

## **Ziegler-Natta Catalyst with High Activity and Good Hydrogen Response**

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### **Abstract**

Ziegler-Natta catalysts were prepared from chemical reaction route comprising of steps of 1) magnesium complex formation between butyloctyl magnesium and 2-ethyl-1-hexanol, 2) MgCl<sub>2</sub> support preparation from the reaction between the magnesium complex and TiCl<sub>4</sub> as chlorinating agent and 3) titanation with TiCl<sub>4</sub>. The catalysts were used for ethylene polymerization using triethylaluminum as a cocatalyst. Effects influencing properties of catalysts and polymerization performance were investigated: triethylaluminum/Mg molar ratio, Ti/Mg molar ratio, addition of electron donor and aging step. Results show that addition of ethylbenzoate as an electron donor resulted in decreased catalytic activity. However it was found that catalytic stability under high pressure was increased, as revealed by higher activity balance. Activity of the catalyst can be improved by performing aging step. High density polyethylene was produced in slurry process.

**Key words:** Ziegler-Natta catalyst, Polyethylene, Magnesium chloride, Hydrogen response

### **Introduction**

Heterogeneous Ziegler-Natta catalysts based on supported on activated MgCl<sub>2</sub> supported with TiCl<sub>4</sub> has widely been used because great success has been achieved in improving catalyst activity and controlling the morphology of the product particles.<sup>(1,2)</sup> MgCl<sub>2</sub> is not only responsible for the dispersion of the titanium atoms over a high surface area, thus increasing the number of active sites, but it is also able to activate the polymerization reaction by increasing the propagation constant with respect to the older TiCl<sub>3</sub>-based systems.<sup>(3)</sup> The preparation method of the catalyst is very important as properties of the polymer are determined by the catalyst active center and its distribution. Each different active center produces polymer with different molecular weight, particle size and bulk density.<sup>(4)</sup> The size and shape of the catalyst particles control the morphology of the resulting polymer particles.<sup>(5)</sup> Many methods have been reported for catalyst preparation.<sup>(6,7,8)</sup> Polyethylene is widely used to make grocery bags, shampoo bottles, toys and many other things. When there is no branching in the polymer structure, it is linear polyethylene (HDPE), which

is stronger than branched polyethylene. When polyethylene is produced, a mixture with a broad molecular weight distribution is developed. For controlling the molecular weight a chain transfer agent, most preferable H<sub>2</sub>, can be added to the reaction mixture. Catalyst efficiency is always lost under high hydrogen concentration and there is a decay in catalytic activity over time caused by thermal deactivation and poisoning of active sites. In production of bimodal polyethylene, a molecular weight component is produced in one stage at a high H<sub>2</sub> concentration and a high molecular weight component is produced in another stage at a low H<sub>2</sub> concentration. The catalyst employed in production must be able to produce the different molecular weights with a high productivity.

In the present work, heterogeneous Ziegler-Natta catalysts were synthesized based on MgCl<sub>2</sub> support. Butyloctyl magnesium and 2-ethyl-1-hexanol were reacted to form magnesium complex which then was chlorinated and titanated. The effect of triethylaluminum/Mg and Ti/Mg molar ratios on the properties of catalysts was then investigated. Thermal treatment and effect of electron donor (ethylbenzoate) addition were studied. The

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resulting catalysts were evaluated in terms of efficiency in polymerization of ethylene in the slurry process. Polymerization performance under different hydrogen pressures (1 and 3 bar) was determined. The stability of the catalyst under high hydrogen pressure was evaluated using activity balance.

## Materials and Experimental Procedures

### Materials

Triethylaluminum (TEA) and 20% butyloctyl magnesium (BOMAG) in heptane were supplied from Chemtura;  $\text{TiCl}_4$  from Akzo Nobel; hexane, ethylene, hydrogen and nitrogen from IRPC PCL, Thailand; 2-ethyl-1-hexanol (2-EHA), ethylbenzoate and other organic solvents from Sigma. Solvents were dried over preactivated molecular sieves (4 Å).

### Characterization

FTIR-spectra were recorded by PERKIN ELMER spectrometer (model 1760X). Average particle size of catalysts was measured using Sympatec HELOS-VARIO/KF (Laser Diffraction, HELOS Sensor R3 for size range of 0.5-175  $\mu\text{m}$ , focal length = 100 mm). Particle size distribution analysis was performed by laser light scattering (Malvern mastersizer microplus). The total Ti content in the catalyst was determined by hydrolyzing the catalyst with 1.0 M  $\text{H}_2\text{SO}_4$ , and then reduced with Zn-amalgam for 10 minutes. After separation of Zn-amalgam, the sample solution was titrated with 0.1 M cerium (IV) sulfate using diphenylamine as an indicator. Ti was separated as hydroxide by adjusting pH of the solution to 4-6. Ti (III) was determined by oxidation of Ti(IV) with 0.1 M  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$  solution. The solution was then treated with  $\text{H}_3\text{PO}_4$  at 70°C and titrated with 0.6 M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution using *N,N'*-diphenylbenzidine as an indicator. A sharp color change from colorless to dark violet occurred at the end point. Mg content was determined following ASTM D511-88. The melt flow index (MFI) of polymer was measured according to ASTM D1238-99 (at 190°C, under 2.16 and 5.00 kg loading) using MPX 62.92 Gottfert Melt Flow Indexer. Bulk density of polymer was measured according to ASTM D1505-98. The hydrogen response of the catalyst was evaluated by calculating the activity balance which is a value expressed by  $AB = [\text{avg. CA} \times \log(\text{MFI}_2^*/\text{MFI}_2)]/|\Delta\text{CA}|$  where  $\text{MFI}_2^*$  = melt flow index at  $\text{H}_2$  pressure 3 bar,  $\text{MFI}_2$  = melt flow index at  $\text{H}_2$  pressure 1 bar, CA = catalyst activity (g PE/g cat).<sup>(9)</sup> Molecular

weight and molecular weight distribution of polymer were performed with gel permeation chromatography (GPC, Senshu SSC-7100) using trichlorobenzene as a solvent. The morphology of the polymeric samples was examined on the surfaces of samples freeze-fractured in liquid nitrogen; the samples were sputter-coated with a fine layer of gold in an Edward Sputter Coater and analyzed with JEOL JSM-6301F electron scanning microscopes.

### Preparation of Catalysts

20 wt% butyloctyl magnesium in heptane (175 mmol) and 200 mL toluene were filled into a 1 L four-neck round bottom flask equipped with motor stirrer. Then triethyl aluminium (TEA) was added in different TEA/Mg molar ratios (0.25, 0.5 and 1.0). Subsequently, 2-ethyl-1-hexanol (2-EHA, 612.5 mmol) was slowly added to a reaction mixture at 30°C. Stirring speed was set at 300 rpm. The reaction mixture was stirred for 30 minutes. Then  $\text{TiCl}_4$  (175 mmol, Ti/Mg molar ratio = 1) was dropped to the reaction mixture at room temperature and stirring speed of 250 rpm. The suspension was stirred for 30 minutes. The solid was separated and washed with heptane and resuspended in 200 mL heptane. After that  $\text{TiCl}_4$  was slowly added in different Ti/Mg molar ratios (2.0, 3.0 and 4.0). At the aging step, aging temperature was varied (80, 85 and 90°C) while stirring at 250 rpm over a course of 3 hours. The mixture was then stirred for different aging times (5, 10 or 15 hours). The resulting solid was isolated and washed several times with dried hexane at 60°C until Ti content in washings was less than 10 mmol/L.

For experiments with addition of electron donor, the same procedure was performed except that ethylbenzoate (EB) was added in EB/Mg molar ratio 0.10-0.15 following the addition of 2-ethyl-1-hexanol.

### Polymerization of Ethylene

All polymerizations of ethylene were carried out in a 2-L stainless steel reactor equipped with a thermostatic system and a mechanical stirrer. The reactor was evacuated and purged with nitrogen 3 times. A required amount of  $\text{Al}(\text{C}_2\text{H}_5)_3$  (cocatalyst) in 1,000 mL hexane (dried and stripped by  $\text{N}_2$ ) was filled into the reactor followed by 0.05 g catalyst (suspension in hexane) at Al/Ti molar ratio of 50. The reactor was heated up to 85°C and pressurized with 1 or 3 bar hydrogen gas and ethylene gas to a

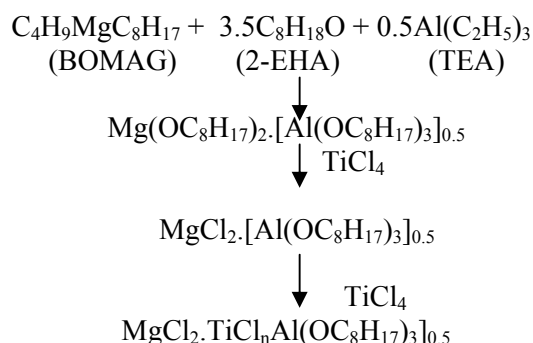
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constant total pressure of 8 bar. The polymerizations were carried out for 2 hours and then were terminated by venting the gaseous monomer and quenching the reaction with a solution of HCl/methanol. The polymers were washed with methanol several times, filtered, dried in vacuum and weighed.

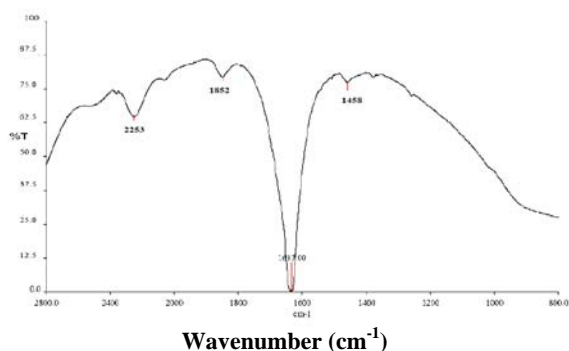
## Results and Discussion

### Preparation and Characterization of Catalysts

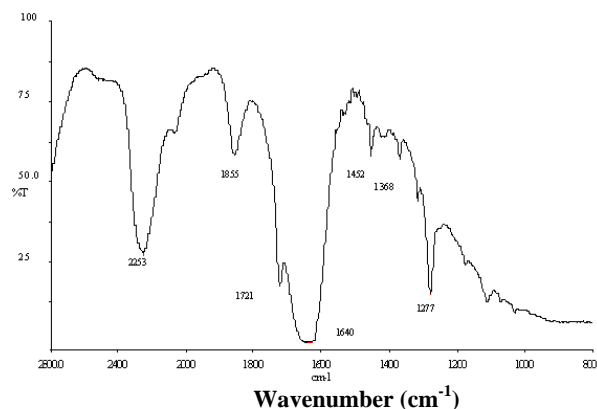
Reaction of BOMAG, 2-EHA and TEA resulted in the formation of magnesium complex. Next, chlorination was performed with  $\text{TiCl}_4$ . Further titanation with  $\text{TiCl}_4$  resulted in Ziegler-Natta catalyst as shown below.



The formation of the Ziegler-Natta catalyst was evidenced by IR spectrum (Figure 1) which shows absorption bands at 1852 and 1633  $\text{cm}^{-1}$  of Mg-Cl stretching.<sup>(4)</sup> Peaks at 2253 and 1458  $\text{cm}^{-1}$  are the  $\text{CH}_2/\text{CH}_3$  deformation vibration of 2-EHA adduct on the surface of  $\text{MgCl}_2$ . When ethylbenzoate was added in the reaction, peaks from ethylbenzoate were observed in the FTIR as shown in Figure 2. A peak at 1721  $\text{cm}^{-1}$  results from C=O stretching, whereas peaks at 1368, 1315, and 1277  $\text{cm}^{-1}$  are assigned to C-O-C asymmetric and symmetric stretching of ester group, indicating coordination of ethylbenzoate with the catalyst.<sup>(10)</sup>



**Figure 1.** FTIR spectrum of Ziegler-Natta catalyst.



**Figure 2.** FTIR spectrum of Ziegler-Natta catalyst with added ethylbenzoate.

### Effect Influencing Properties of Catalyst and Polymerization

In this work parameters affecting the property of catalyst and catalytic activity in the polymerization of ethylene were investigated. The parameters studied are: TEA/Mg molar ratio, Ti/Mg molar ratio, aging time and aging temperature. Results are summarized as follows:

#### a. Effect of TEA/Mg Molar Ratio

Experiments were carried out using different TEA/Mg molar ratios (0.25, 0.50 and 1.00). In this first step, triethylaluminium (TEA) was used in order to control viscosity of the catalyst suspension. The results are shown in Table 1. At TEA/Mg molar ratio of 0.25, the catalysts became sticky. This might be due to the formation of amorphous species reported previously.<sup>(12)</sup> At TEA/Mg molar ratio = 0.5 and 1.0, good dispersion of the catalyst in heptane can be obtained. Therefore, the ratio of 0.5 was chosen to use in further experiments.

**Table 1.** Properties of catalysts at different TEA/Mg molar ratios

TEA/Mg molar ratio used	Appearance of catalyst
0.25	sticky
0.5	good dispersion
1.0	good dispersion

## b. Effect of Ti/Mg Molar Ratio

In the chlorination step  $TiCl_4$  (Ti/Mg molar ratios = 2.0, 3.0 and 4.0) was used as chlorinating agent and the optimized TEA/Mg molar ratio of 0.50 which was determined. The results are shown in Table 2. When the Ti/Mg molar ratio used was increased from 2.0 to 3.0, Ti content fixed on the  $MgCl_2$  support was increased as revealed by an increasing analyzed Ti/Mg molar ratio. The maximum Ti content was obtained at a Ti/Mg molar ratio of 3.0. Ti amount fixed on magnesium chloride support has strong affect on the efficiency of the catalyst. It was found that the catalytic activity is also maximum (20,990 g PE/g cat) at Ti/Mg molar ratio 3.0. When the Ti/Mg molar ratio used was further increased to 4.0, the Ti content slightly dropped and catalytic activity was decreased to 10,950 g PE/g catalyst. The catalytic activity is noticeably influenced by the oxidation state of Ti on the catalyst. It was shown from content of Ti(III) (in percentage) analyzed that the optimum Ti/Mg molar ratio of 3.0 resulted in a higher percentage of Ti(III) 73% compared to other molar ratios.

**Table 2.** Properties of catalysts at different Ti/Mg molar ratios (TEA/Mg molar ratio = 0.50)

Ti/Mg molar ratio used	Ti/Mg molar ratio analyzed	%Ti(III)	Activity (g PE/g cat.) at 1 bar $H_2$
2.0	0.18	27	7,854
3.0	0.35	73	20,990
4.0	0.30	40	10,950

## c. Effect of Electron Donor Addition on Activity and Hydrogen Response of the Catalyst

The electron donor in this work is ethylbenzoate. It was added at different EB/Mg molar ratios (0.10 and 0.15). Results are shown in Table 3. It was found that EB decreased the fixation of Ti on the  $MgCl_2$  support. This can be explained by the fact that the electron donor occupies some active sites on the  $MgCl_2$  support, preventing  $TiCl_4$  from coordination on  $MgCl_2$  crystal faces.<sup>(15)</sup> The adverse effect of EB was shown in polymerization performance of the catalyst. The catalytic activities were measured under both 1 and 3 bar  $H_2$  conditions. It can be seen that the activities decreased significantly when ethylbenzoate was added.

**Table 3.** Property of catalysts with ethylbenzoate (EB) addition (TEA/Mg molar ratio 0.50 and Ti/Mg molar ratio 3.0)

EB/Mg molar ratio used	Ti/Mg molar ratio analyzed	Activity (g PE/g cat.) 1 bar $H_2$	Activity (g PE/g cat.) 3 bar $H_2$
0	0.35	20,990	14,249
0.12	0.10	4,558	4,505
0.25	0.08	2,080	2,155

For industries, high catalytic activity and high molecular weight polymer were required. A good catalyst should still possess high activity at both low and high hydrogen pressures. In other words, it was not deactivated at high hydrogen pressure. Activity balance (AB) proposed by Garolf, *et al.* (2002) was used to compare the hydrogen response of the catalyst. It was calculated from both activities and melt flow indices at two hydrogen pressures (1 and 3 bar). In this work, the activity balance of the catalyst with EB addition was compared to the one without addition as shown in Table 4. The catalysts with EB/Mg molar ratio of 0.12 and 0.25 show higher high value of AB (52.2 and 17.2, respectively) than the one without EB addition (2.7). Therefore, it can be shown that EB enhanced the stability of the catalyst under high hydrogen pressure (3 bar). Moreover, it was also observed that the catalyst size increased from 7.2 to 13.3-16.6  $\mu m$ , which indicated that EB enhanced the mechanical stability of catalyst particles by preventing fragmentation. As the EB/Mg molar ratio of 0.12 gave the highest AB value, it was used in a further experiment.

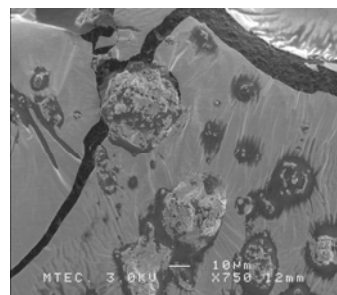
**Table 4.** Melt flow indices, activity balance and size of catalysts with and without ethylbenzoate (EB) addition

EB/Mg molar ratio used	MFI <sub>2</sub> (g/10 min) 1 bar $H_2$	MFI <sub>2</sub> (g/10 min) 3 bar $H_2$	Activity balance (AB)	Catalyst size ( $\mu m$ )
0	1.7	54.5	2.7	7.2
0.12	1.0	18.0	52.2	16.6
0.25	2.0	6.2	17.2	13.3

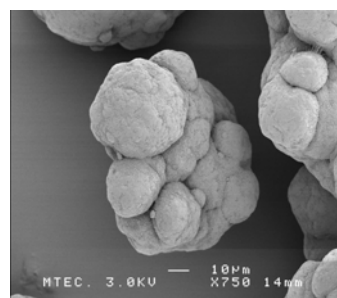
Activity balance,  $AB = [\text{avg. CA} \times \log(\text{MFI}_2^*/\text{MFI}_2)]/|\Delta CA|$  where  $\text{MFI}_2^*$  = melt flow index at  $H_2$  pressure 3 bar,  $\text{MFI}_2$  = melt flow index at  $H_2$  pressure 1 bar, CA = catalyst activity (g PE/g cat)

## d. Effect of Aging

It was found that the activity balance of the catalyst can be enhanced by addition of electron donor, but the catalytic activity was decreased significantly. Therefore, an attempt was made to improve the activity by performing aging step. Under the optimized conditions, the reaction mixture after ethyl benzoate and  $\text{TiCl}_4$  added was stirred at  $85^\circ\text{C}$  for required periods of aging time (5, 10 and 15 hours). The influence of aging on catalyst activity is shown in Table 5. It was found that when the catalyst was aged, its activity was higher than that from the unaged catalyst (4,558 and 4,505 g PE/g cat at 1 and 3 bar  $\text{H}_2$ ) under the same condition. When increasing aging time, catalyst activity was increased. This can be due to the increase in Ti content in the catalyst. The maximum activity was achieved at an aging time of 10 hours. At a longer aging time, a drop in activity was observed, probably due to over-reduction of Ti. Table 5 shows the melt flow indices, activity balance and size of the catalysts at different aging times. At 5, 10 and 15 hours aging time, the activity balances were 57.0, 21.8 and 2.3, respectively. The catalyst sizes are similar (12-15  $\mu\text{m}$ ). It was thus demonstrated that the catalyst undergoing thermal treatment with appropriate aging time can give high activity (23,096 and 22,376 at 1 and 3 bar, respectively) with moderate activity balance.



(a) catalyst



(b) polyethylene

**Figure 3.** SEM micrographs of (a) catalyst and (b) polyethylene (x 750 magnification).

### Conclusions

The  $\text{MgCl}_2$ -supported Ziegler-Natta catalysts were synthesized from the *in situ*-prepared  $\text{MgCl}_2$ . Addition of electron donor (ethylbenzoate) was found to increase the stability of the catalyst under high  $\text{H}_2$  pressure even though the catalyst activity

**Table 5.** Property of catalysts at different aging times (TEA/Mg molar ratio 0.50, Ti/Mg molar ratio 3.0 and EB/Mg molar ratio 0.12, aging temperature  $85^\circ\text{C}$ )

Aging time (h)	Ti/Mg molar ratio analyzed	Activity (g PE/g cat.) 1 bar $\text{H}_2$	Activity (g PE/g cat.) 3 bar $\text{H}_2$	MFI <sub>2</sub> (g/10 min) 1 bar $\text{H}_2$	MFI <sub>2</sub> (g/10 min) 3 bar $\text{H}_2$	Activity Balance (AB)
5	0.10	5,505	6,630	1.1	9.4	57.0
10	0.18	23,096	22,376	0.8	5.1	21.8
15	0.18	20,467	13,400	0.6	4.6	2.3

### Morphology of the Catalyst and Polymer

The morphology of the catalyst and the polymer produced was examined by SEM. The SEM micrographs are shown in Figure 3. The polymer granules produced in the polymerization replicated the spherical shape of the catalyst particles.<sup>(16)</sup> Polyethylenes produced have a density of 0.9591 which is in the range of high density polyethylene (HDPE, 0.9591-0.9594  $\text{g}/\text{cm}^3$ ).  $M_w$  and  $M_n$  determined by GPC were 30,000 and 192,000  $\text{g}/\text{mol}$  and molecular weight distribution was 6.4.

was decreased. It was verified that aging or thermal treatment during the preparation of these catalysts can improve catalyst activity. The catalyst is suitable for producing HDPE in slurry process.

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