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A comparative study of SiO_2- and ZrO_2-supported zirconocene/MAO catalysts on ethylene/1-olefin copolymerization

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Abstract

In this present study, the use of silica and zirconia as a support for zirconocene/MAO catalyst for copolymerization of ethylene/1-olefin (1-hexene, 1-octene, and 1-decene) was investigated. First, MAO as the cocatalyst was impregnated onto the support. Then, copolymerization of ethylene/1-olefin was performed. It was found that the use of zirconia support showed promising activities compared to those of the silica. Increased activities can be attributed to higher amount of $[Al]_{MAO}$ present on the zirconia support coupled with strong interaction between the $O_{support}$–$Al_{cocatalyst}$ linkage. In addition, the use of zirconia also resulted in higher degree of 1-olefin insertion and decreased T_m of copolymers produced.

Keywords: Silica; Zirconia; Zirconocene; MAO; Copolymerization; Metallocene

1. Introduction

The discovery of metallocene catalyst along with a methylaluminoxane (MAO) cocatalyst essentially led to the development of the highly active for homogeneous polymerization of α-olefin [1,2]. It is obvious that these active metallocene catalysts can compete with the conventional Ziegler–Natta catalysts. In particular, these catalysts are also capable of producing a variety of polyethylene copolymers, all with different chain compositions and architecture. However, to apply metallocene catalysts in the modern gas phase and slurry olefin polymerization processes, they need to be heterogenized on a support.

As known, the homogeneous metallocene catalysts have two major disadvantages; (i) the lack of morphology control and (ii) reactor fouling. Therefore, binding these metallocene catalysts onto inorganic supports as supported metallocene catalysts can overcome those drawbacks. Many inorganic supports such as SiO_2, Al_2O_3, TiO_2 and $MgCl_2$ have been investigated [3–14]. It has been reported that silica is perhaps the most attractive support employed for supported metallocene catalysts so far. However, the properties of silica itself may not be completely satisfied for all purposes based on the polymerization activity and properties of the obtained polymers. In order to increase an efficiency of supported metallocene catalysts, the modification of silica can be made [9,12] or alternative supports would be further investigated. Among various inorganic supports, zirconia (ZrO_2) has been widely used in many areas of chemistry such as in ceramics and catalysis. As catalysts, it was found that zirconia exhibited high catalytic activities for isomerization of olefins [15] and epoxides [16]. It was also used for isosynthesis via hydrogenation of CO as well [17]. The application of zirconia as a catalyst support has shown promising results in various catalytic reactions such as CO_2 hydrogenation [18], CO oxidation [19], and Fischer–Tropsch reaction [20–23]. Although the properties of zirconia as a catalytic support are promising in different areas of catalytic reaction, there has not been

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the literature reported on the use of zirconia as a support for metallocene catalytic system so far.

In this present study, the use of zirconia as a support for zirconocene/MAO catalyst for ethylene/1-olefins (1-hexene, 1-octene, and 1-decene) copolymerization was investigated and compared with that obtained from the conventional silica support. The properties of supports were characterized using N_2 physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDX), and thermal gravimetric analysis (TGA). The obtained copolymers were further characterized by means of SEM/EDX, ^{13}carbon nuclear magnetic resonance (^{13}C NMR), and differential scanning calorimetry (DSC).

2. Experimental

All chemicals [silica gel (Fuji Silasia, Cariact P-10), zirconium (IV) oxide powder (Aldrich), toluene (EXXON), *rac*-ethylenebis(indenyl) zirconium dichloride, *rac*-Et(Ind)$_2$-ZrCl$_2$) (Aldrich), methylaluminoxane, MAO, 2.667 M in toluene (Tosoh Akso), trimethylaluminum, TMA [Al(CH$_3$)$_3$] 2.0 M in toluene (Nippon Aluminum Alkyls), 1-hexene, 99% (Aldrich), 1-octene, 98% (Aldrich), and 1-decene, 98% (Fluka Chemie)] were manipulated under an inert atmosphere using a vacuum glove box and/or Schlenk techniques.

2.1. Materials

First, the support (SiO_2 and ZrO_2) was heated under vacuum at 400 °C for 6 h. Then, 1 g of the heated support was reacted with the desired amount of MAO in 10 ml of toluene at ambient temperature for 30 min. The solid part was separated and washed five times with 20 ml of toluene, followed by drying in vacuum at room temperature to obtain the catalyst support precursor MAO/SiO_2 and MAO/ZrO_2.

2.2. Polymerization

The ethylene/1-olefin [(1-hexene, EH), (1-octene, EO), and (1-decene, ED)] copolymerization reactions were carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 0.2 g of the supported MAO ($[\mathrm{Al}]_{\mathrm{MAO}}/[\mathrm{Zr}]_{\mathrm{cat}} = 2270$) and 0.018 mole of 1-olefin along with toluene (to make the total volume of 30 ml) were put into the reactor. The desired amount of Et(Ind)$_2$ZrCl$_2$ (5×10^{-5} M) and TMA ($[\mathrm{Al}]_{\mathrm{TMA}}/[\mathrm{Zr}]_{\mathrm{cat}} = 2500$) was mixed and stirred for 5 min aging at room temperature, separately, then was injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction for 15 min and then the reactor was evacuated to remove argon. The reactor was heated up to polymerization temperature (70 °C). By feeding the fixed amount of ethylene (0.018 mole $\sim$ 6 psi) into the reaction mixtures, the ethylene consumption can be observed corresponding to the ethylene pressure drop. The polymerization reaction was stopped and the reaction time used was recorded when all ethylene (0.018 mole) was totally consumed. After all ethylene was consumed, the reaction was terminated by addition of acidic methanol (0.1% HCl in methanol) and stirred for 30 min. After filtration, the obtained copolymers denoted as EH, EO, and ED (white powder) were washed with methanol and dried at room temperature.

2.3. Characterization

2.3.1. Characterization of supports

N_2 physisorption: Measurement of BET surface area, average pore diameter and pore size distribution of supports were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system.

X-ray diffraction: XRD was performed to determine the bulk crystalline phases of samples. It was conducted using a SIEMENS D-5000 X-ray diffractometer with Cu Kα ($\lambda = 1.54439$ Å). The spectra were scanned at a rate of 2.4° min^{-1} in the range $2\theta = 20$–$80°$.

Scanning electron microscopy and energy dispersive X-ray spectroscopy: SEM and EDX were used to determine the sample morphologies and elemental distribution throughout the sample granules, respectively. The SEM of JEOL mode JSM-5800LV was applied. EDX was performed using Link Isis series 300 program.

Thermal gravimetric analysis: TGA was performed to prove the interaction between the $[\mathrm{Al}]_{\mathrm{MAO}}$ and various supports. It was conducted using TA Instruments SDT Q 600 analyzer. The samples of 10–20 mg and temperature ramping from 50 to 600 °C at 5 °C min^{-1} were used in the operation. The carrier gas was N_2 UHP.

2.3.2. Characterization of polymer

Scanning electron microscopy: SEM was performed to study morphologies of polymers produced. The same equipment as mentioned above was employed.

Differential scanning calorimetry: The melting temperature of ethylene/1-olefin copolymer products was determined with a Perkin–Elmer diamond DSC. The analyses were performed at the heating rate of 20 °C min^{-1} in the temperature range of 50–150 °C. The heating cycle was run twice. In the first scan, sample was heated and then cooled to room temperature. In the second, sample was reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

Nuclear magnetic resonance: ^{13}C NMR spectroscopy was used to determine comonomer incorporation and polymer microstructure. Comparison of the positions of peak in the ^{13}C NMR spectrum of polymer sample with characteristic leads to identification of the sequence of the comonomer incorporation. The ^{13}C NMR spectra were recorded at 100 °C using BRUKER magnet system 400 MHz/54 mm. The copolymer solutions were prepared using 1,2-dichlorobenzene as solvent and benzene-d$_6$ for an internal lock.