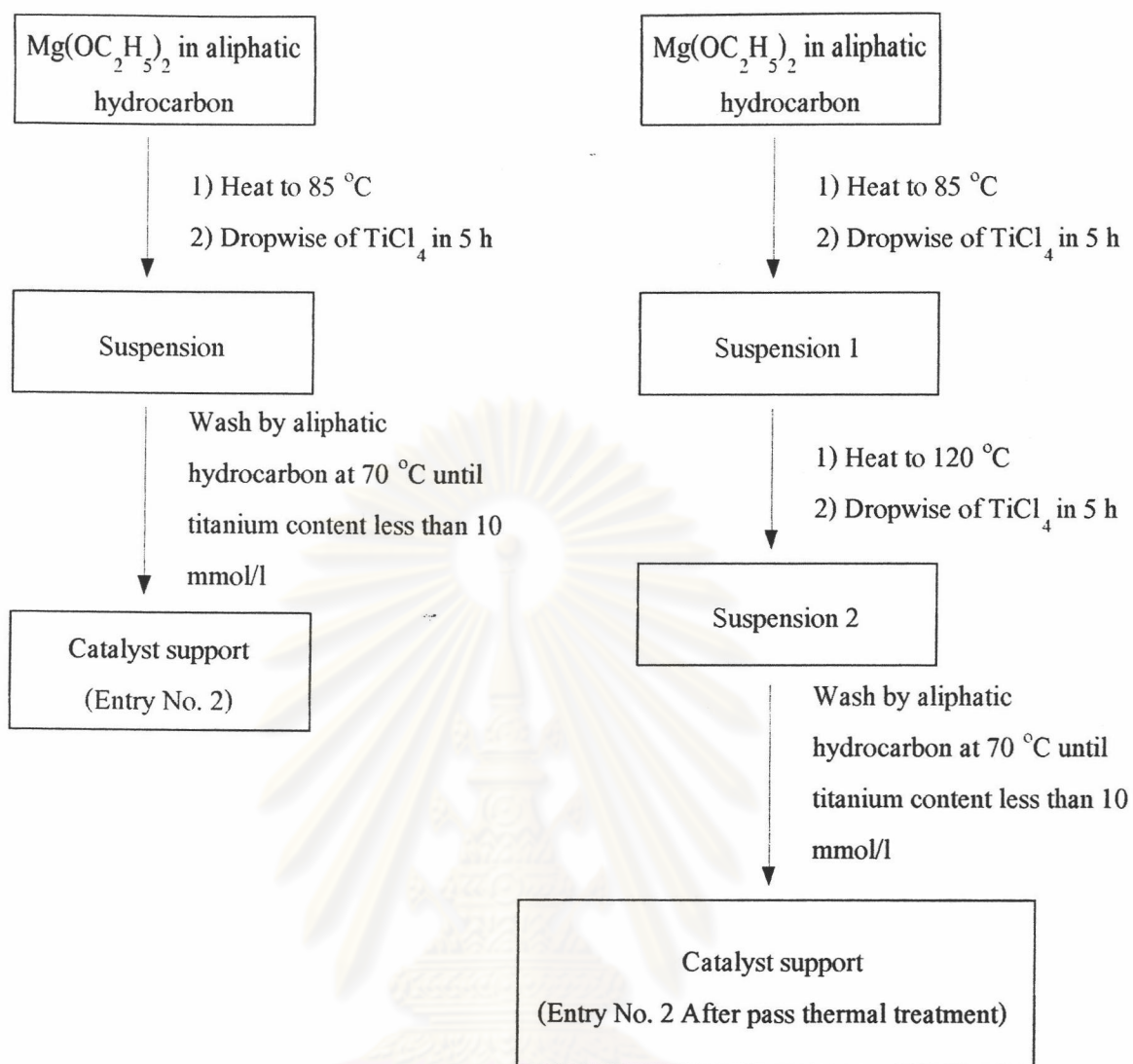
### 4.3 Z/N Catalyst for Producing High Molecular Weight HDPE

As revealed in Section 4.2, the most appropriate ratio of  $\text{TiCl}_4/\text{Mg}(\text{OC}_2\text{H}_5)_2$  for producing low molecular weight HDPE was 2.5. Since it gave high catalyst activity and more reliable, it was thus taken for further modification to be the catalyst for producing high molecular weight HDPE. Bosowska had discovered that the Z/N catalyst containing higher  $[\text{Ti}]/[\text{Mg}]$  gave higher molecular weight HDPE. Therefore this study has been designed in order to enhance the titanium content on catalyst support.

#### 4.3.1 Thermal Treatment of Catalyst Support

In section 4.1.1, it was found that the most suitable temperature during addition of  $\text{TiCl}_4$  was at  $85\text{ }^\circ\text{C}$ . However, increasing temperature after complete addition of  $\text{TiCl}_4$  might enable chemisorption of titanium on catalyst support. Therefore, the reaction, Entry No. 2, was repeated and compared with the one after thermal treatment without washing of suspension. Figure 4.3 shows different catalyst support preparation.

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**Figure 4.4** Catalyst support preparation by using Entry No. 2 compared with catalyst support preparation by modification of Entry No. 2 by thermal treatment

Titanium content of catalyst support from both catalyst support preparations was increased from 0.17 to 0.58 molar ratios with magnesium as shown in Table 4.3. After reacting the supported catalyst with TEA, Z/N catalyst was used for ethylene slurry polymerization. Higher activity of Entry No. 2 was obtained indeed.

**Table 4.3** Comparison of titanium content of catalyst support by variation of titanium concentration in aliphatic hydrocarbon before washing

Supported catalyst	[Ti]/[Mg]	Average activity of supported catalyst (kg PE × g <sup>-1</sup> Ti × h <sup>-1</sup> )
Entry No. 2	0.17	356.9
Entry No. 2	0.58	62.3

after thermal treatment

These results exhibit that increasing in temperature can improve chemisorption efficiency. High titanium concentration in supernatant of suspension 1 could enhance titanium content of supported catalyst at 120 °C. However, it does not mean that highest titanium content in supported catalyst could lead to lowest molecular weight of HDPE. Therefore, the most suitable of washing time before thermal treatment was varied for preparation of Z/N catalyst that was used for producing low molecular weight of HDPE.

#### 4.3.2 Effect of Washing before Thermal Treatment on Titanium Content of Catalyst Support

It was found that higher titanium content of catalyst support could be obtained by thermal treatment at 120 °C but catalyst support from this supported catalyst showed much lower activity on polymerization than the one without thermal treatment. It means that [Ti]/[Mg] should be readjusted. Therefore, the removal of titanium compound in supernatant before thermal treatment was investigated. This was performed by washing the resulted reaction mixture (suspension 1) with hot aliphatic hydrocarbon.<sup>[20]</sup> The number of washing was varied 1-8 times. The analysis of titanium content in supernatant and [Ti]/[Mg] in catalyst support, Table 4.4, indicated that

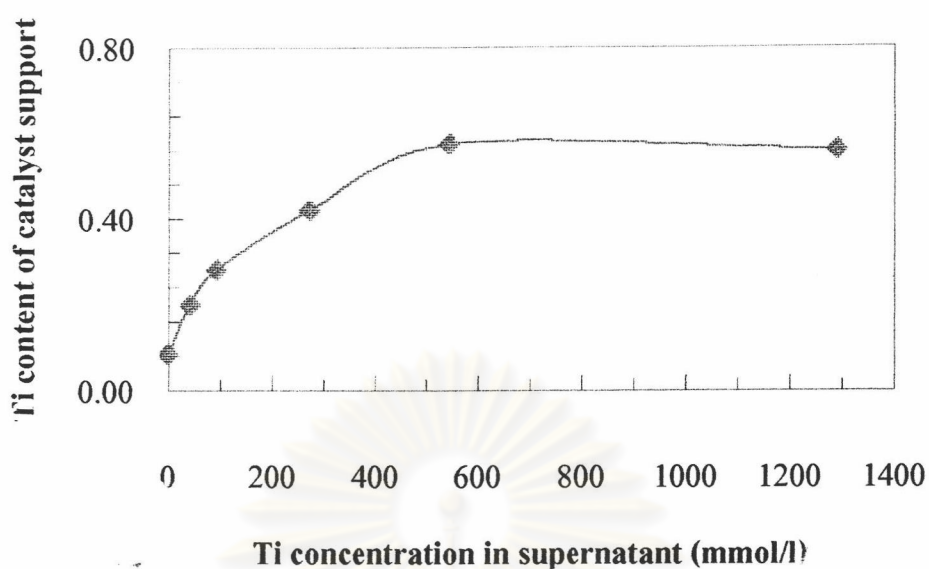
higher titanium content in catalyst support resulted when titanium content in supernatant was high.

**Table 4.4** Variation of the number of washing and titanium content in supernatant and support

Catalyst	[Ti] in supernatant (mmol/l)	[Ti]/[Mg] in catalyst support
W0	1290.5	0.56
W1	545.0	0.57
W2	272.5	0.42
W3	92.5	0.28
W4	41.0	0.20
W10	<10	0.08

This was probably attributed to the availability of titanium compound in supernatant and its absorption was enhanced by heating at 120 °C. However, Figure 4.4 explained that the highest titanium content in catalyst support was achieved at the concentration of supernatant around 400 mmol/L.

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**Figure 4.5** Effect of titanium concentration in supernatant on titanium content of catalyst support

### 4.3.3 Conversion of Ti(IV) to Ti(III) of Supported Catalyst

It has been known that the high molecular weight HDPE resulted from ethylene polymerization using Z/N catalyst depends on the oxidation state of titanium. Ti(III) lead to high molecular weight while Ti(IV) will provide lower molecular weight HDPE. Therefore, Ti(III) in the supported catalyst is required for producing high molecular weight HDPE. Table 2.4 clearly demonstrated that high molecular weight HDPE could be obtained from Ti(III) in all samples. Therefore, catalyst support, Section 4.3.2 was separated into two parts. Each part was reacted with TEA, at room temperature and 120 °C, respectively, for 2 hours. Table 4.5 shows that at higher temperature could be generated higher percentage of Ti(III) in supported catalyst was obtained.

**Table 4.5** Percentage of Ti(III) in supported catalyst for producing high molecular weight HDPE

Catalyst	Percentage of Ti(III) in supported catalyst	
	Redox reaction at room temperature	Redox reaction at 120 °C
	(RT)	(HT)
W0	51.75	65.10
W1	44.90	61.20
W2	42.63	52.10
W3	41.76	64.07
W4	35.02	43.09
W10	31.95	52.55

From Table 4.5, redox reaction at 120 °C gave higher efficiency than at room temperature for all cases. Consequently, the catalyst for producing high molecular weight HDPE should be prepared with redox reaction at 120 °C.

#### 4.3.4 Effect of Catalyst Support Composition on Their Activity

After redox reaction of catalyst support with TEA, each Z/N catalyst was used for ethylene slurry polymerization as described in Section 3.4.2. Table 4.6 reveals that lower titanium content of catalyst was led to higher activity of supported catalyst.



**Table 4.6** Catalyst activity of supported catalyst for producing high molecular weight HDPE

Catalyst	[Ti]/[Mg] in catalyst support	Average activity of supported catalyst ( $\text{kg PE} \times \text{g}^{-1}\text{Ti} \times \text{h}^{-1}$ )	
		Redox reaction at room temperature	Redox reaction at 120 °C
		(RT)	(HT)
W0	0.56	62.3	82.6
W1	0.57	55.0	58.6
W2	0.42	96.8	86.3
W3	0.28	97.2	80.7
W4	0.20	113.6	109.6
W10	0.08	214.1	210.8

Highest catalyst activity was resulted in both case, redox reactions at room temperature and 120 °C, of W10 catalyst while its was 0.08 molar ratios of [Ti]/[Mg]. These results confirmed that titanium compound that adhered on catalyst support had less activity. Although W10HT and W10RT had highest catalyst activity but  $\text{MFI}_5$  should be considered as well.

#### 4.3.5 Relationship of Titanium Oxidation State with Melt Flow Index

As discussed in Section 4.3.3, it was found that all redox reactions between titanium in catalyst support and TEA at 120 °C gave the higher percentage of Ti(III) than at room temperature.  $\text{MFI}_5$  of resulted HDPE could be used for investigation of the relation between molecular weight and Ti(III). Table 4.7 indicated that with redox reaction at 120 °C, lower  $\text{MFI}_5$  of HDPE was obtained comparing to the one with redox reaction at 120 °C.

**Table 4.7** MFI<sub>5</sub> of HDPE from supported catalyst for producing high molecular weight HDPE that obtained from different preparation condition

Catalyst	Average MFI <sub>5</sub> (g/10 min)	
	Redox reaction at room temperature	Redox reaction at 120 °C
	(RT)	(HT)
W0	12.6	13.1
W1	13.6	11.7
W2	15.5	10.5
W3	14.4	12.9
W4	15.9	14.0
W10	17.4	17.3

It is clear that the supported catalyst prepared with redox reaction at room temperature contained highest amount of titanium does not provide lowest MFI<sub>5</sub> and thus molecular weight. Therefore, the amount of Ti(III) in catalyst was considered. W0HT and W1HT catalysts were used to produce HDPE with higher MFI<sub>5</sub> than W2HT. This effect may due to too high titanium content on catalyst support derived from titanium compound in supernatant. Generally, soluble catalyst can lead to lower molecular weight polymer than supported catalyst. Furthermore, too much titanium content came from soluble part. It means that they should have low molecular weight catalytic efficiency. However, W3HT, W4HT and W10HT could provide higher MFI<sub>5</sub> of HDPE than W2HT. This result shows the same trend as in Section 4.2 and the reason had discussed previously. Consequently, MFI<sub>5</sub> of HDPE using W2HT in Table 4.7 was the lowest and would be appropriate for mixing.

#### 4.4 Z/N Catalyst for Broad MWD HDPE

##### 4.4.1 Activity of Mixed Catalyst on Polymerization

Aim of this study is to producing broad MWD HDPE by using the mixture of Z/N catalyst for producing low molecular weight and Z/N catalyst for producing high molecular weight. Two most important criteria for choosing the appropriate catalysts for mixing are catalyst activity and  $MFI_5$  of resulted HDPE. Table 4.8 presents the comparison of  $MFI_5$  and catalyst activity of each catalyst from Sections 4.2 and 4.3, respectively. R1 and R2 catalysts exhibited out of consideration because the resulted HDPE had lower activity regardless of their close  $MFI_5$ . R4 and R5 catalysts were also not chosen because of their unreliable reproducibility as shown by their activity. Thus, most suitable catalyst for producing low molecular weight HDPE is R3 catalyst. The case of the catalyst for producing high molecular weight HDPE,  $MFI_5$  of HDPE using W0HT was the lowest. Accordingly, two catalysts that were chosen for producing broad MWD HDPE were R3 and W2HT catalysts.

**Table 4.8** Catalyst activity and MFI<sub>5</sub> of HDPE from Sections 4.2 and 4.3

Catalyst	Catalyst code	MFI <sub>5</sub> (g/10 min)	Average catalyst activity (kg PE × g <sup>-1</sup> Ti × h <sup>-1</sup> )
For producing low molecular weight HDPE	R1	20.3	61.2 ± 8.3
	R2	19.7	246.8 ± 16.3
	R3	19.0	356.9 ± 24.4
	R4	18.9	537.1 ± 120.9
	R5	15.0	676.0 ± 199.2
For producing high molecular weight HDPE with redox reaction at room temperature	W0RT	12.6	62.3 ± 6.4
	W1RT	13.6	55.0 ± 7.1
	W2RT	15.5	96.8 ± 17.0
	W3RT	14.4	97.2 ± 15.9
	W4RT	15.9	113.6 ± 14.1
	W10RT	17.4	214.1 ± 18.2
For producing high molecular weight HDPE with redox reaction at 120 °C	W0HT	13.1	82.6 ± 2.9
	W1HT	11.7	58.6 ± 3.1
	W2HT	10.5	86.3 ± 17.1
	W3HT	12.9	80.7 ± 20.4
	W4HT	14.0	109.6 ± 18.4
	W10HT	17.3	210.8 ± 36.3

The chosen catalyst, R3 and W2HT catalysts were mixed in several ratios by calculation from their total titanium of each supported catalyst. Table 4.9 demonstrated the ratio of total titanium concentration of R3 ( $[Ti]_{R3}$ ) and total titanium concentration of W2HT ( $[Ti]_{W2HT}$ ).

**Table 4.9** Variation of R3 and W2HT molar ratio and their activity

R3:W2HT	$[\text{Ti}]_{\text{R3}}/[\text{Ti}]_{\text{W2HT}}$ (molar ratio)	Average catalyst activity (kg PE $\times$ g <sup>-1</sup> Ti $\times$ h <sup>-1</sup> )
1:9	0.11	89.9
3:7	0.43	109.8
5:5	1.00	164.1
7:3	2.33	185.9
9:1	9.00	203.5

Table 4.9 exhibited that catalyst exhibited catalyst activity was improved as R3 catalyst increased. This indicates that both catalysts do not affect on active site of the other. Therefore, increasing of R3 catalyst indicated to good catalyst activity.

#### 4.4.2 Molecular Weight and Molecular Weight Distribution of HDPE

Mw and MWD of HDPE from ethylene slurry polymerization by using mixed catalyst between R3 and W2HT catalysts were analyzed. Table 4.10 shows that, molecular weight of HDPE decreased as the amount of R3 catalyst increased. This effect confirmed that active sites of W2HT catalyst did not interfere the kinetic of initiation and propagation steps in ethylene polymerization using R3 catalyst.

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**Table 4.10** Molecular weight and molecular weight distribution of HDPE using mixed catalyst

R3 : W2HT	Mn	Mw	MWD
1:9	23,300	117,900	5.0
3:7	17,100	76,300	4.5
5:5	15,200	88,400	5.8
9:1	9,400	66,800	7.1

The GPC chromatogram, Figure E5 in Appendix E, shows the shoulder belonging to low molecular weight of HDPE in case of using R3 and W2HT catalyst ratio of 9:1. There is shoulder peak at low molecular weight and high activity of mixed catalyst was appeared. This can be explained that R3 and W2HT catalysts might have different catalytic activity but could produce much-closed molecular weight HDPE. In the change of HDPE molecular weight with time in polymerization, R3 catalysts could increases HDPE molecular weight for an initial period of polymerization time and then reaches a constant while W2HT catalyst could continually increased the molecular weight throughout the duration of polymerization although the rate of this increase diminishes with time.