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Catalytic behaviors of SiO_2-supported various aluminoxanes as coactivator in $MgCl_2/DEP/TiCl_4$–TEA catalysts for propylene polymerization

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ABSTRACT

The study showed that the use of silica-supported aluminoxanes as coactivator can alter the catalytic behaviors of $MgCl_2$/diethylphthalate (DEP)/$TiCl_4$ catalyst with triethylaluminum (TEA) as an activator for propylene polymerization. It was found that the catalytic activities were ranged between 380 and 760 kg PP/mol.Ti.h within the order of dMMAO/SiO_2 > MAO/SiO_2 > MMAO/SiO_2 > dMMAO > no coactivator > SiO_2. The TGA analysis revealed that the strong interaction between aluminoxane compounds and support apparently resulted in a decreased catalytic activity. Based on the polymer microstructure, it indicated that an enhanced activity can be attributed to the increase in active site concentration.

1. Introduction

The Ziegler-Natta catalyst, which comprises of $TiCl_4$, $MgCl_2$ and an electron donor, constitutes the majority of global polyolefin production during the past several decades [1]. The discovery of $MgCl_2$-supported $TiCl_4$ catalyst in the late 1960s leads not only to the substantial enhancement of catalyst activity, but also results in polymers with morphology control [2]. In particular, the use of spherical $MgCl_2$ adducts as the catalyst support afforded significant progress in controlling polymer morphology as spherical particles and brought about revolutionary industrial developments [3,4]. Afterwards, various generations of electron donor (Lewis base) including monoester, diester, alkoxysilane, diether and succinates were sequentially developed and now become the most promising compound, which is indispensable for producing polymer with high stereoregularity so that highly isotactic polypropylene could be achieved [5]. However, highly active Ziegler-Natta catalyst is still the important issue for catalyst research. Modification of catalyst supports [6] and introduction of other components such as Grignard reagent [7,8] have been applied to enhance polymerization activity. Recently, trimethylaluminum-free methylaluminoxane (MAO) together with a certain amount of an alkylaluminum showed a notable effect on activity improvement for propylene polymerization at high temperature [9,10]. In fact, MAO is a particularly prominent activator for metallocene catalyst system. The formation of active sites undergoes by alkylation of transition metal complexes subsequent to methyl anion abstraction to yield cationic transition metal species which is active for olefin polymerization [11,12]. Nevertheless, alkylaluminum cocatalyst serves as alkylating agent in a similar way as MAO, but greater capability. Moreover, it further reduces Ti oxidation state to lower valence species and possibly form bimetallic complexes with Ti species [13,14]. Therefore, the activation mechanism of the combination between aluminoxane compound and alkylaluminum component might differ from the conventional activation process and it perhaps generates new active species, which gives high activity and novel polymer properties.

In this study, several SiO_2-supported alkylaluminums, such as MAO, modified MAO (MMAO), dried-MMAO (dMMAO) and unsupported dMMAO were prepared and used as coactivator to perform propylene polymerization using $MgCl_2/DEP/TiCl_4$ catalyst in combination with triethylaluminum (TEA) as an activator. The influence of the supported aluminoxanes on the catalytic activity and polymer properties were investigated and discussed further.

2. Experimental

2.1. Chemicals

Polymerization-grade propylene and triethylaluminum (TEA), donated from PTT Chemical Plc., were used as received. Methylaluminoxane (MAO) and modified methylaluminoxane (MMAO) in toluene were donated by Tosoh Akzo Corp. Cariact P-10 Silica gel (specific surface area 300 m^2/g), supplied by Fuji Silasia Chemical, was heated at 400 °C under vacuum for 6 h before use. $TiCl_4$ was

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purchased from Merck Ltd. Anhydrous $MgCl_2$ was supplied from Sigma–Aldrich Inc., Phthalic anhydride, diethylphthalate (DEP, used as an internal donor), *n*-heptane, *n*-decane and 2-ethyl-1-hexanol were purchased from Fluka Chemie A.G. Switzerland. *n*-Hexane and toluene were donated by Exxon Chemical Thailand Ltd. and were purified by refluxing over sodium/benzophenone under argon atmosphere prior to use. Ultra high purity argon (99.999%) was obtained from Thai Industrial Gas Co., Ltd. and was further purified by passing through molecular sieves 3 Å, ASF catalyst R3-11G, NaOH and phosphorus pentoxide (P_2O_5) in order to remove traces of oxygen and moisture. All chemicals and catalyst preparation were carried out under an inert atmosphere of argon using a vacuum glove box and/or standard Schlenk techniques.

2.2. Catalyst preparation

A catalyst of type $MgCl_2$/DEP/$TiCl_4$ was synthesized according to a reported procedure [15]. Under an argon atmosphere and magnetic stirring, a mixture of 0.476 g (5 mmol) of anhydrous $MgCl_2$ and 2.5 ml of *n*-decane were treated with 2.34 ml (15 mmol) of 2-ethyl-1-hexanol at 130 °C for 2 h then added 0.1089 g (0.74 mmol) of phthalic anhydride and held at the temperature for one more hour. After the system was cooled to −20 °C, about 20 ml (182.2 mmol) of $TiCl_4$ was injected dropwise before heating slowly to 110 °C followed by treatment of the solution in the presence of 0.26 ml (1.3 mmol) of diethylphthalate (DEP) at 110 °C for 2 h. The resulting solid product was separated by filtration and the addition of 20 ml of $TiCl_4$ was repeated at room temperature. After heating and keeping the solution at 120 °C for 2 h, the liquid was siphoned off and the solid part was washed twice with 10 ml of *n*-decane and three portions of *n*-hexane 10 ml, respectively. The obtained solid catalyst was vacuum dried at 40 °C for 30 min and contained 3% Ti by means of ICP analysis.

2.3. Preparation of SiO_2-supported aluminoxanes

Silica gel was heated under vacuum at 400 °C for 6 h. Then, 1 g of heated silica was reacted with 40 ml of MAO or MMAO in additional 10 ml of toluene for 30 min at room temperature. The solid part was washed twice with toluene and then dried under vacuum to obtain MAO/SiO_2 or MMAO/SiO_2 powder. For preparation of dMMAO/SiO_2, dMMAO was carried out according to the method as described in the literature [16]. The toluene solution of 40 ml MMAO was vacuum dried at ambient temperature for 6 h followed by dissolving with *n*-heptane and dried under vacuum for removing the residue of TMA and *i*-Bu_3Al (TIBA). Based on this technique, only about 40% of TMA was removed [16]. After repeat this procedure for 4 times, the obtained solid particle (dMMAO) was treated with 1 g of SiO_2 in toluene solution for 30 min and again evacuated to give a final white powder of dMMAO/SiO_2.

2.4. Propylene polymerization

Propylene polymerization was carried out in a 100 ml stainless steel autoclave reactor equipped with a magnetic stirrer. The prescribed amount of hexane (30 ml), TEA (Al/Ti molar ratio = 167), the selected SiO_2-supported aluminoxanes (MAO/SiO_2, MMAO/SiO_2, dMMAO/SiO_2) or dMMAO with the $Al_{aluminoxane}$/Ti mole ratio of 13 and catalyst were respectively added into the reactor. Polymerization was initiated by continuous feeding of propylene at constant pressure of 60 psi and temperature of 60 °C. After 30 min of polymerization, the reaction was then terminated by the addition of acidified methanol and the product was precipitated with a large amount of methanol. The resulting polymer was then filtered off and dried under vacuum at 60 °C for 6 h.

2.5. Characterization

2.5.1. Characterization of supported aluminoxanes

2.5.1.1. N_2 physisorption. Measurement of BET surface area, average pore diameter and pore size distribution of SiO_2-supported aluminoxanes were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system.

2.5.1.2. Scanning electron microscopy and energy dispersive X-ray spectroscopy. SEM and EDX were used to determine the morphologies and elemental distribution throughout the supported SiO_2, respectively. The SEM of JEOL mode JSM-6400 was applied. The EDX was performed using Link Isis series 300 program.

2.5.1.3. Thermogravimetric analysis. TGA was performed using TA Instruments SDT Q 600 analyzer. The samples of 10–20 mg and a temperature ramping from 40 to 800 °C at 10 °C/min were used in the operation. The carrier gas was N_2 UHP.

2.5.2. Characterization of polymer

2.5.2.1. ^{13}C NMR spectroscopy. ^{13}C NMR spectroscopy was used to determine the *mmmm* pentad of polymer obtained. Sample solution was prepared by dissolving 70 mg of polymer in 1,2,4-trichlorobenzene and benzene-d_6. The spectra were taken at 110 °C using BRUKER AVANCE II 400 operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

2.5.2.2. Differential scanning calorimetry. DSC (Perkin–Elmer DSC7) was used to examine melting temperatures and crystallinity of polymers at a ramping rate of 10 °C/min in temperature range of 30–200 °C. The thermogramme was recorded in the second heating run in order to remove the thermal history.

3. Results and discussion

The characteristics of different silica-supported aluminoxanes, such as $[Al]_{aluminoxanes}$ content, surface area, and number of Al atoms/nm^2 are shown in Table 1. As seen, the Al contents based on EDX measurement in various supported coactivators apparently increased in the following order: MAO/SiO_2 < MMAO/SiO_2 < dMMAO/SiO_2. These behaviors could be due to the adsorption ability between the different aluminoxanes and the silica support employed. Since the surface hydroxyl groups of SiO_2 have high reactivity towards exchange reaction, thus it results in high capability to be tailored by interaction with the external agents. In these regards, it is possible for the aluminoxane compounds to be able to bind on the SiO_2 surface by reactions with the hydroxyl groups [17]. As also shown in Table 1, the heterogenization caused

Table 1
Characteristics of different silica-supported aluminoxane and activity.

System	% Al[a]	Surface area (m^2/g)	Number of Al[b] (atoms/nm^2)	Activity[c] (kg PP/mol.Ti.h)
SiO_2	–[d]	211	–[d]	380
MAO/SiO_2	7.3	282	6	630
MMAO/SiO_2	8.7	250	8	560
dMMAO/SiO_2	10.2	254	9	760
dMMAO	20.1	–[d]	–[d]	500
No coactivator	–[d]	–[d]	–[d]	430

[a] Determined by EDX analysis.

[b] Calculated by Al contents and specific surface area of final support.

[c] Measured for propylene polymerization using catalyst = 10 mg, cocatalyst (Al_{TEA}/Ti) = 167, $Al_{aluminoxane}$/Ti = 13, solvent = n-hexane (30 ml), *P* = 60 psi, *T* = 60 °C, and polymerization time = 30 min.

[d] Not applicable.