

Observation on Different Reducing Power of Cocatalysts on the Ziegler–Natta Catalyst Containing Alkoxide Species for Ethylene Polymerization

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ABSTRACT: In this work, the effects of three types of cocatalyst having different alkyl groups, such as triethylaluminum (TEA), triisobutylaluminum (TiBA), and trioctylaluminum (TnOA), and their concentrations on the catalytic activity and polymer properties were investigated for the Ziegler–Natta catalyst containing alkoxide species. The drastic escalation of catalytic activity was observed when the ratio of Al/Ti was increased only for TEA because of its good diffusivity as proven by the electron spin resonance technique. Moreover, it was found that the characteristic of the alkyl group in cocatalyst affected on the chain transfer ability. The chain transfer ability of TnOA was found to be equal to the TiBA in spite of its concentration was higher. By the way, the cocatalyst types and their concentrations did not affect on the variety of active sites as seen in molecular weight distribution of polymer. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40884.

KEYWORDS: catalysts; polyolefins; processing; synthesis

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INTRODUCTION

Due to a large demand of polyethylene (PE) and polypropylene (PP), there are many attempts to enhance the productivity of these polyolefins. Ziegler–Natta catalyst is the first choice for both PE and PP production although there are the others two common types, single-site catalyst and chromium catalyst because of its lower production cost and less poison. Many research fields have involved with this kind of catalyst including improvement of catalytic activities,¹ characterization techniques,² and development of a novel support.³ In addition, numerous related factors such as polymerization temperature, cocatalyst types, and Al/Ti ratios^{4–6} are also crucial to optimize for the enhancement of catalytic activity.

Normally, alkylaluminum compounds are used as cocatalyst or activator in polymerization process. It is known that the oxidation state of titanium is critical for olefin polymerization. The Ti³⁺ species can polymerize both of ethylene and propylene whereas the Ti²⁺ species can polymerize only ethylene.⁷ Thus, the selection of cocatalyst is one of the principle factors accounting for high catalytic activity achievement. For this reason, the effects of cocatalysts on Ziegler–Natta catalyst activity and polymer properties have been widely studied; however, the

precursor used is only titanium tetrachloride (TiCl₄).^{4,5} From the previous work,⁸ it was found that triethylaluminum (TEA) could perform higher catalytic activity than triisobutylaluminum (TiBA) because of its higher reducing power on MgCl₂/SiO₂/TiCl₄/diester type catalyst for ethylene/propylene copolymerization. Moreover, Nooijen⁶ also found that the catalytic activity of MgCl₂/TiCl₄ catalyst was changed with different cocatalyst types in the order; TEA > TiBA > trioctylaluminum (TnOA) > isoprenylaluminum (IPRA).

Up to now, TiCl₄ has been chosen for a long time as Ziegler–Natta catalyst precursor because of its crystal structure, which is proper with MgCl₂ support⁹ and also provides fairly high catalytic activity. However, due to the special requirement of PE properties such as good mass flow rate and excellent impact resistance, which cannot be achieved by only TiCl₄, so the classical TiCl₄ catalyst has to be modified. It was found that titanium alkoxide [Ti(OR)₄] species as a catalyst precursor can provide those required properties of PE,¹⁰ but its activity is still low. Moreover, many of previous works also showed that the addition of titanium alkoxide species could lead to the reduction of cocatalyst amount compared to the industrial condition.¹⁰ Thus, the combination of TiCl₄ and Ti(OR)₄ precursors to be catalyst is expected to succeed in higher activity and

flexibility of polymer properties than the use of a sole precursor. Unfortunately, the use of TiCl_4 and $\text{Ti}(\text{OR})_4$ mixture as an effective catalyst in the heterogeneous system has been limitedly studied,^{11–13} especially the effect of incorporation of various cocatalysts and biprecursor catalyst on catalytic activity and polymer properties in heterogeneous system.

In this study, the effect of different cocatalyst types and Al/Ti ratios in biprecursor catalyst system was observed to optimization between the catalytic activity and polymer properties such as melt index (MI) and molecular weight distribution (Mw/Mn) in the Ziegler–Natta catalyst system.

EXPERIMENTAL

Materials

All reactions were performed under purified argon atmospheres using a standard glove box and Schlenk techniques. Polymerization grade ethylene and argon were purchased from Linde Co., butylchloride (BuCl), titanium(IV) chloride, titaniumisopropoxide [$\text{Ti}(\text{OiPr})_4$], and hexane were purchased from Sigma-Aldrich Co. TEA, TiBA, and TnOA were donated by Thai Polyethylene Co.

Catalyst Preparation

First, 100 mL of hexane was filled into the reaction flask at room temperature. Magnesium powder (10 g) was transferred into the flask. Then, I_2 was added dropwise into the solution mixture (gray color) while stirring until the solution mixture turned into purple. Then, the desired amount of $\text{Ti}(\text{OiPr})_4$ was added into the solution mixture while stirring, followed by BuCl addition. The solution was still purple. After that, the solution mixture was heated up to 60°C while stirring for 1 h. As observed, the color apparently changed into brown.

After the solution mixture was cooled down to 40°C , $\text{Ti}(\text{OiPr})_4$ and TiCl_4 (equimolar) were added into the solution mixture and stirred for 1 h. Then, the resulting product was cooled down to 30°C with lower stirring speed and kept for another 1 h. The slurry of catalyst was formed. Finally, it was washed with hexane for five times and the solvent was evacuated. The dark brown powder of catalyst was obtained.

Polymerization Procedure

Polymerization, the ethylene polymerization, was performed in 2-L autoclave reactor connected with the lines available for argon, hydrogen, and ethylene and also the hexane feed line. The reactor and all connected feed lines were cleared humid and oxygen by evacuation, and then followed by purging with the argon many times. First, 1 L of hexane was filled and heated to 80°C . The desired amount of cocatalyst was injected into the reactor subsequently by the injection of desired amount of catalyst. Then, the reactor was pressurized with 1 bar of argon followed by pressurizing with 2.5 bar of hydrogen partial pressure and finally pressurizing with ethylene gas. The total pressure was 8 bars.

Catalyst and Polymer Characterization

All of catalyst characterization techniques were used under argon atmosphere to prevent deactivation of catalyst. The functional groups contained in catalyst were observed by FT-IR using a THERMO model Nicolet 6700. The crystal structure of

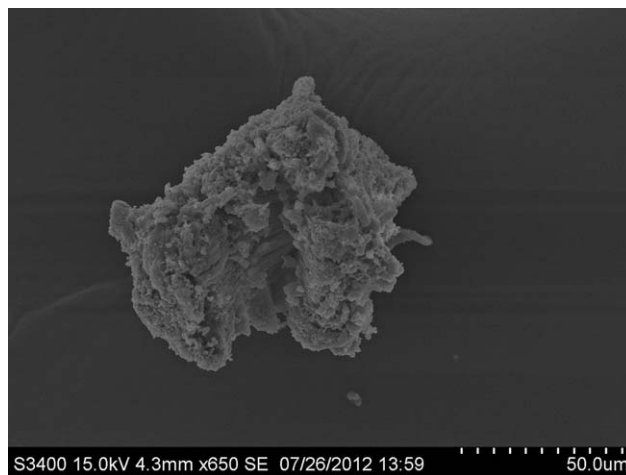


Figure 1. The morphology of catalyst particle.

catalyst was observed by x-ray diffraction (XRD) using a SIEMENS D-5000 X-ray diffractometer with CuK_α ($\lambda = 1.54439 \times 10^{-10}$ m). The sample was placed on holder and sealed with mylar film by grease. The Ti^{3+} content of the catalysts was observed by the electron spin resonance (ESR) technique. The catalyst samples were prepared in a glove box and activated by TEA, TiBA, and TnOA. The ESR equipment was JEOL model JES-RE2X and used under argon atmosphere at room temperature and held for 120 min. DPPH standard was used for g-factor calibration. The external surface of the catalysts and their morphologies were evaluated by scanning electron microscopy (SEM) with a JEOL model S-3400. The elemental composition of catalyst was measured by the inductively coupled plasma mass spectrometry technique. For polymer properties, molecular weight was evaluated by two techniques, melt index (MI) with a DYNISCO polymer test with 2.16 and 10 kg loading, and a high temperature gel permeable chromatography (GPC; Waters 150-C) equipped with a viscometric detector.

RESULTS AND DISCUSSION

Catalyst Characterization

The synthesized catalyst was characterized by inductively coupled plasma - mass spectrometry (ICP-MS) for evaluating the amount of titanium and magnesium content in the catalyst. The results showed that titanium and magnesium content were 6.20 and 15.51 wt %, respectively. The morphology of catalyst is shown in Figure 1. The catalyst surface was rough and cracked as usually be observed. Moreover, the size of catalysts was not uniform. Also, the catalysts were analyzed to reveal the functional groups contained as seen in Figure 2. The wavenumber of 1071 cm^{-1} confirmed the existence of titanium chloride alkoxide species.¹⁴ The XRD patterns (Figure 3) show the peak around $2\theta \approx 50$ indicating the structure of $\delta\text{-MgCl}_2$ ¹⁵ produced by magnesium powder and TiCl_4 .

For comparison, the commercial catalysts synthesized in the previous work were also probed.^{16,17} Although, the morphology of synthesized catalysts was not uniform and the distribution was broad, comparing to the magnesium ethoxide based Ziegler–Natta catalyst that produced well spherical shape catalysts

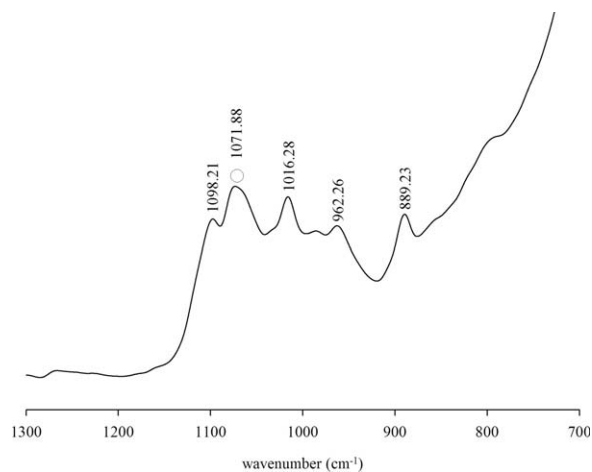


Figure 2. FT-IR spectrum of the catalyst, C—O bond in titanium alkoxide species (○).

and narrow particle size distribution, the simplicity of synthesis procedure used in this research seemed to overwhelm where the high activity of catalyst was achieved using very low amount of cocatalysts.

Catalytic Activity

During polymerization, cocatalyst types and Al/Ti molar ratios were varied. For the cocatalyst type, Nooijen⁶ proposed the relation between cocatalyst size and catalytic activity. It was found that the size of cocatalyst directly affected on diffusivity ability of cocatalyst to titanium active centers. The large size of cocatalyst anticipated slow diffusion. In this work, three types of cocatalyst such as TEA, TiBA, and TnOA were investigated. The bulky and size of cocatalyst can be arranged by TnOA > TiBA > TEA. Thus, the expected sequence of catalytic activity was TEA > TiBA > TnOA. The noticeable difference of catalytic activity among these three cocatalyst types was observed as seen in many previous works^{4,5,8,18} using only TiCl₄ as a titanium precursor. The obtained sequence can be explained by polymerization method. We had introduced hexane, cocatalyst, and catalyst before the polymerization reaction

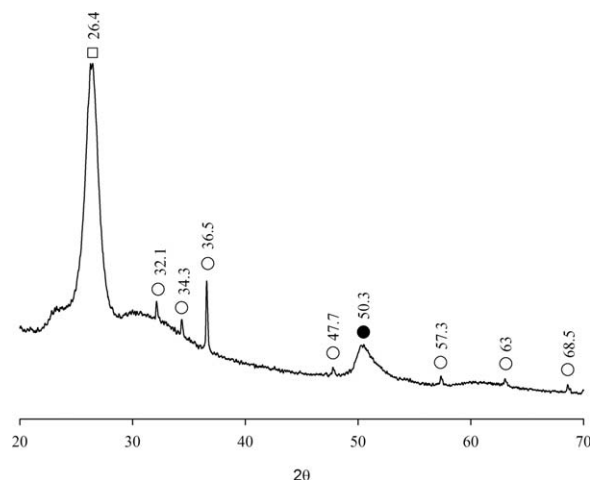


Figure 3. XRD patterns of the catalyst. Mylar film (□), δ-MgCl₂ (●), and Magnesium powder (○).

Table I. Catalytic Activities with Different Cocatalyst Types and Al/Ti Molar Ratios

Cocatalyst	Al/Ti molar ratio	Catalytic activity (kgPE/molTi.h)
TEA	2	543
	3	623
	5	780
TiBA	2	504
	3	498
	5	535
TnOA	2	506
	3	547
	5	552

Polymerization was performed in 2-L autoclave, reaction temperature = 80°C, Ti = 0.3 mmol, reaction time = 2 h, under argon, hydrogen, and ethylene partial pressure of 1, 2.5, and 4.5 bars, respectively.

started, so the active centers were simultaneously formed. When the ethylene was fed, the polymerization could start immediately.

The numerical experimental results can be seen in Table I. The activity obtained from TEA was the highest while that obtained from TiBA and TnOA was almost equal. This result was also observed when the Al/Ti ratio was changed. This phenomenon is probably due to the existence of alkoxide species contained in the catalyst. The surface of catalyst apparently contained alkoxide species as proven by FT-IR (Figure 2). We believed that the bulkiness of alkoxide group on the surface of catalyst is the main factor affecting on the catalytic activity. The branches of alkyl group, isopropyl, can obstruct cocatalyst. Therefore, the large size of cocatalyst cannot completely activate titanium into the active center. The ESR technique was used for proving this assumption. The ESR spectrum (Figure 4) shows the g-value of 1.94, which refers to the six-coordinated Ti³⁺ dissolved in MgCl₂¹⁹ or the isolated octahedral coordinated Ti³⁺.²⁰ For quantitative study, the spectra were double integrated and the obtained area referring to the Ti³⁺ amount was plotted in the terms of relative area as seen in Figure 5. The Ti³⁺ amount of TnOA tended to increase with time while the trend of TiBA increased within 45 min, and then remained constant. This suggested that TnOA did not finish forming the active sites within

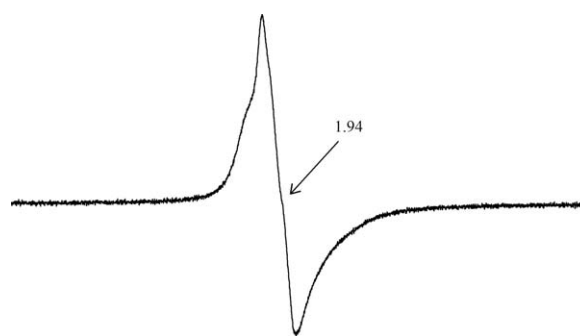


Figure 4. The typical ESR spectrum of the catalyst.

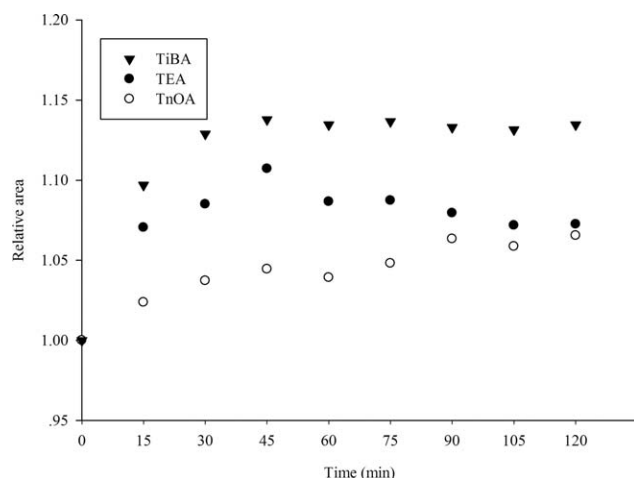


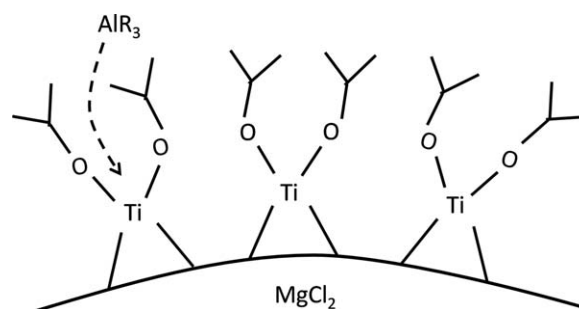
Figure 5. The relative amount of Ti^{3+} with the Al/Ti molar ratio of 2.

2 h due to its difficulty of diffusion to active centers, which is more difficult than TiBA. For TEA, the Ti^{3+} was maximized in the first 45 min, and then continuously decreased. This was probably due to TEA that can efficiently diffuse through alkoxide barrier, and then reduced Ti^{3+} to Ti^{2+} , which was more active for ethylene polymerization²¹ resulting in the highest catalytic activity among these three cocatalyst. In addition, this explanation was also able to describe the reason of lower relative area of TEA than TiBA. Furthermore, high concentrations of cocatalyst increased the opportunity of its diffusion to the titanium center. Thus, in case of TEA, the higher concentration led to the more active sites and various active species formed, while the addition of TnOA and TiBA can slightly enhance the activity. This indicated that they only generated a few active centers.

Polymer Characterization

The properties of polymer can be seen in Table II. The result when the Al/Ti ratio changed can be also explained by the obstruction of alkoxide group on the catalyst surface. The conceptual model on the catalyst surface can be drawn in Scheme 1.

We purposed that TEA size was small enough to diffuse through the alkoxide barrier while the partial TnOA and TiBA could not



Scheme 1. Conceptual model on the obstruction of *i*-propoxide to cocatalyst.

pass because of their size and bulkiness. Thus, higher concentration of TEA led to an increase of formation of active sites and then resulted in a decrease of particle size of polymer (Table II). Moreover, GPC and MI measurements showed the concordant trend of molecular weight. Normally, the change of molecular weight of polymer depends on chain transfer ability. Chain transfer to hydrogen is a main route for termination reaction.²² Also, monomer, solvent, and cocatalyst can perform as the chain transfer agent. In this work, interestingly, only TnOA was noticeably changed the molecular weight as mentioned in Table II. The increase of TnOA concentration led to a noticeable decrease of molecular weight while TEA and TiBA slightly affected on the molecular weight. The effect of cocatalyst on the chain transfer ability could be independently considered. The less bulky cocatalyst such as TEA was classified as the first group. Most TEA molecules were believed that they could pass through the barrier and activate the titanium active centers. Thus, the main route for chain transfer was from hydrogen.²³ The second group was more bulky cocatalysts such as TiBA and TnOA, which only a few molecules can pass through the alkoxide barrier because of their bulkiness. Thus, the increase of their concentration was similar with increased amount of chain transfer to cocatalyst agent. From previous study,⁷ it showed that chain transfer ability of cocatalyst depended on the bulkiness of alkyl group in cocatalyst. The *n*-octyl of TnOA is more bulky than the *i*-butyl in TiBA, so the chain transfer to TnOA is slower than to TiBA. This resulted in the evidence that the molecular weight of polymer from TnOA is higher than that

Table II. Properties of Polymers Upon Different Cocatalyst Types and Al/Ti Molar Ratios

Cocatalyst	Al/Ti molar ratio	Mw × 10 ⁻⁵ (g/mol)	Mn × 10 ⁻⁴ (g/mol)	Average size ^a (μm)	Mw/Mn	Bulk density (g/mL)	MI (g/10 min)
TEA	2	1.43	2.79	111	5.14	0.25	0.833
	3	1.21	2.22	97	5.46	0.28	1.606
	5	1.26	2.23	82	5.65	0.30	1.406
TiBA	2	1.10	2.02	162	5.47	0.27	2.852
	3	1.02	1.95	150	5.23	0.23	3.346
	5	1.06	2.04	138	5.21	0.23	2.793
TnOA	2	1.92	3.60	166	5.34	0.25	0.250
	3	1.55	2.93	149	5.30	0.23	0.608
	5	1.01	1.72	157	5.88	0.24	3.289

^aEvaluated by SEM.

obtained from TiBA. Moreover, the concentration of cocatalyst also confirmed the chain transfer ability. The molecular weight of polymer showed that the chain transfer ability of TnOA at the Al/Ti ratio of 3 was equal to the TiBA at the Al/Ti ratio of 5. However, it was worth to point that the amount of cocatalyst scarcely affected on the molecular weight distribution. This revealed that the active site species of catalyst containing two species of titanium precursors were not affected by the cocatalyst amount.

CONCLUSIONS

Three types of cocatalyst were found to affect on both catalytic activity and polymer properties. The effect of cocatalyst was different when the catalyst was synthesized from bititanium precursors. Only TEA was found to noticeably enhance the catalytic activity because its size was small enough to diffuse through the alkoxide barrier. The bulkiness of alkyl group in cocatalyst was found to affect on its chain transfer ability. The chain transfer routes can be considered into two cases; (i) for TEA, the chain transfer to hydrogen is dominant and (ii) for TiBA and TnOA, the chain transfer ability of TiBA is more pronounced than TnOA. The bulky cocatalyst tends to be an inefficient chain transfer agent. However, both of cocatalyst type and concentration did not affect on the molecular weight distribution of polymer in this catalyst system.

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