Journal of Metals, Materials and Minerals, Vol.19 No.1 pp.17-23, 2009.

Effect of Electron Donor on PE Polymerization

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Abstract

Received Mar. 2, 2009
Accepted Apr. 27, 2009

Ziegler-Natta catalyst was prepared from colloidal $MgCl_2$ (from reaction between magnesium ethyl carbonate and aluminium sesquichloride, $Al_2Et_3Cl_3$) followed by contact with $TiCl_4$. Al/Mg and Ti/Mg molar ratios were studied as parameters affecting the catalyst synthesis. Catalytic performance and effect of electron donor on ethylene polymerization were investigated. Results showed that addition of electron donor (ethyl benzoate) increased activity balance when polymerizations were performed under hydrogen pressure of 1 bar and 3 bars. The morphology of the polymer can be improved while fine content of the polymer was reduced by addition of dicyclopentyl dimethoxysilane. A productivity of 17.3 and 15.0 kg PE/g cat. was obtained at 1 and 3 bar H_2. High density polyethylenes with molecular weight of $2.43x10^5$ g/mol, molecular weight distribution of 11.9 and high bulk density (0.36 g/cm^3) can be obtained.

Key words : Ziegler –Natta catalyst, HDPE, Magnesium chloride

Introduction

Ziegler-Natta catalyst has played an essential role in the production of polyolefin plastics. The conventional Ziegler-Natta catalyst consists of a $MgCl_2$ support and $TiCl_4$ together with the cocatalyst. The capability of the catalysts to replicate their morphology into the morphology of polymer granules is an important feature of the heterogeneous Ziegler-Natta polymerization.(1,2) Morphology-controlled polyolefins made directly in reactors (so-called reactor polyolefin granules) are polyolefin granules that have spherical shape, high bulk density, high flowability, large size and low content of fines. Commercial production of reactor polyolefin granules is carried out in multistage processes, for example the SPHERIPOL and SPHERILENE processes. (3, 4)

The supported Ziegler-Natta catalyst should contain activated $MgCl_2$ and small primary crystallize size and a disordered crystallographic structure.(5) $MgCl_2$ 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 $TiCl_3$-based systems. Several different techniques are used to manufacture $MgCl_2$ particles suitable for catalyst preparation, including (a) recrystallization of $MgCl_2$ from a mixture of ethanol, methyl siloxane oil, and paraffin oil at low temperature;(6) (b) precipitation of complexes of $MgCl_2$ from polar solvents;(7) (c) chemical method(8) and (d) spray crystallization.(9) The active component ($TiCl_4$) can be fixed on the $MgCl_2$ support by one of the various methods, one of which is impregnation and refluxing.(10) The common used method in industry is by cooling emulsions of molten $MgCl_2.nEtOH$ adducts in paraffin oil and reaction with $TiCl_4$.(11)

The present paper reports on the preparation of Ziegler-Natta catalyst from colloidal magnesium ethyl carbonate. The performance of the catalysts was evaluated in slurry ethylene polymerization, using triethylaluminum as cocatalyst. The effect of the electron donors: ethyl benzoate

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and dicyclopentyl dimethoxysilane as well as heat treatment on catalyst performance were investigated. Catalyst stability under different hydrogen pressures was determined in terms of activity balance.

Materials and Experimental Procedures

Materials

Magnesium ethoxide (particle size 700 micron in diameter) from Degussa; ethyl aluminium sesquichloride ($Al_2Et_3Cl_3$), diethyl aluminium chloride ($AlEt_2Cl$) and triethyl aluminium (TEA) from Chemtura; $TiCl_4$ from Ti oxide UK Limited; hexane, ethylene, hydrogen and nitrogen from IRPC PCL, Thailand; carbon dioxide (99.999 %) from Lab center; ethyl benzoate from Fluka and dicyclopentyl dimethoxysilane (DCPDMS) (99.99%) from Xiangyang; ethanol and other solvents from Merck. Solvents were dried over preactivated molecular sieve 4 Å.

Preparation of Catalyst

Magnesium ethyl carbonate was formed by suspending 0.25 mol of magnesium ethoxide in ethanol (ethanol/magnesium ethoxide molar ratio was varied in the range of 1-4) and 400 ml. of toluene, feeding 40 psi CO_2 at ambient temperature until the magnesium ethoxide was dissolved. Two types of precipitating agent ($Al_2Et_3Cl_3$ or $AlEt_2Cl$) were compared at Mg/Al molar ratio of 0.50. Addition of precipitating agent resulted in precipitated solids. $Al_2Et_3Cl_3$/Mg molar ratio was also varied. For experiments with addition of ethyl benzoate (EB), EB was added in various EB/Ti molar ratios. Then the resulting solids were reacted with different amount of $TiCl_4$ at 110°C for 2 h with an agitation speed of 400 rpm. After that the solid catalyst was separated and washed several times with toluene until the titanium content in washing was lower than 10 mmol/L. During the washings temperature was controlled at 65°C. Another experiment was conducted in the same manner (using the same reagents and reaction condition) but with addition of dicyclopentyl dimethoxysilane (DCPDMS) to the solution of magnesium ethyl carbonate.

Polymerization of Ethylene

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. $Al(C_2H_5)_3$ in 1 L hexane (dried and stripped by N_2) was filled into the reactor. Then it was charged with catalyst (suspension in hexane). The Al/Ti molar ratio used was 50. The reactor was heated up to 85°C and pressurized with hydrogen gas (1 or 3 bar) and ethylene gas. The total pressure of the reactor was kept constant at 8 bar. After 2 h polymerization, gas was vented. The reaction was quenched by adding HCl/methanol solution. The polymer powder was separated and dried in vacuum at 80°C and weighed.

Characterization

The Mg content was determined following ASTM D511-88. For total Ti content, the catalyst sample was digested with sulfuric acid and oxidized with hydrogen peroxide and analyzed by visible spectrophotometry (λ = 410 nm). FTIR-spectra were recorded by PERKIN ELMER spectrometer (model 1760X). Average particle size and particle size distribution (PSD) of catalysts were measured using Sympatec HELOS-VARIO/KF (Laser Diffraction, HELOS Sensor R3 for size range of 0.5-175 μm, focal length = 100 mm). Particle size distribution analysis was performed by laser light scattering (Malvern mastersizer microplus). 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. Melt flow index (MFI) 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. Molecular weight (MW) and molecular weight distribution (MWD) of polymer were measured using a PL-GPC high temperature chromatograph with differential refractive index detector and viscometric detector. Bulk density of polymer was measured according to ASTM D1505-98. The hydrogen sensitivity of the catalyst was evaluated by calculating activity balance which is a value expressed by $AB = [\text{avg.}CA \times \log(MFI_2^*/MFI_2)]/|\Delta CA|$, where MFI_2^* = melt flow index at H_2 pressure 3 bar, MFI_2 = melt flow index at H_2 pressure 1 bar, CA = catalyst activity (g PE/g cat).(12)

Results and Discussion

Preparation and Characterization of Catalysts

Magnesium ethoxide was suspended in a mixture of ethanol/toluene. After adding CO_2 it was dissolved and formed magnesium ethyl carbonate. This paper demonstrates the minimum $EtOH/Mg(OEt)_2$ molar ratio (3) to obtain a clear solution. The very low amount of alcohol needed in this method is different from that used in other works in which larger amounts of alcohol were needed to form magnesium chloride alcohol adduct. Active magnesium chloride was finally obtained after alcohol evaporation which needed long time in removing ethanol. (13, 14)

The addition of $Al_2Et_3Cl_3$ (or $AlEt_2Cl$) in the Mg/Al molar ratio of 0.5 resulted in formation of solids and magnesium chloride as shown in the equation below. It was observed that precipitated particles were obtained when using $Al_2Et_3Cl_3$ while $AlEt_2Cl$ gave puffy particles. Therefore $Al_2Et_3Cl_3$ was chosen in further experiments.

$$\begin{tikzcd} Mg(OEt)_2 + CO_2 \arrow[r, "\text{ethanol/toluene}"] & Mg(OEt)(OCOOEt) \arrow[d, "Al_2Et_3Cl_3 \text{ orA } lEt_2Cl"] \\ & MgCl_{2-x}\{Mg(OEt)(OCOOEt)\}_x \end{tikzcd}$$

The formation of magnesium ethyl carbonate was confirmed by TGA and FT-IR, as shown in Figures 1 and 2, respectively. In Figure 1 the TGA curve of the magnesium ethyl carbonate compared to magnesium ethoxide showed weight loss at lower temperature, indicating formation of magnesium ethyl carbonate. (15)

FTIR spectrum of the magnesium ethyl carbonate in Figure 2 showed strong bands belonging to C=O and C-O peaks of ester group at 1646 and 1326 cm^{-1}, respectively. A band of ethoxy group appeared at 1449 cm^{-1}.

The magnesium ethyl carbonate was reacted with ethyl aluminium sesquichloride ($Al_2Et_3Cl_3$) and contacted with $TiCl_4$ to result in $MgCl_2$ supported Ziegler-Natta catalyst. Its FT-IR spectrum (Figure 3) showed bands of Mg-Cl at 1636, 1852 and 2252 cm^{-1} together with bands of Ti-Cl at 466 and 618 cm^{-1}. (16)

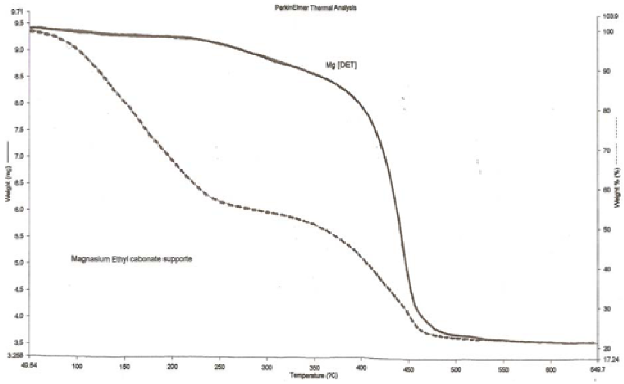


Figure 1. Differential TGA of magnesium ethoxide (continuous line) and magnesium ethyl carbonate support (dot line).

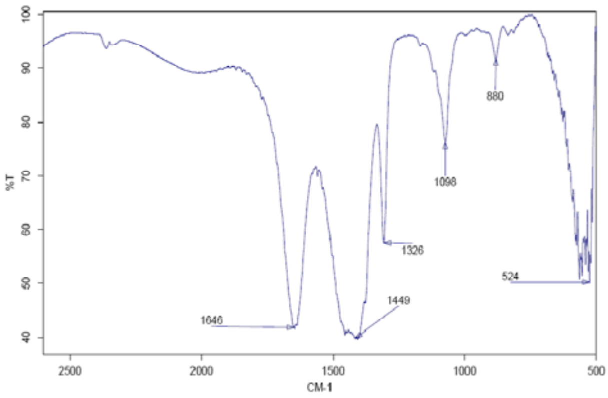


Figure 2. FT-IR spectrum of magnesium ethyl carbonate.

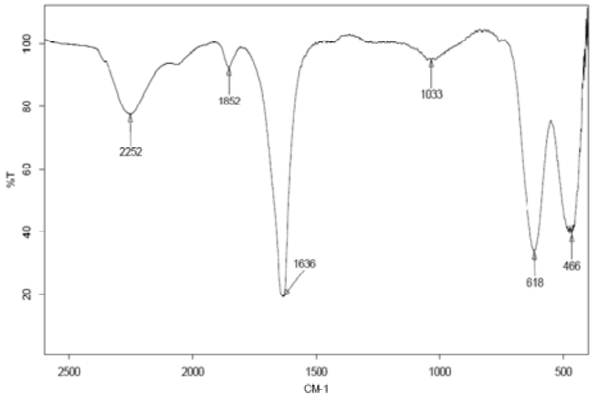


Figure 3. FT-IR spectrum of $MgCl_2$ supported Ziegler-Natta catalyst.

Effect of Al2Et3Cl3/Mg Molar Ratio

The effect of $Al_2Et_3Cl_3$ concentration on Ti fixation onto the catalyst was studied. A different amount of $Al_2Et_3Cl_3$ was used, while other reaction parameters were fixed: Ti/Mg molar ratio of 3.00, Al/Ti molar ratio of 50, polymerization temperature at 85°C and time 2 h. Ti and Mg contents on the supported catalyst were analyzed and are shown in Table 1. It can be seen that the Ti/Mg molar ratio was slightly decreased when the $Al_2Et_3Cl_3$ amount was increased, $Al_2Et_3Cl_3$/Mg molar ratio from 0.06 to 0.50. At higher Ti/Mg molar ratios used (0.75-1.00), the Ti/Mg molar ratio analyzed was found to increase. This is in good agreement with previous report.(17) Comparison of activity of the catalysts in polymerization of ethylene showed that optimum activity (20.1 kg PE/g catalyst) occurred at $Al_2Et_3Cl_3$/Mg molar ratio of 0.50. This high activity is due to the fact that more Ti (IV) ions were reduced to Ti(III) or Ti(II) with an increase of $Al_2Et_3Cl_3$ as the $Al_2Et_3Cl_3$ was not only used as precipitating, but it also acted as a reducing agent. However, at higher $Al_2Et_3Cl_3$/Mg molar ratio (1.00) the activity was decreased. This might be due to overreduction of Ti (IV). Therefore, an optimum ratio is acquired as was previously reported.(18) The optimum $Al_2Et_3Cl_3$/Mg molar ratio found in this work was at 0.50. Averaged catalyst particle sizes were in range of 9.3-12.6 μm.

Effect of Ti/Mg Molar Ratio

As a much higher Ti/Mg molar ratio has usually been used for good polymerization performance, Job, 2003 in this work the effect of the Ti/Mg molar ratio (2.00-4.00) was investigated. Results are shown in Table 2. The Ti/Mg molar ratio at 3.00 showed higher activity than those ratios at 2.00 and 4.00. Ti amount fixed on the support was increased with an increase in the Ti/Mg molar ratio. At ratio of 2.00, catalytic activity was low. On the contrary, at ratio of 4.00, even though there was more Ti on the support, catalytic activity turned out to be lower than that at 3.00. This fact might be explained by different oxidation state of Ti on the catalyst.

Effect of Ethylbenzoate

The electron donor was usually used to activate the support, e.g. by increasing its surface area.(20) In this work, the electron donor ethylbenzoate was added into the reaction mixture in the step before $TiCl_4$ addition. The reaction mixture was then

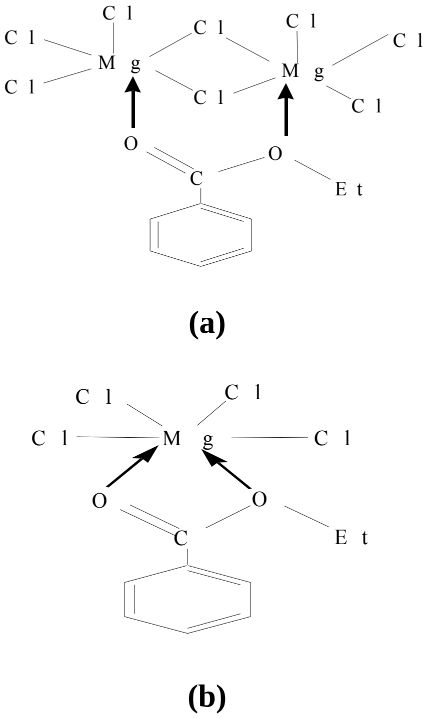
Table 1. Catalytic activities at different $Al_2Et_3Cl_3$/Mg molar ratios (Ti/Mg molar ratio of 3.00, Al/Ti molar ratio of 50, agitation speed 400 rpm, polymerization temperature at 85°C and time 2 h)

$Al_2Et_3Cl_3$/Mg molar ratio	Ti/Mg molar ratio used	Ti/Mg molar ratio analyzed	Averaged catalyst particle size (μm)	Activity (kg PE/g cat.) at 1 bar of H_2
0.06	3.00	0.11	9.3	6.7
0.12	3.00	0.09	9.7	9.3
0.25	3.00	0.07	9.8	13.1
0.50	3.00	0.07	11.0	20.1
0.75	3.00	0.11	12.0	13.7
1.00	3.00	0.20	12.6	10.2

Table 2. Catalytic activities at different Ti/Mg molar ratios ($Al_2Et_3Cl_3$/Mg molar ratio of 0.50, Al/Ti molar ratio of 50, agitation speed 400 rpm, polymerization temperature at 85°C and time 2 h)

Ti/Mg molar ratio used	Ti/Mg molar ratio analyzed	Averaged catalyst particle size (μm)	Activity (kg PE/g cat.) at 1 bar of H_2
2.00	0.04	9.2	6.2
3.00	0.07	11.0	20.1
4.00	0.09	8.0	11.5

stirred at 110°C for 2 h. The result showed that the catalyst contained a lower amount of Ti (Ti/Mg molar ratio was decreased). This was due to displacement of $TiCl_4$ with ethylbenzoate to the surface of $MgCl_2$. The coordination of ethylbenzoate was theoretically studied (Figure 4).(21)



(a)

(b)

Figure 4. Possible models for EB coordination on the (100) (a) and (110) (b) faces of $MgCl_2$.

In this work, the reaction mixture was performed by heat treatment at 110°C for 2 h. The heat treatment created different active sites on the catalyst and chlorotitanate ($-Ti(OR)_nCl_{4-n}$) converted into titanoxane (Ti-O-Ti).(22)

The addition of ethylbenzoate did not have much effect on average catalyst particle size, it was in the range of 12.2-13.5. On the contrary, % fine content of the polymer prepared with EB addition decreased significantly from 50 to 28.

Activity Balance

For industries, high catalytic activity and high molecular weight polymer were required. A good catalyst should still possess high activity at low and high hydrogen pressures. In other words, it was not deactivated at high hydrogen pressure. Activity balance (AB) proposed by Garolf et al. (12) was used to compare hydrogen response of the catalyst. It was calculated from both activities and melt flow indices at two hydrogen pressures (1 and 3 bar). The results in Table 3 show that at high hydrogen pressure (3 bar) the activity of catalyst and molecular weight of polymer were decreased. The highest value of AB (6.1) was obtained in the catalytic system with an EB/Mg molar ratio of 0.12. This means that the catalyst system was still stable under high H_2 pressure. However, the catalyst activity was decreased to 9.5 and 8.3 kg PE/g cat. at 1 and 3 bar H_2, respectively. An attempt to improve this was successful by increasing the time from 2 to 5 h (after ethyl benzoate and $TiCl_4$ were added, the reaction mixture was stirred at 110°C for 5 h). The result show that the obtained catalyst has a Ti/Mg molar ratio of 0.07 and averaged particle size of 12.5 μm. Furthermore, the activity can be enhanced to 17.3 and 15.0 kg PE/g cat. and melt flow index (MFI) were 0.98 and 10.3 g/10 min. at 1 and 3 bar H_2, respectively. The calculated activity balance was high (7.2).

Table 3. Catalytic activities with ethyl benzoate (EB) addition ($Al_2Et_3Cl_3$/Mg molar ratio = 0.50, Ti/Mg molar ratio = 3.00, agitation speed 400 rpm, temperature 110°C and time 2 h)

EB/Mg molar ratio added	Ti/Mg molar ratio analyzed	Averaged catalyst particle size(μm)	Activity (kg PE/g cat.) at 1 bar of H_2	$MFI_{2.16}$ (g/10min) at 1 bar of H_2	Activity (kg PE/g cat.) at 3 bar of H_2	$MFI_{2.16}$ (g/10 min) at 3 bar of H_2	Activity Balance (AB)	Fine content (%)
0.00	0.07	11.0	20.1	1.05	14.7	9.5	3.1	50
0.06	0.06	13.5	11.5	1.56	9.2	10.5	3.7	32
0.12	0.05	13.1	9.5	1.86	8.3	12.3	6.1	28
0.25	0.04	12.2	4.8	2.00	1.8	20.1	1.1	31

*AB = [average CA x $\log[(MFI_2^*/MFI_2)]/|\Delta CA|$ where MFI_2^* = melt flow index at H_2 pressure 3 bar, MFI_2 = melt flow index at H_2 pressure 1 bar, CA = catalyst activity

Effect of Dicyclopentyl Dimethoxysilane

Dicyclopentyl dimethoxysilane (DCPDMS) was also added to the reaction mixture after addition of ethylbenzoate (EB/Mg molar ratio = 0.12). The DCPDMS/Mg molar ratio used was 0.25. The result showed that the introduction of DCPDMS increased the average catalyst particle size to 33 μm. This revealed that DCPDMS played the role of a binding agent Figure 5, making small support particles to aggregate as well as preventing mechanical fragment of support during polymerization.

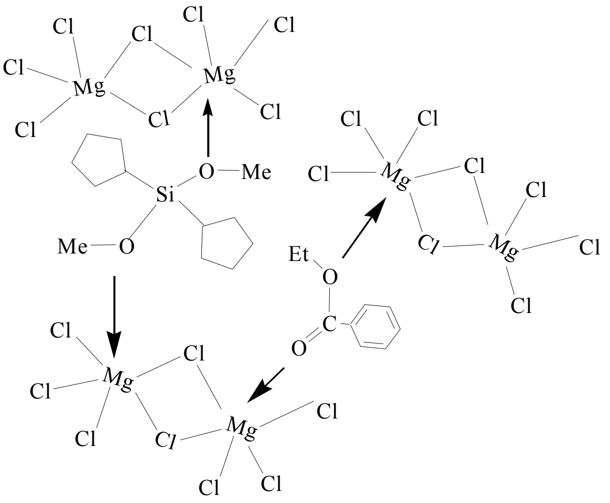
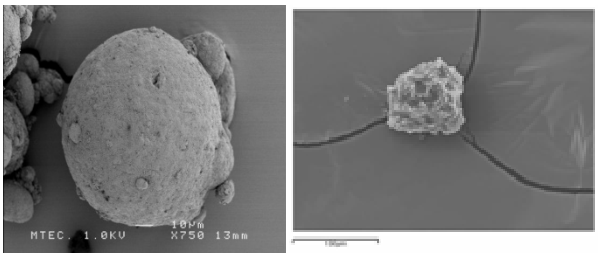
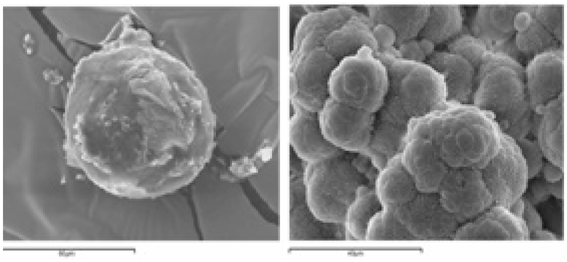


Figure 5. Binding of DCPDMS and EB with $MgCl_2$.

The SEM micrograph of polyethylene produced with addition of both EB and DCPDMS is shown in Figure 6, compared to the polyethylene with only EB addition. Polymer with fibril nature in bigger size ~135 μm was observed in the system with addition of both EB and DCPDMS. Moreover, the use of DCPDMS has the advantage of reducing % fine content of polymer to only 7%. The molecular weight of polyethylene was 2.43×10^5 g/mol which is in range of HDPE. The molecular weight distribution was 11.9. Bulk density of polymer was determined to be 0.36 g/cm^3.



(a)



(b)

Figure 6. SEM micrographs of catalyst and polyethylene (a) with EB addition (b) with EB and DCPDMS addition

Conclusion

The Ziegler-Natta catalyst was prepared from colloidal $MgCl_2$ which resulted from the reaction of magnesium ethyl carbonate and chlorinating agent. It showed good activity in slurry polymerization of ethylene under optimized condition to produce HDPE with low fine content.

The catalyst was active at low and high pressures, demonstrating its stability or high activity balance.

Acknowledgments

The authors would like to thank the Graduate School, Chulalongkorn University for financial support.

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