Investigation of Effective Factors on the 4th Generation Ziegler-Natta Catalyst Activity by Design of Experiments

Zahra Sekhavat Pour, Abbas Shockravi, and Ali Sabzevari Zadeh

Abstract—This study presents the influence of triethylaluminium as cocatalyst, cyclohexylmethylmethoxysilane as external electron donor, and interaction between these two factors on catalyst activity in propylene polymerization with a 4th generation Ziegler-Natta catalyst. The experiments were performed by a two factor factorial design (concentration of triethylaluminium and cyclohexylmethylmethoxysilane) and the analysis of variance was used to evaluate the results by Minitab14 software. This experimental design enabled us to investigate the main effects or individual effects of each factor and determine whether the factors had interaction or not. It was found that triethylaluminium had significant effect on catalyst activity but cyclohexylmethylmethoxysilane donor was not individually effective on catalyst activity.

Index Terms—Catalyst Activity, Cocatalyst, External Electron Donor, Design of Experiments.

I. INTRODUCTION

Ever since its discovery in the 1950s, the Ziegler-Natta catalyst has played a fundamental role in the production of polyolefin plastics. Ziegler-Natta catalysts enabled the preparation of polyolefin plastics under conditions of low pressure and temperature. The conventional Ziegler-Natta polypropylene (PP) catalysts consist of TiCl₄ and microcrystals of MgCl₂ as support. TiCl₄ is very often used together with the cocatalyst which is usually an aluminium alkyl, such as triethylaluminium (TEA). Al/Ti mole ratio is an effective factor in propylene polymerization that can affect catalyst activity, polymerization rate and final property of products. Electron donors play a fundamental role in modern Ziegler-Natta catalyst systems for propylene polymerization. The internal donor is added during the catalyst preparation and the external donor, together with the cocatalyst, to polymerization reactor. Electron donors are used to control the stereospecificity. For the fourth generation Ziegler-Natta catalyst internal electron donor is an alkylphthalate and external electron donor is a silane compound.

Effect of cocatalyst and external electron donors with different structures on propylene polymerization with Ziegler-Natta catalyst was studied by many researchers [1-11]. Studies show that all types of external donors easily form complexes with cocatalyst [1], but these complexes are more stable with silane compound [2].

In studies on the complexity of different alkoxy silanes with triethylaluminium Iskola et al. [12] found that, at room temperature, TEA and alkoxy silane instantly form a 1:1 complex independent of the number of alkoxy groups in the silane. The stability of the complex depends on the structure of the alkoxide, Al/Si mole ratio, temperature and time. Under typical polymerization conditions, the greatest part of the complex seems to persist in its original form. Spitz et al. [3] studied the effect of triethylaluminium and triethoxyphenylsilane concentration and Al/Si mole ratio on MgCl₂/dibutylphthalate/TiCl₄. It was found that at increasing silane content, the activity increased up to a maximum and then decreased. The rate of isotactic polymer production had the same behavior and the production of atactic polymer continuously decreased. Seppala and Harkonen [4] selected nineteen silane compounds of structure \( R_nSi(OR)_4 \) where \( n=1-4, R=C_6H_{13}, \text{alkyl or } H; \text{and } R'=C_{10}-C_{20}\text{-alkyl as external donors. They reported decrease of catalyst activity with increase of silane external donor. Busico et al. [5] also reported this decreasing trend for catalyst activity with increase of triethoxyphenylsilane as external donor. Garrof et al. [6] did several polymerizations with increase of dicyclopentyldimethoxysilane/Ti mole ratio. Catalyst activity increased at first but at high donor/Ti mole ratio a gradual decrease in the activity was observed. Increase in the activity was explained by increased complexation of the external donor to the catalyst and hence decrease in the number of donor-free sites. Decrease in activity was demonstrated by exchange reaction between ethoxy and ethyl ligand.

In most publications, each effective factor such as cocatalyst or external electron donor has been investigated by one factor at a time approach. The major disadvantage of the one factor at a time strategy is that it fails to consider any possible interaction between the factors. Interactions between factors are very common, and if they occur, the one factor at a time strategy will usually produce poor results. The correct approach to deal with several factors is to conduct a factorial design. This is an experimental strategy in which factors are varied together instead of one at a time [13].

In this work we report effects of triethylaluminium as cocatalyst and cyclohexylmethylmethoxysilanes ((Cy)(Me)Si(OMe)₂ or CHMDMS) as external donor on catalyst activity. A factorial design with two factors...
consisting of TEA and CHMDMS concentration was selected. Experiments were performed randomly and each test was repeated twice. The analysis of variance (ANOVA) was used for investigation of the tests’ results by Minitab14 software.

II. EXPERIMENTAL PROCEDURE

A. Materials

In this study, a 4th generation Ziegler-Natta catalyst manufactured by Basell Company under the trade name GTF2 was used. This catalyst was donated by Navid Zar Petrochemical Company. Its concentration was 230 g catalyst per liter.

Hydrogen and propylene (donated by Bandar Imam Khomeini Petrochemical Company (BIPC)) were used with further purification. Hexane (donated by BIPC) was extra dried by passing through molecular sieve. Concentration of TEA solution (donated by BIPC) was determined by titration with 0.1 molar butanol solution in heptane. CHMDMS (Merck) was used as external electron donor.

B. Slurry polymerization of propylene

Propylene (10 bar) was polymerized in a Buchi stainless steel reactor with Ziegler-Natta catalyst (0.03 mol Ti) in hexane (1 liter) at 70 °C for 90 minutes. The conditions of each test from viewpoint of TEA and CHMDMS concentrations are given in Table I. Hydrogen (100 ml) was introduced into the reactor as chain transfer agent [14]. After 90 minutes, residual gases were removed from the reactor and the reaction was stopped. The solid polymer was filtered and dried. Each test was repeated twice, so 24 slurry polymerizations were carried out in these test series. The catalyst activity for each test was calculated by measuring the total mass of polymer produced in the test divided in the amount of the catalyst used in each test.

III. RESULT AND DISCUSSION

A. Catalyst Activity

Table I shows the catalyst activities reached in the test series measured as g PP/g catalyst. A two factor factorial experiment with design factors at four different concentrations of TEA and three different concentrations of CHMDMS was considered. Analysis of results was difficult by means of Table I, and therefore the ANOVA and Minitab14 software were used for the analysis of experiments’ results.

Before the conclusions from the ANOVA are adopted, the adequacy of the model was checked by residual analysis [13]. We evaluated the normality, the independence and equality of variances of residuals for model adequacy checking.

TABLE I: EFFECTS OF DIFFERENT CONCENTRATIONS OF TEA AND CHMDMS ON CATALYST ACTIVITY

<table>
<thead>
<tr>
<th>[TEA] (mmol/l)</th>
<th>[CHMDMS] (mmol/l)</th>
<th>Catalyst activity (g PP/g Catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.35</td>
<td>0.2</td>
<td>5250</td>
</tr>
<tr>
<td>4.35</td>
<td>0.4</td>
<td>4857.5</td>
</tr>
<tr>
<td>4.35</td>
<td>0.6</td>
<td>5350</td>
</tr>
<tr>
<td>6</td>
<td>0.2</td>
<td>5305</td>
</tr>
<tr>
<td>6</td>
<td>0.4</td>
<td>6650</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>5220</td>
</tr>
<tr>
<td>10</td>
<td>0.2</td>
<td>5562.5</td>
</tr>
<tr>
<td>10</td>
<td>0.4</td>
<td>5787.5</td>
</tr>
<tr>
<td>10</td>
<td>0.6</td>
<td>6675</td>
</tr>
<tr>
<td>13</td>
<td>0.2</td>
<td>5777.5</td>
</tr>
<tr>
<td>13</td>
<td>0.4</td>
<td>6142.5</td>
</tr>
<tr>
<td>13</td>
<td>0.6</td>
<td>5282.5</td>
</tr>
</tbody>
</table>

A. Model adequacy checking

1) The normality assumption

The first assumption in model adequacy checking is normality of residuals. Residuals are differences between resulting amounts of response variable (catalyst activity) in experiments and fitted value by regression model. Normal probability plot of the residuals was obtained for effect of TEA and CHMDMS on catalyst activity by Minitab 14 software and it has been shown in Fig. 1. Since given points have considerable distance from the central line of the standard normal distribution, the normality assumption is not concluded. Hence, reciprocal transformation was used for increasing the accuracy of the ANOVA results. In the other word, 1/(g PP/g catalyst) was used instead of g PP/g catalyst. Fig. 2 shows normal probability plot of the residuals for the transformed variable. In this figure, given points have short and admissible distance from the central line, so the normality assumption is confirmed for the transformed variable.

![Normal Probability Plot of the Residuals](image.png)
2) The independence assumption

Fig. 3 shows residuals versus the order of the data for the transformed variable. It is easy to see from this figure, there is not any special trend such as ascending, descending or sine trend. Thus, the residuals are structureless and independency of residuals is verified.

3) Equality of variances

The third assumption for using the ANOVA is equality of variances. Bartlett’s test was used to check this assumption. Bartlett’s test is sensitive to the normality assumption, so it can only be used for normal residuals. Fig. 4 depicts the equality of variances, because P value of Bartlett’s test is more than error type I (0.963>0.1). Note that, throughout this paper we considered 10 percent for error type I.

TABLE II: MINITAB OUTPUT FOR 1/(g PP/g CATALYST)

Analysis of Variance for 1/(g PP/g catalyst), using Adjusted SS for Tests:

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA</td>
<td>3</td>
<td>2683544</td>
<td>894515</td>
<td>2.64</td>
<td>0.078</td>
<td></td>
</tr>
<tr>
<td>CHMDMS</td>
<td>2</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.29</td>
<td>0.310</td>
</tr>
<tr>
<td>TEA×CHMDMS</td>
<td>6</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>4.33</td>
<td>0.015</td>
</tr>
<tr>
<td>Error</td>
<td>20</td>
<td>6781215</td>
<td>339061</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>23</td>
<td>9464758</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 582.3 R-Sq = 28.35% R-Sq(adj) = 17.61%

According to Table III, TEA concentration has significant effect on catalyst activity because of P value<0.1. Fig. 5 shows the box plot of TEA concentrations on catalyst activity. As this figure shows increase of TEA concentration initially causes to increase in catalyst activity, but there is a maximum in [TEA]=10 mmol/l, further addition of cocatalyst decreases catalyst activity.

Fig. 5: Box plot of TEA concentrations on catalyst activity

TEA needs for alkylation and activation of catalyst and transforms the catalyst site to active site. A little amount of TEA eliminates impurity and catalyst poisons such as H2O and O2 in the polymerization. There is no doubt that Ti4+ undergoes an extensive reduction whenever the catalyst is treated with TEA. According to scientist thought, Ti5+ and Ti3+ are active in propylene polymerization [11]. So catalyst activity increases with increasing TEA concentration because catalyst poisons are removed, Ti5+ species are increased and polymerization centers are activated. Increase of catalyst activity continues until all polymerization centers become active. Further increase in TEA decreases the catalyst activity because high TEA concentration causes further reduction of
Effect of TEA as cocatalyst and CHMDMS as external electron donor on catalyst activity in propylene polymerization with a 4th generation Ziegler-Natta catalyst was investigated. A factorial design with two factors was selected. The analysis of variance and Minitab 14 software were used for investigation of results. In this research, not only effect of each factor but also interplay between them was evaluated. Two factor factorial design revealed that TEA concentration and its interaction with CHMDMS have significant effect on catalyst activity and CHMDMS did not affect it. In the real world when one factor actually has not significant effect, its interaction with other factor is not also effective. So the one-way ANOVA was used for investigation of TEA effect on catalyst activity and ineffective CHMDMS was abandon.

Increase of TEA up to certain concentration in polymerization enhanced the yield of obtained polymers and catalyst activity because; TEA reduced Ti^{4+} to Ti^{3+} active species and activated the catalyst. Further increase of TEA caused to reduction of Ti^{4+} species even to Ti^{2+} that were inactive in propylene polymerization. Hence, TEA had an optimum concentration in polymerization.

REFERENCES

Zahra Sekhavat Pour was born in Dezful, Iran, in 1984. She received both B.Sc (2006) and M.Sc (2009) degree in Applied Chemistry from Tarbiat Moallem University, Tehran, Iran. She is an invited instructor at University of Applied Science and Technology, Ahvaz, Iran. Her journal papers are: 1) Effect of hydrogen on operation of 4th generation of Ziegler-Natta catalyst in slurry polymerization of propene” Iran. J. Chem. & Chem. Eng., 29 (2), Pages 41-51, 2010. 2) Investigation of aluminium alkyl and alkoxysilane effects on the 4th generation Ziegler-Natta catalyst using design of experiments”, Iran. J. Chem. & Chem. Eng., submitted for publication.


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