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Effect of methylaluminoxane/transition-metal ratio on the physical properties and chemical composition distributions of ethylene–hexene copolymers produced by a *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst

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Abstract

A silica–magnesium bisupport (SMB) was prepared by a sol–gel method for use as a support for the impregnation of TiCl$_4$ and *rac*-Et(Ind)$_2$ZrCl$_2$. The prepared *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO(methylaluminoxane)/SMB catalyst was applied to the ethylene–hexene copolymerization under the conditions of variable Al(MAO)/Zr ratio and fixed Al(TEA, triethylaluminum)/Ti ratio. The effect of Al(MAO)/Zr ratio on the physical properties and chemical composition distributions of ethylene–hexene copolymers produced by a *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst was investigated. The catalytic activity of *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB was steadily increased with increasing Al(MAO)/Zr ratio from 200 to 500. The ethylene–hexene copolymer produced with Al(MAO)/Zr = 300, 400, and 500 showed two melting points at around 110 °C and 130 °C, while that produced with Al(MAO)/Zr = 200 showed one melting point at 136 °C. The number of chemical composition distribution (CCD) peaks was increased from 4 to 7 and the short chain branches of ethylene–hexene copolymer were distributed over lower temperature region with increasing Al(MAO)/Zr ratio. The lamellas in the copolymer were distributed over lower temperature region and the small lamellas in the copolymer were increased with increasing Al(MAO)/Zr ratio. The *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst preferably produced a ethylene–hexene copolymer with non-blocky sequence ([EHE]) with increasing Al(MAO)/Zr ratio.

Keywords: Silica–magnesium bisupport; Metallocene/Ziegler–Natta hybrid catalyst; Ethylene–hexene copolymer; Chemical composition distribution; Physical property; Al(MAO)/Zr ratio

1. Introduction

Metallocene catalysts have attracted much attention as next generation catalysts because of their high catalytic activity and excellent ability of comonomer incorporation in the olefin polymerization

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[1–5]. Although polymers produced by a metallocene catalyst have excellent mechanical and optical properties, they have limitation in polymer processing due to their narrow molecular weight distribution (MWD). On the other hand, polymers produced by a Ziegler–Natta catalyst have advantages in polymer processing due to their broad molecular weight distribution (MWD) [6,7]. Ziegler–Natta catalysts used in commercial polymerization processes are heterogeneous catalyst system, while metallocene catalysts are homogenous catalyst system [8,9]. Therefore, it is desirable to heterogenize the metallocene catalysts in order for use in the existing commercial processes such as slurry and gas phase processes.

For this purpose, inorganic materials such as silica, zeolite, and alumina have been used as a support for metallocene catalysts [10,11]. A mixture of metallocene and Ziegler–Natta catalysts has been also employed to improve the physical properties of polymers [12,13]. Another promising method for utilizing both metallocene and Ziegler–Natta catalysts is to hybrid these catalysts by impregnating these two components on a single support [14–19]. It was reported that a polyethylene produced by a metallocene/Ziegler–Natta hybrid catalyst supported on $MgCl_2$ showed a bimodal molecular weight distribution (MWD) and two melting temperatures, indicating the existence of two different active sites on the support [14,15]. A silica–magnesium bisupport (SMB) prepared by a sol–gel method has been also used to impregnate both metallocene and Ziegler–Natta catalysts [16–19]. The existence of two different active sites in this hybrid catalyst system was confirmed by the observation of a bimodal molecular weight distribution and two melting temperatures of resulting polymer.

In this work, a silica–magnesium bisupport (SMB) was prepared by a sol–gel method and it was then treated with methylaluminoxane (MAO) prior to the impregnation of $TiCl_4$ and *rac*-Et $(Ind)_2ZrCl_2$. The prepared *rac*-Et$(Ind)_2ZrCl_2$/$TiCl_4$/MAO/SMB catalyst was applied to the ethylene–hexene copolymerization under the conditions of variable methylaluminoxane (MAO)/transition metal (Zr) ratio and fixed triethylaluminum (TEA)/transition metal (Ti) ratio. The effect of Al(MAO)/Zr ratio on the physical properties and chemical composition distributions (CCDs) of ethylene–hexene copolymers produced by a *rac*-Et$(Ind)_2ZrCl_2$/$TiCl_4$/MAO/SMB catalyst was investigated.

2. Experimental

2.1. Materials

High purity ethylene (World Gas) and nitrogen (Daesung Gas) were further purified by sequential passage through columns containing molecular sieve 5A (Kokusan Chemical Works) and anhydrous P_2O_5 (Yakuri Chemicals). Toluene (Samjun Chemicals) and 1-hexene (Aldrich) were purified by distillation over sodium metal. $MgCl_2$ (Junsei Chemical), colloidal SiO_2 (LUDOX HS-40, Aldrich), *rac*-Et$(Ind)_2ZrCl_2$ (Strem), $TiCl_4$ (Aldrich), methylaluminoxane (MAO, Albermale), and triethylaluminum (TEA, Aldrich) were used without further purification.

2.2. Preparation of silica–magnesium bisupport (SMB)

The silica–magnesium bisupport (SMB) treated with methylaluminoxane (MAO) was prepared according to the similar method in a previous report [18]. $MgCl_2$ was dissolved in distilled water (100 ml), and pH of the solution was adjusted at 6.4 by adding H_2SO_4. The solution was introduced into corn oil (2.5 l), and it was stirred at 2000 rpm for uniform dispersion. Colloidal silica (80 ml) was then introduced into the mixed solution of corn oil and $MgCl_2$. The agglomerated particles separated from the solution were washed seven times with toluene, and they were dried at 110 °C in a nitrogen stream to yield silica–magnesium bisupport. The silica–magnesium bisupport (SMB) (6 g) was suspended in toluene (100 ml), and then methylaluminoxane (MAO, 10 wt% in toluene) (100 ml) was introduced into the slurry for 2 h at 0 °C. The mixture was stirred at 0, 20, 40, and 60 °C for 30 min each, and then finally at 80 °C for 2 h. The MAO-treated SMB (MAO/SMB) was washed seven times with toluene and dried under vacuum.

2.3. Preparation of supported hybrid catalyst

The MAO-treated SMB (MAO/SMB) (2 g) was suspended in toluene (100 ml), and it was reacted with $TiCl_4$ (2 ml) at 50 °C for 2 h. The resulting slurry was washed seven times with toluene (100 ml), and then it was dried under vacuum to obtain $TiCl_4$/MAO/SMB. The $TiCl_4$/MAO/SMB suspended in toluene (20 ml) was further reacted with *rac*-Et$(Ind)_2ZrCl_2$ dissolved in toluene