Recycling of Methylaluminoxane (MAO) Cocatalyst in Ethylene Polymerization with Supported Metallocene Catalyst

Jae Seung Oh†, Bun Yeoul Lee* and Tai Ho Park**

LG Chemical Ltd./Research Park, Moonji-dong 104-1, Yuseong-ku, Daejeon 305-380, Korea

Abstract−The economy of the metallocene catalyst system in olefin polymerization depends more on the cost of methylaluminoxane (MAO) cocatalyst rather than on the catalyst cost since high ratio of cocatalyst to catalyst is required to have sufficient activity. The conditions to minimize the consumption of MAO have been studied for the ethylene polymerization with supported metallocene catalyst. By introducing the prepolymerization step, in which the supported metallocene catalyst is activated at high MAO concentration before polymerization, the MAO could be recovered after the prepolymerization and recycled repeatedly for the subsequent activation with marginal decrease in activity. No extra MAO was needed during the main polymerization. The addition of small amount of MAO or less expensive alkylaluminum at each recycle step kept the catalyst activity to the initial level. It compensates the MAO losses occurring both by the incomplete decantation of MAO solution and by the reaction with metallocene complex or impurities. As a result, the actual consumption ratio of Al/Zr in moles in commercial applications could be reduced to about 30 without sacrificing the activity. This value is significantly low considering that conventionally an Al/Zr ratio of 1,000 is required for sufficient activity.

Key words: Metallocene Catalyst, Supported Catalyst, Ethylene Polymerization, Methylaluminoxane, Cocatalyst Recycle

INTRODUCTION

Metallocene compounds activated by cocatalysts such as aluminoxanes or borates have been extensively investigated as a new generation of catalysts for polyolefins [Togni and Halterman, 1998; Scheirs and Kaminsky, 2000]. The metallocene catalyst has single-site characteristics producing polymers with narrow molecular weight distribution [Cho et al., 2000] and uniform comonomer incorporation. The stereo-structure of polymer can also be controlled by the molecular geometry of the catalyst. During the last 10 years, the metallocene catalyst has been successfully applied to most commercial polyolefin processes. Nevertheless, the cost of metallocene catalyst is still considered much higher than the conventional Ziegler-Natta catalyst [Sullivan, 1998; Brockmeier, 1998]. When methylaluminoxane (MAO) is used as a cocatalyst, the economy of metallocene catalyst system depends more on the MAO cost rather than on the catalyst cost since a large excess of MAO is required to have high catalyst activity. Generally, the ratio of MAO/metallocene catalyst is represented by Al/Zr molar ratio when zirconocene is used as a catalyst. In conventional applications its range for sufficient activity is more than 1,000 [Chien and Sugimoto, 1991; Coevoet et al., 1998; Han et al., 1999; Jeong et al., 2003]. Some previous studies claim that all or part of MAO used in polymerization could

be replaced with less expensive alkylaluminum [Panin et al., 2001], but MAO is still used as a major cocatalyst in the metallocene catalyst systems of industrial importance.

MAO has various roles in the metallocene-catalyzed polymerization of olefins. MAO activates metallocene compound by alkylation and cation-formation and stabilizes it as a non-coordinating anion [dos Santos et al., 1999; Pedeutour et al., 2001]. It also protects the activated catalyst from impurities by scavenging them. A high concentration of MAO is required mainly for the purpose of catalyst activation. Therefore, the use of MAO may be optimized if the catalyst is activated in the prepolymerization step before main polymerization, and the polymerization is carried out separately with the prepolymerized active catalyst [Oh et al., 2002]. A high concentration of MAO is employed only at the prepolymerization step and no MAO is added during the main polymerization in this method. The major portion of MAO in the prepolymerization step can be recovered and reused for the next activation reaction since only small portion of the added MAO is consumed during the activation. By following this idea the conditions to minimize the consumption of MAO cocatalyst in the ethylene polymerization have been investigated in this report.

For the slurry or gas phase process, in which the morphology and the bulk density of the polymer particles need to be controlled, homogenous catalysts like metallocene compounds should be immobilized on solid support [Chung et al., 2002]. It is more convenient with this supported metallocene catalysts to apply the prepolymerization method for the recycling of MAO. Various silica-supported zirconocenes so prepared were activated in the prepolymerization step with high concentration of MAO (zirconocene/silica+MAO). Then the prepolymerized active catalysts were injected to the reactor without the addition of extra MAO for main polymerization. Their catalyst activities were compared with the conven-
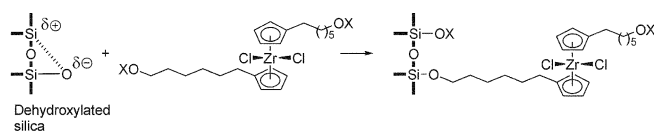
†To whom correspondence should be addressed.
E-mail: jsoh@lgchem.co.kr
*Present address: Department of Molecular Science and Technology, Ajou University, Suwon 442-749, Korea
**Present address: Department of Chemistry, University of Illinois at Urbana-Champagne, Illinois 61801, U.S.A.
‡This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

X=(EtO)(Me)$_2$Si-, Me$_3$Si-, H(Me)$_2$Si-, or t-Butyl-.

Scheme 1. Anchoring metallocene compound by the reaction with siloxane group on silica.

tional direct polymerization method where MAO exists in polymerization medium.

EXPERIMENTAL

1. Catalyst Anchoring

Among the various ways of immobilization of homogeneous metallocene catalysts [Ribeiro et al., 1997; Hlatky, 2000], one of the most promising methods may be the reaction between a functional group of metallocene compound and a functional group on solid surface to form a strong covalent bonding. An electron-deficient strained siloxane group of silica, after dehydroxylation over 900 K, could be used for anchoring by a simple reaction (Scheme 1). The synthesis of metallocene complexes having acetal, ketal, or t-butyl ether groups as a substituent on the cyclopentadienyl ring was described elsewhere [Lee and Oh, 2000; Oh et al., 2002]. Dehydroxylated silica was prepared by calcining silica (Grace Davison XPO 2412, mean particle size 21 µm) at 800 °C for 15 hours under vacuum. The anchored metallocene catalysts were prepared by the reaction of metallocene compound (0.10 g) with dehydroxylated silica (1.0 g) in hexane (30 mL) at 85 °C for 4 hours. Nothing was detected in the decanted hexane, indicating that all metallocene complex added was immobilized on the solid surface and the Zr content on silica determined on an ICP was in agreement with the added amount.

2. Catalyst Activation and Polymerization

Polymerization was conducted with or without prepolymerization and the methods are described in Fig. 1. For the polymeriza-

tion conducted without prepolymerization (Fig. 1a), hexane (200 mL), predetermined MAO (Akzo MMAO-3, Al 7.3 wt% in heptane solution), and the anchored catalyst (100 mg) were added to a 500 mL glass reactor successively. The reactor was immersed in an oil bath, whose temperature had been set at 80 °C, and agitated for 5 minutes. Ethylene was fed continuously to the reactor under the pressure of 2.76 bar for 1 hour. Polymerization was stopped by venting the ethylene gas. The precipitated polyethylene particles were filtered and dried under vacuum.

For the polymerization conducted with prepolymerization (Fig. 1b), hexane (100 mL), predetermined MAO (Akzo MMAO-3, Al 7.3 wt% in heptane solution), and the anchored catalyst (100 mg) were added to a 500 mL glass reactor successively. Prepolymerization was carried out by feeding ethylene gas (625 mg) at room temperature for 10 minutes through a mass flow controller (feeding rate, 50 mL/min). As soon as the ethylene gas was added, it was consumed completely and no ethylene pressure was built. The prepolymerized active catalyst particles were settled down and the hexane containing unreacted MAO was decanted by a cannular without contacting air to the reservoir. Then hexane (200 mL) containing triethylaluminum (0.3 mmol) as a scavenger was added to the reactor having the prepolymerized catalysts and the reactor was immersed in an oil bath (80 °C). After the temperature of hexane reached 80 °C, ethylene gas was fed continuously under 2.76 bar for 1 hour. Polymerization was stopped by venting the ethylene gas. The precipitated polyethylene particles were filtered and dried under vacuum. Hexane used in the polymerization was dried by passing it through a column packed with activated 4A molecular sieve.

3. Cocatalyst Recycle

MAO recyclability was tested for both polymerization conducted without prepolymerization and polymerization conducted with prepolymerization. In the case of the polymerization conducted without prepolymerization [Fig. 1(a)], the hexane solution containing unreacted MAO was decanted after the main polymerization via cannula and the decanted hexane solution was used as a solvent for the next polymerization reaction.

In the case of polymerization conducted with prepolymerization [Fig. 1(b)], the hexane solution containing unreacted MAO was decanted right after the prepolymerization and reused for the next prepolymerization. Only 90 mL hexane out of the 100 mL hexane initially charged could be decanted from the prepolymerized slurry. To compensate MAO reacted in the first prepolymerization reaction and the loss occurred by incomplete decantation, 10 mL hexane containing predetermined amount of MAO or alkylaluminum, depending on the test condition, was added in the second prepolymerization reactor. This procedure was repeated several times to test the efficiency of the MAO recyclability.

RESULTS AND DISCUSSION

1. Catalyst Activity as a Function of Al/Zr Ratio and MAO Concentration

The Al/Zr molar ratio is a common index of MAO use in metallocene catalyst. The catalyst activity of the conventional ethylene polymerization is plotted as a function of Al/Zr molar ratio in Fig. 2. Though a bell-shaped relationship between the catalyst activity and Al/Zr ratio was reported [Chien and Sugimoto, 1991; Herfert

1. Hexane (200 mL) and MAO
2. Supported catalyst (100 mg)
3. Ethylene (2.76 bar, 80°C, 1 hr)

(a)

1. Hexane (100 mL) and MAO
2. Supported catalyst (100 mg)
3. Ethylene (625 mg): Prepolymerization

4. Decantation of hexane containing unreacted MAO

5. Hexane (200 mL) and triethylaluminum (0.3 mmol)
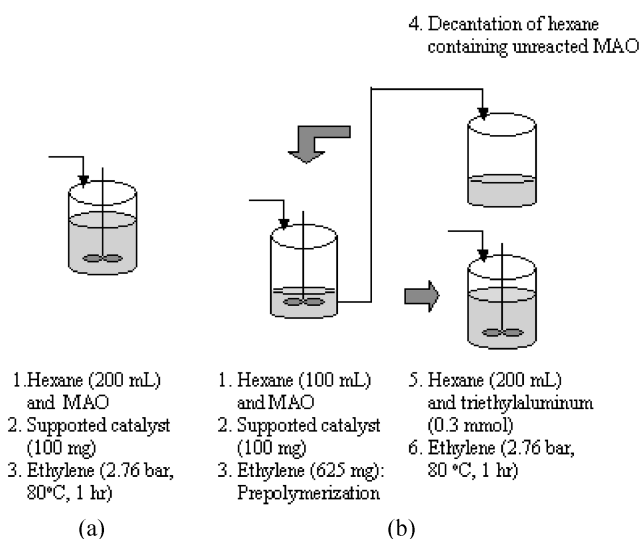6. Ethylene (2.76 bar, 80 °C, 1 hr)

(b)

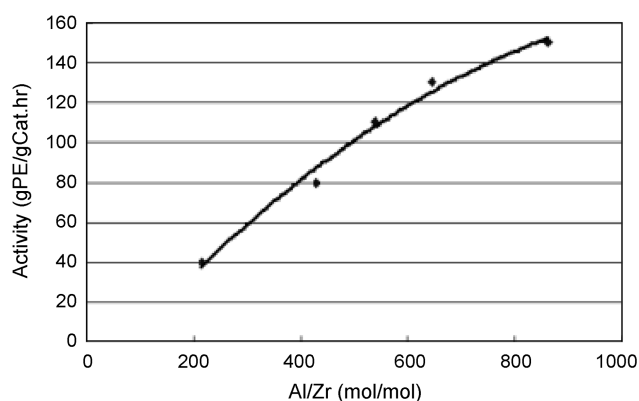**Fig. 1. Polymerization methods: (a) conducted without prepolymerization, and (b) conducted with prepolymerization.**

Fig. 2. Activity of supported catalyst as a function of Al/Zr molar ratio. Polymerization condition: catalyst (100 mg), [(EtO)(Me)$_2$SiO-(CH$_2$)$_6$-C$_5$H$_4$]$_2$ZrCl$_2$ supported on silica calcined at 800 °C; 80 °C; 2.76 bar; 1 hr.

and Fink, 1992; Haag et al., 2001], almost linear increase of the catalyst activity with Al/Zr molar ratio was observed within the experimental range of this study.

The activation of catalyst may be regarded as a chemical reaction between the metallocene compound and the MAO cocatalyst [Khrushch and Bravaya, 2000]. Then the efficiency of catalyst activation reaction depends directly on the MAO concentration. The MAO concentration may be quite low even at high Al/Zr ratio if a large volume of solvent is employed. Hence, those data of catalyst activity with Al/Zr molar ratio reported previously in the literature cannot be compared directly unless the size of the polymerization system is specified. Table 1 compares the effect of the Al/Zr ratio and MAO concentration on the catalyst activity. When the polymerization was conducted without prepolymerization (runs 1 and 2), the catalyst activity increased twice by increasing the amount of

MAO twice in the same volume of hexane (200 mL). In this case, both Al/Zr molar ratio and MAO concentration were increased twice. When the polymerization was conducted with prepolymerization (run 3), four times higher activity could be achieved with the addition of the same amount of MAO as the run 1. In this case, only half of the hexane (100 mL) was used in the prepolymerization step and hence the MAO concentration in the activation reaction was twice higher than that of the run 1, even though the Al/Zr molar ratio had not been changed. These observations illustrate that the prepolymerization method is more efficient in the catalyst activation compared with the conventional direct polymerization conducted without prepolymerization. Its effect is quite larger than that of the simple increase of MAO concentration.

2. Effects of Anchored Catalysts and Prepolymerization

Various functional groups for anchoring metallocene catalyst on silica surface have been developed [Lee and Oh, 2000]. Only slight difference in the catalyst activity was observed for the functional groups as shown in Table 2. On the other hand, the effect of prepolymerization was so significant that the twice the catalyst activity could be achieved with the addition of half amount of MAO (runs 4-7 versus runs 8-11). These results are in agreement with the observation in Table 1. For the polymerization conducted without prepolymerization (runs 4-7), the catalyst activation and polymerization were conducted with the addition of 4.0 mmol Al of MAO in 200 ml of hexane. For the polymerization conducted with prepolymerization (runs 8-11), the catalyst was activated in the prepolymerization step in the presence of 2.0 mmol Al of MAO in 100 ml hexane. Hence, the amount of added MAO was half in the cases of the polymerizations conducted with the prepolymerization, even though the MAO concentration was the same in both polymerizations (0.02 mmol Al/mL). The activation of catalyst in small volume of solvent has the benefits of both higher MAO concentration and less chance of exposure of naked active catalyst to the impuri-

Table 1. Polymerization results showing the effects of [MAO] and prepolymerization[a]

Run	Prepolymerization	MAO (mmol Al)	Hexane (mL)	Al/Zr (mol/mol)	[MAO] (mol Al/L)	Activity (gPE/gCat.hr)
1	No	2.0	200	220	0.01	40
2	No	4.0	200	440	0.02	80
3	Yes	2.0	100[b]	220	0.02[b]	152

[a]Polymerization condition: catalyst (100 mg), [(EtO)(Me)$_2$SiO-(CH$_2$)$_6$-C$_5$H$_4$]$_2$ZrCl$_2$ supported on silica calcined at 800 °C; 80 °C, 2.76 bar, 1 hr. [b]Hexane volume used in the prepolymerization.

Table 2. Polymerization results showing the effects of functional groups and prepolymerization[a]

Run	Prepolymerization	Functional group	Al/Zr (mol/mol)	[MAO] (mol Al/L)	Activity (gPE/gCat.hr)
4	No	(EtO)(Me)$_2$SiO-	430	0.02	86
5	No	Me$_3$SiO-	410	0.02	74
6	No	H(Me)$_2$SiO-	390	0.02	78
7	No	t-Butyl-O-	380	0.02	80
8	Yes	(EtO)(Me)$_2$SiO-	220	0.02	152
9	Yes	Me$_3$SiO-	200	0.02	138
10	Yes	H(Me)$_2$SiO-	200	0.02	140
11	Yes	t-Butyl-O-	190	0.02	145

[a]Polymerization condition: catalyst (100 mg), [X-(CH$_2$)$_6$-C$_5$H$_4$]$_2$ZrCl$_2$ supported on silica calcined at 800 °C, where X denotes the functional group; 80 °C; 2.76 bar; 1 hr.

ties. It is well known that the metallocene catalysts are very sensitive to polar impurities such as water, carbon monoxide, acetylene, etc. in polymerization processes. When the naked catalyst is prepolymerized, it is surrounded by polyethylene, which might protect the active catalyst from polar impurities and hence the higher activities were observed.

3. MAO Recycle

Though a high concentration of MAO is required for high catalyst activity, only small portion of the added MAO is actually consumed during the polymerization. Theoretically only one equivalent of MAO molecule, which may be composed of 15-30 aluminum atoms, is consumed to form active ion-paired complex if the role of scavenging impurities is excluded. Therefore, a large portion of unreacted MAO could be present in the solvent after polymerization or prepolymerization if rigorously purified solvent is used. It was envisaged that the unreacted MAO present in the solvent might be decanted and reused for another polymerization or prepolymerization reaction. Fig. 3 shows the possibility of the MAO recycle. In the case of polymerization conducted with the prepolymerization, hexane containing unreacted MAO was decanted and reused in the prepolymerization step and the main polymerization was carried out after adding hexane (200 mL) and triethylaluminum (0.3 mmol) as a scavenger. In the case of polymerization conducted without the prepolymerization, the hexane containing MAO was decanted after the main polymerization and reused. As shown in Fig. 3, the MAO solutions were reused 3 times with limited decrease in activity for both of the polymerizations conducted with and without prepolymerization. Since only 90% of hexane containing unreacted MAO could be decanted after the precipitation of polymer particles or prepolymerized catalyst particles, the apparent amount of MAO in solution, as well as the Al/Zr ratio, was decreased at least by 10% with each recycle in Fig. 3. In addition, some of MAO should have been reacted to activate the metallocene complexes and may have been lost by the reaction with impurities. Therefore, the actual concentration of MAO in the recycle solution should be lower than the apparent concentration of MAO. That may explain the slight decrease of activity for each recycle.
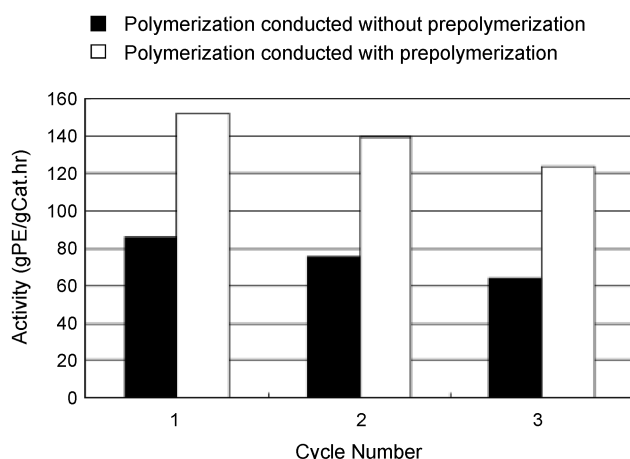
In case of polymerization conducted without prepolymerization, a slight reactor fouling was observed with lower bulk density of polymer particles in the 2nd and 3rd cycles. These observations indicate that a small portion of activated catalyst may be leached out from the supported catalyst during the polymerization. The active species present not only on the surface of the reactor but in the solution produces polymers having bad morphology and these give rise to the reactor fouling and low bulk density. Reactor fouling creates major problems in commercial operation. Neither fouling nor decrease in bulk density was observed when the MAO was recycled in the prepolymerization step. After all, the MAO recycle in the prepolymerization step is more desirable than the recycle in the main polymerization.

The compensation method for MAO loss in each recycle was studied for the polymerization conducted with prepolymerization. The loss might be due to both the incomplete decantation and the reaction with metallocene compound or impurities. As shown in Table 3 and Fig. 3, the catalyst activity decreased successively for each recycle when extra MAO was not added (runs 12-14). However, when small amount of extra MAO (0.2 mmol Al) in hexane (10 mL) was added to the decanted hexane (90 mL) for the next prepolymerization reaction, no decrease in activity was observed in the second cycle (run 16). When the same amount of extra MAO (0.2 mmol Al) in hexane (10 mL) was added to the decanted hexane from the second cycle, no decrease in activity was also observed in the third cycle (run 17). Theses results indicate that, even though an excess amount of MAO may be required to activate metallocene catalyst to have sufficient activity, the actual consumption of MAO is less than 10% of original MAO.

Low-cost alkylaluminums are used as a cocatalyst and scavenger in Ziegler-Natta catalysis. It is also reported that MAO can be partially replaced by common alkylaluminums without severe loss of activity [Chien and Wang, 1988; dos Santos et al., 1999; Pedeutour et al., 2001]. If unreacted MAO - enough to activate metallocene catalyst in the next run - is left in the decanted solution, the MAO consumed by scavenging impurities, at least, may be replaced by a

- ■ Polymerization conducted without prepolymerization
- □ Polymerization conducted with prepolymerization

Fig. 3. Activity of supported catalyst by using decanted hexane containing unreacted MAO. Polymerization condition: catalyst (100 mg), [(EtO)(Me)$_2$SiO-(CH$_2$)$_6$-C$_5$H$_4$]$_2$ZrCl$_2$ supported on silica calcined at 800 °C; 80 °C; 2.76 bar; 1 hr.

Table 3. Polymerization results showing the effect of addition of extra MAO[a]

Run	Cycle no.	Extra MAO[b]	Hexane (mL)[c]	Activity (gPE/gCat.hr)
12	1	-	100	145
13	2	No	90[d]	132
14	3	No	80[d]	116
15	1	-	100	145
16	2	Yes	100[e]	143
17	3	Yes	100[e]	144

[a]Polymerization condition: catalyst (100 mg), [t-Butyl-O-(CH$_2$)$_6$-C$_5$H$_4$]$_2$ZrCl$_2$ supported on silica calcined at 800 °C; conducted with prepolymerization; 80 °C; 2.76 bar; 1 hr.
[b]Extra MAO (0.2 mmol Al) in hexane (10 mL) was added to the decanted hexane.
[c]Hexane used for the prepolymerization.
[d]Decanted amount from the previous run.
[e]Decanted amount from the previous run and extra added amount

Table 4. Polymerization results showing the effect of addition of extra alkylaluminum[a]

Run	Cycle no.	Pre-polymerization*	Alkylaluminum (mmol)[b]	Activity (gPE/gCat.hr)
18	1	Yes	-	150
19	2	Yes	TMA (0.2)	147
20	3	Yes	TMA (0.2)	145
21	1	Yes	-	145
22	2	Yes	TEA (0.2)	143
23	3	Yes	TEA (0.2)	142
24	1	Yes	-	149
25	2	Yes	TIBA (0.2)	148
26	3	Yes	TIBA (0.2)	144
27	1	No	-	57
28	2	No	TIBA (0.4)	43
29	3	No	TIBA (0.4)	30

[a]Polymerization condition: catalyst (100 mg), [t-Butyl-O-$(CH_2)_6$-$C_5H_4]_2ZrCl_2$ supported on silica calcined at 800 °C; 80 °C; 2.76 bar; 1 hr.

[b]Extra alkylaluminum in hexane (10 mL) was added to the decanted hexane solution (TMA, trimethylaluminum; TEA, triethylaluminum; TIBA, triisobutylaluminum).

common alkylaluminum. Table 4 shows that the catalyst activity can be sustained by adding the same amount of inexpensive extra alkylaluminum (0.2 mmol) instead of MAO. Trimethylaluminum (TMA), triethylaluminum (TEA), and triisobutylaluminum (TIBA) were working similarly to show almost the same activities. Prepolymerization played a crucial role as well in obtaining high activity in these cases (runs 24-26 versus runs 27-29). When the polymerization was conducted without prepolymerization (runs 27-29), the catalyst activity decreased more significantly even though twice of TIBA was added compared with prepolymerized cases (runs 24-26). This result indicates that the expensive MAO may be substituted with low-cost alkylaluminums in cocatalyst recycle system if the prepolymerization step is included.

Deffieux et al. [Coevoet et al., 1998] showed by UV-vis spectroscopy that an Al/Zr ratio of at least 150 is required to form the homogeneous active metallocene catalyst. Even though this guideline is kept, the consumption of MAO can be minimized by the MAO recycling method disclosed in this article, especially by recycling MAO in the prepolymerization step and the addition of small amount of extra alkylaluminum or MAO for another activation reaction. The Al/Zr ratio in the prepolymerized catalyst was determined to be about 30 by ICP analysis.

CONCLUSIONS

The cocatalyst MAO is required in excess quantities to activate metallocene catalysts with high activity. A method to minimize the MAO consumption keeping the same high activity is proposed and confirmed by experiments: (1) the prepolymerization of catalyst at high concentration of MAO in small volume of hexane so that the total added amount of MAO is minimized while keeping the MAO

concentration high, (2) decantation of hexane containing unreacted MAO after prepolymerization and its reuse for another prepolymerization reaction, and (3) the extra addition of small amount of MAO or alkylaluminum to compensate the MAO loss occurring not only by incomplete decantation but also by the reaction with metallocene compound or impurities. The prepolymerized catalysts prepared according to this method may be applied to both commercial slurry and gas phase olefin polymerization processes.

REFERENCES

Brockmeier, N. F., "Polypropylene Reinvented-Cost of Using Metallocene Catalysts, Metallocene Catalyzed Polymers-Materials, Properties, Processing and Markets, Benedikt, G. M. and Goodall, B. L., eds., Plastics Design Library, Norwich, NY (1998).

Chien, J. C. W. and Wang, B. P., "Metallocene-Methylaluminoxane Catalysts for Olefin Polymerization. I. Trimethylaluminum as Coactivator," *J. Polym. Sci.: Part A: Polym. Chem.*, **26**, 3089 (1988).

Chien, J. C. W. and Sugimoto, R., "Kinetics and Stereochemical Control of Propylene Polymerization Initiated by Ethylene Bis(4,5,6,7-Tetrahydro-1-Indenyl) Zirconium Dichloride/Methyl Aluminoxane Catalyst," *J. Polym. Sci.: Part A: Polym. Chem.*, **29**, 459 (1991).

Cho, H. S., Choi, K. H., Choi, D. J. and Lee, W. Y., "Control of Molecular Weight Distribution (MWD) for Polyethylene Catalyzed over Ziegler-Natta/Metallocene Hybrid Catalysts," *Korean J. Chem. Eng.*, **17**(2), 205 (2000).

Chung, J. S., Tairova, G., Zhang, Y., Hsu, J. C., McAuley, K. B. and Bacon, D. W., "Polymer-Supported Metallocene Catalysts for Gas-Phase Ethylene Polymerization," *Korean J. Chem. Eng.*, **19**(4), 597 (2002).

Coevoet, D., Cramail, H. and Defieux, A., "U.V./visible Spectroscopic Study of the rac-Et(Ind)$_2$ZrCl$_2$/MAO Olefin Polymerization Catalytic System, 1. Investigation in Toluene," *Macromol. Chem. Phys.*, **199**, 1451 (1998).

dos Santos, J. H. Z., da Rosa, M. B., Krug, C., Stedile, F. C., Haag, M. C., Dupont, J. and Forte, M. C., "Effects of Ethylene Polymerization Conditions on the Activity of SiO$_2$-Supported Zirconocene and on Polymer Properties," *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 1987 (1999).

Haag, M. C., Krug, C., Dupont, J., de Galland, G. B., dos Santos, J. H. Z., Uozumi, T., Sano, T. and Soga, K., "Effects of Al/Zr Ratio on Ethylene-Propylene Copolymerization with Supported-Zirconocene Catalysts," *J. Mol. Cat. A: Chem.*, **169**, 275 (2001).

Han, T. K., Seo, T. S., Choi, H. K. and Woo, S. I., "Cocatalytic Activities of Methylaluminoxane Prepared by Direct Water Addition Method in Ethylene Polymerization over Cp$_2$ZrCl$_2$," *Korean J. Chem. Eng.*, **16**(2), 156 (1999).

Herfert, N. and Fink, G., "Elementartprozesse der Ziegler-Katalyse, 6: Ethylen- und Propenhomopolymerisation mit den stereorigiden Katalysatorsystemen iPr[FluCp]ZrCl$_2$/MAO und Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO," *Makromol. Chem.*, **193**, 1359 (1992).

Hlatky, G. G., "Heterogeneous Single-Site Catalysts for Olefin Polymerization," *Chem. Rev.*, **100**, 1347 (2000).

Jeong, B. G., Nam, D. W., Hong, S. D., Lee, S. G., Park, Y. W. and Song, K. H., "Influence of Process Parameters on Ethylene-Norbornene Copolymers Made by Using [2,2'-Methylenebis(1,3-dimethylcyclopentadienyl)]-Zirconium Dichloride and MAO," *Korean J. Chem. Eng.*, **20**(1), 22 (2003).

Khrushch, N. E. and Bravaya, N. M., "Interaction of Zirconocenes with Polymethylalumoxane. Kinetics of Methane Liberation," *J. Mol. Cat. A: Chem.*, **156**, 69 (2000).

Lee, B. Y. and Oh, J. S., "Preparation of Anchored Metallocene Complexes on Dehydroxylated Silica and Their Use in the Polymerization of Ethylene," *Macromolecules*, **33**, 3194, (2000).

Panin, A. N., Dzhabieva, Z. M., Nedorezova, P. M., Tsvetkova, V. I., Saratovskikh, S. L., Babkina, O. N. and Bravaya, N. M, "Triisobutylaluminum as Cocatalyst for Zirconocenes. II. Triisobutylaluminum as a Component of a Cocatalyst System and as an Effective Cocatalyst for Olefin Polymerization Derived from Dimethylated Zirconocenes," *J. Polym. Sci.: Part A: Polym. Chem.*, **39**, 1915 (2001).

Pedeutour, J.-N., Radhakrishnan, K., Cramail, H. and Deffieux, A., "Reactivity of Metallocene Catalysts for Olefin Polymerization: Influence of Activator Nature and Structure," *Macromol. Rapid Commun.*, **22**, 1095 (2001).

Ribeiro, M., Deffieux, A. and Portela, M. F., "Supported Metallocene Complexes for Ethylene and Propylene Polymerizations: Preparation and Activity," *Ind. Eng. Chem. Res.*, **36**, 1224 (1997).

Oh, J. S., Lee, B. Y., Oum, Y. H. and Park, T. H., "Method for Olefin Polymerization with Recycling of Cocatalyst," US Patent 6,340,728 (2002).

Scheirs, J. and Kaminsky, W., "Metallocene-Based Polyolefins," Vol. 1 and 2, Wiley, Chichester (2000).

Sullivan, J. M., "Economic Factors for the Production of Metallocene and Perfluorinated Boron Cocatalysts," Metallocene Catalyzed Polymers-Materials, Properties, Processing and Markets, Benedikt, G. M. and Goodall, B. L., eds., Plastics Design Library, Norwich, NY (1998).

Togni, A. and Halterman, R. L., "Metallocene Synthesis Reactivity Applications," Vol. 1 and 2, Wiley/VCH, Weinheim (1998).