Journal of Molecular Catalysis A: Chemical 386 (2014) 120–125

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Control of the molecular structure of ethylene-1-hexene copolymer by surface functionalization of SBA-15 with different compositions of amine groups

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ARTICLE INFO

Article history:
Received 3 March 2013
Received in revised form 11 August 2013
Accepted 21 January 2014
Available online 5 February 2014

Keywords:
SBA-15
Metallocene
Organosilane
Dual-functionalization
Ethylene polymerization

ABSTRACT

The surface of SBA-15 was functionalized with mixtures of two different silanes, *N*-[(3-trimethoxysilyl) propyl]ethylenediamine (NS) and 4-(triethoxysilyl)butyronitrile (NCy), after which $(n\text{-BuCp})_2ZrCl_2$ and methylaluminoxane (MAO) were grafted onto the amine-functionalized SBA-15 to examine its effect on ethylene homopolymerization and ethylene-1-hexene copolymerization. As the NCy/NS molar ratio in the feed decreased, the Zr content in the supported catalyst and ethylene homopolymerization activity increased owing to the strong interaction between NS and $(n\text{-BuCp})_2ZrCl_2$, whereas dual-silane functionalized catalysts showed little difference as regards the activity of ethylene-1-hexene copolymerization. The molecular weight (MW), polydispersity index (PDI) and chemical compositional distribution (CCD) were significantly influenced by the composition of the two silanes in feed. The MW of the homo- and copolymers increased as the molar ratio of NCy/NS in the supported catalyst increased. The presence of NCy in the supported catalyst made the PDI and MW narrower and larger, respectively. NCy was found to have a tendency to form more homogeneous active sites during the grafting process compared to the NS. Therefore, a change in the NCy/NS molar ratio can control the MW and PDI of the resulting polyethylene. From the results of a TREF analysis, it was also found that the nature of active species grafted onto the amine groups can be controlled by the type of amine group and by the NCy/NS molar ratio on the surface of SBA-15. Conclusively, the controllability of PDI, CCD and MW during ethylene-1-hexene polymerization was demonstrated using dual-silane functionalized catalysts.

1. Introduction

The commercial use of the metallocene/methylaluminoxane (MAO) catalyst system has opened a new frontier in olefin polymerization [1–3]. Metallocene, the most successful type of single-site catalyst, has been studied extensively due to its different properties compared to those of Ziegler–Natta catalysts [4–6]. It is well known that the mechanical and thermal properties of polymers considerably depend on their molecular weight, polydispersity index (PDI) and chemical compositional distributions (CCD) [7–10].

We reported the application of a mesoporous material as a type of support for a metallocene [11–14]. SBA-15 is known as well-defined and designable mesoporous materials possessing a narrow pore size distribution, large nanopore surface area and hexagonal arrangement of uniformly sized cylindrical pores (1.5 to 10 nm) [11]. Especially, the surface area of SBA-15 (>600 m^2/g) is much larger than that of amorphous silica (<300 m^2/g) which is mainly employed as a support for metallocene immobilization. The larger surface area can give opportunity to increase the supporting amount of metallocene and MAO compared to silica. According to the previous studies, the effect of nanopores of metallocene-confined mesoporous materials such as SBA-15 on copolymerization of ethylene-α-olefin was reported that regular and cylindrical nanopores of mesoporous materials caused an increase in the activity and a change in the chemical compositional distribution due to the different comonomer concentration inside the nanopore in comparison to amorphous silica [11,12].

The larger surface area of SBA-15 can also give an opportunity to increase the functionalized surface area than silica, and the functionalized surface can be applied to the efficient metallocene immobilization and for the variation of catalyst performance. SBA-15 functionalized with amine groups such as *N*-[(3-trimethoxysilyl)propyl]ethylenediamine (NS) or 4-(triethoxysilyl)butyronitrile (NCy) and other silane compounds have been applied for the immobilization of $(n\text{-BuCp})_2ZrCl_2$ and MAO. Interestingly, the Zr contents in the prepared supported catalysts were strongly dependent on the nitrogen content on the functionalized SBA-15 due to the strong interaction between

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http://dx.doi.org/10.1016/j.molcata.2014.01.015

(n-BuCp)$_2$ZrCl$_2$ and amine or nitrile groups on the surface of SBA-15 [13]. Another noteworthy finding was that NS could interact with (n-BuCp)$_2$ZrCl$_2$ strongly in comparison with NCy due to the greater number of amine groups and the formation of stable active species [14]. The polymerization activities of (n-BuCp)$_2$ZrCl$_2$ supported on NS or NCy-functionalized SBA-15 increased with an increase in the nitrogen and Zr contents of the supported catalyst. SBA-15/NCy/(n-BuCp)$_2$ZrCl$_2$ also showed a different chemical compositional distribution of ethylene-1-hexene copolymer from that of SBA-15/NS/(n-BuCp)$_2$ZrCl$_2$. It was explained that the difference in the nature of the active species arose due to the different electric environment of the nitrile group compared to the amine group [13].

In addition, spherical SBA-15 as spherical silica which is the usual support for metallocene can be formed in a spray drying method for the application to commercial plants. The textual properties of SBA-15 can also be controlled to apply it to the commercial plants.

In this study, we demonstrate the controllability of the CCD and PDI of polyethylene by introducing a combination of NS and NCy which showed the different CCD from each other in a previous report [13]. The controllability of them is considered to be very crucial in the polyolefin industry to meet a variety of polyethylene properties depending on their applications. To investigate the effect of a dual-functionalized system, SBA-15 was functionalized with NS and NCy with different molar ratios and supported metallocene was then prepared with this dual-silane functionalized SBA-15. The effects of the dual-silane functionalized surface of SBA-15 on the catalyst performance during polymerization and on the molecular structure of the resulting polymer were investigated in detail.

2. Experimental

2.1. Materials

All manipulations were carried out under an inert atmosphere of nitrogen. SBA-15 was synthesized according to previously reported procedures [15]. For the surface functionalization, *N*-[(3-trimethoxysilyl)propyl]ethylenediamine ($H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$, NS, Aldrich) and 4-(triethoxysilyl)butyronitrile ($CNCH_2CH_2CH_2Si(OCH_2CH_3)_3$, NCy, Aldrich) were employed, as shown in Fig. 1. Bis(n-butylcyclopentadienyl)zirconium dichloride ((n-BuCp)$_2$ZrCl$_2$, Aldrich) was used without purification. Methylaluminoxane (MAO, Albemarle) and triethylaluminum (TEAL, Aldrich) were used as cocatalysts without purification. 1-Hexene (Aldrich) was dried over a 13X molecular sieve. Ethylene (SK energy, Korea) and nitrogen were purified using two columns of Fisher RIDOX and a 5A/13X molecular sieve. Toluene (J.T Baker) and hexane (SK energy) were purified by refluxing over sodium metal.

2.2. Surface functionalization with silanes

To observe the difference in the polymer properties, we synthesized a series of dual-functional materials in which the molar ratio between NS and NCy was varied from 100% NS to 100% NCy with the total amount of NS and NCy fixed at 2 mmol.

1.0 g of as-synthesized SBA-15 was dispersed in 100 mL of dried toluene and NS and NCy mixtures (total 2.0 mmol) were added to the suspension. The mixture was stirred and the temperature kept at 105 °C for 2 h. The resulting solid was recovered by filtration, washed with ethanol, and dried at 100 °C for 12 h.

2.3. Catalyst synthesis

1.0 g of dual-silane functionalized SBA-15 was suspended in 30 mL of dried toluene. 0.35 mmol (n-BuCp)$_2$ZrCl$_2$ was dissolved in 8 mmol of MAO and the mixture was stirred. Subsequently, amino-functionalized SBA-15 was reacted with a mixture of 0.35 mmol (n-BuCp)$_2$ZrCl$_2$ and 8 mmol of MAO. After being stirred for 3 h at 70 °C, the solid part was collected and washed several times with toluene and dried in vacuum. All manipulations were performed in a nitrogen atmosphere.

2.4. Polymerization

Ethylene polymerization was performed in a 500 mL steel high-pressure reactor. 280 mL of hexane, comonomer and TEAL were introduced into the reactor, and the temperature was increased to the polymerization temperature. The catalyst suspension in hexane was injected into the reactor with a syringe and was then saturated with ethylene. After ethylene saturation, polymerization was started by agitation. The polymerization temperature (70 °C) and total pressure of the ethylene (7 bar) were maintained during the reaction. The polymerization process was stopped after a designed polymerization time and the polymer was filtered, washed with ethanol, and dried. The ethylene and 1-hexene concentrations in the liquid phase were calculated with Aspen plus^{TM}.

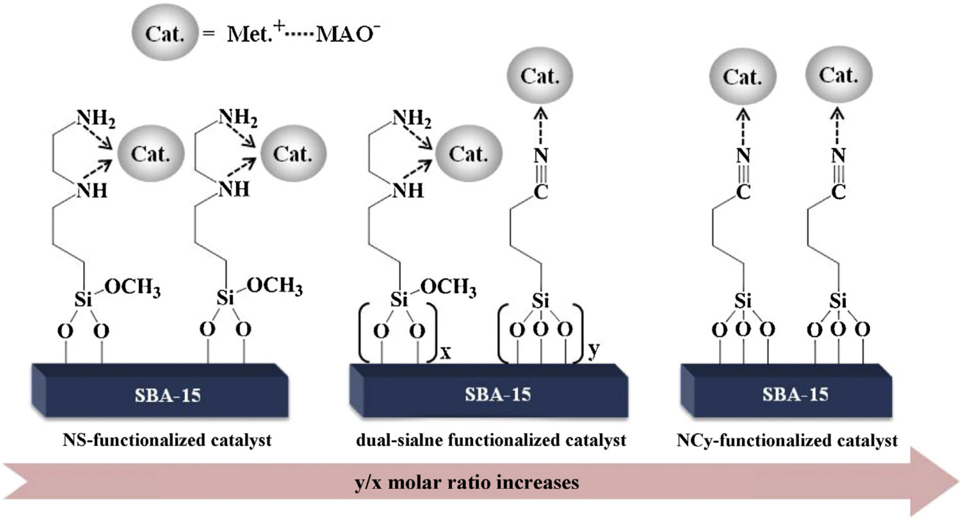

Fig. 1. Plausible structure of the interaction between the dual-silane functionalized surface of SBA-15 and the immobilized (n-BuCp)$_2$ZrCl$_2$ and MAO on SBA-15.