Full Length Article

Broadening molecular weight polyethylene distribution by tailoring the silica surface environment on supported metallocenes

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ABSTRACT

The synthesis of nonporous monodisperse chemically modified spherical silica particles was carried out according to the Stöber method. The resulting hybrid silicas were employed in the preparation of supported Cp_2ZrCl_2. The resulting metal loading, determined by Rutherford Backscattering Spectrometry (RBS), was between 0.15 and 0.48 wt% Zr/SiO_2. The systems were evaluated in ethylene polymerization with MAO as the co-catalyst. The presence of ligands can increase catalyst activity and the nature of the employed organosilane ligand on the hybrid silicas were shown to affect the molecular weight distribution leading to polyethylenes with broad polydispersity (Mw/Mn = 3.8) and even with bimodality (Mw/Mn = 12.6).

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1. Introduction

The use of heterogenous catalyst systems on polyolefin production, where the catalyst is supported on an inorganic matrix, leads to advantages on the resulting polymers, such as better control over size and morphology. Furthermore, better properties are achieved due to the presence of these inorganic particles, which may act as fillers resulting in nanocomposites [1–6]. Therefore, many research efforts have focused on the optimization of the supported metallocene system, using a variety of different inorganic supports such as alkylammonium-AlPO-kanemites [1], silica nanotubes [2], silica and zeolite core@LDH [3], reduced graphite oxide [4] and α-Ti(HPO$_4$)$_2$ [5], among others.

The improvement of polymeric processability on polymers produced by single-site catalysts by broadening polydispersity or by producing a bimodal molecular weight distribution is another important issue to consider when the catalytic system is concerned [7,8].

The choice of a support is of great importance once its surface characteristics, such as its textural profile (specific area, particle size, porous size, porous volume and morphology) as well as its mechanic resistance, are determinant factors in olefin

polymerizations [9,10]. Support morphology is also of great importance because of the replica phenomenon, meaning that the surface influences the shape of the final polymer [9]. Despite the fact that heterogenization often leads to a decrease in the employed Al/Zr ratio when compared to the homogeneous system, a decrease in the catalyst activity is observed. This reduction of catalyst activity occurs because some active sites may be deactivated on the support in combination with monomer diffusion restriction caused by the support itself. A method to overcome these drawbacks may be chemical modification of the support prior to metallocene impregnation or grafting [11,12].
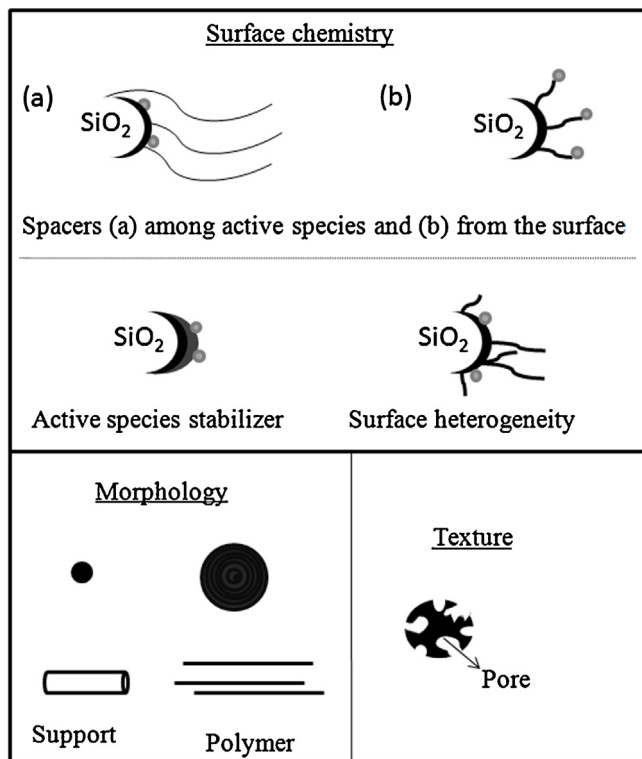
By far, silica is the most investigated support because of its stability at high temperatures and its low cost. Furthermore, it is commercially available in a variety of different ranges of particle sizes and specific areas [9,13]. Characteristics including the textural, morphologic and chemical treatment (Scheme 1) of a support are determinant factors, which can act and interfere with catalyst activity and polymer characteristics [11,14–18].

As shown in the first quadrant of Scheme 1, supports can be chemically modified with ligands acting as spacers (a) among active species or (b) far from the surface [16]. Such a procedure can directly affect catalyst activity, once the spaced catalyst species decrease bimolecular deactivation and therefore enhance catalytic performance. Another support chemical treatment reported in the literature is the dehydroxylation of the surface and the grafting of the co-catalyst in order to stabilize the active species to improve

Support effect

Surface chemistry

(a) SiO$_2$
(b) SiO$_2$

Spacers (a) among active species and (b) from the surface

SiO$_2$
SiO$_2$

Active species stabilizer
Surface heterogeneity

Morphology

Support
Polymer

Texture

Pore

Scheme 1. Support effect on catalyst active site and polymer morphology.

catalyst activity [13,17]. The nature of the support as well as its morphology and texture has a crucial influence on the catalyst behavior. The morphology of the support determines the polymer particles by replica phenomenon [2,10], while textural properties, like microporous and mesoporous supports, influence the structure of the supported metallocenes and, therefore, their catalytic activity [10,18].

To investigate specifically the effect of silica functionalized with different organosilane groups, a nonporous silica was synthesized. This nonporous silica was synthesized in order to arrange the organic groups directly on the external surface and to investigate the behavior of the organic groups on the surface, minimizing the effect of porosity on the catalyst performance. Therefore, in the present study, spherical silica particles were synthesized by sol precipitation, using TEOS according to the Stöber method, and modified with different organosilane groups, varying the chain size (from C_1 to C_{18}), chain type (aliphatic and cyclic) and its reactivity (vinyl group) of these groups. Functionalized supports were used to immobilize metallocene (Cp$_2$ZrCl$_2$) to ethylene via polymerization, and the ligand effect was evaluated on the polydispersity of the final polymer.

2. Experimental procedures

2.1. Materials

The hybrid materials were prepared using ammonium hydroxide P.A. (NH$_4$OH, Nuclear 29%), cyclohexyltriethoxysilane (CHS, 98%), octadecyltrimethoxysilane (ODS, 90%) and methyltriethoxysilane (MS, 99%) from Sigma Aldrich; tetraethoxysilane (TEOS, Acros > 98%), octyltriethoxysilane (OS, 85%), phenyltrimethoxysilane (Ph > 85%) and vinyltrimethoxysilane (Vy > 85%) from Dow Corning were used as received. Catalyst immobilization was conducted under an inert atmosphere (Argon;

99.99%; Air Liquid) using the Schlenk technique. Toluene and hexane were distilled with metallic sodium and benzophenone. Methylaluminoxane (MAO; 5 wt% Al solution in toluene; Chemtura Europe), triethylaluminum (TEA; 23 wt.% Al, Akzo) and cyclopentadienyl zirconium dichloride (Cp$_2$ZrCl$_2$; Sigma Aldrich) were used as received.

2.2. Synthesis of hybrid silicas

Hybrid silicas were synthesized by precipitation, following the Stöber method with NH$_4$OH as the catalyst. All silicas were used TEOS (45 mmol) as a starting material with a 90:10 ratio of TEOS:organosilane. In a beaker containing a magnetic stirrer, 40 mL of NH$_4$OH was diluted in 100 mL of ethanol and the suitable amount of TEOS. After stirring the mixture for 2 h at room temperature, 5 mmol of the chosen organosilane for surface functionalization was added. The suspension was stirred for more 2 additional hours. The suspension was then filtered and washed several times with ethanol and dried under a vacuum at 60 °C for 12 h.

2.3. Catalyst immobilization

Prior to zirconocene immobilization, 1.5 g of the resulting hybrid silica was treated with TEA (10 wt% Al) and magnetic stirring for 2 h. Then, the suspension was washed with 3 aliquots of 10 mL of hexane, and the treated support was dried under a vacuum. A solution of Cp$_2$ZrCl$_2$ in toluene (0.5 wt% corresponding to Zr/SiO$_2$) was added to the treated support and stirring was maintained for 30 min. The suspension was then transferred to a fritted disk, and the solid was washed with 15 aliquots of 2 mL of toluene. Then, the catalyst was dried under a vacuum for 12 h.

2.4. Polymerization procedure

Ethylene polymerization was performed in a 100 mL stainless steel reactor (Parr) equipped with a mechanical stirrer and an external heater to control the desired temperature. For all experiments, 30 mL of toluene was used as the solvent; 20 mL of toluene was added with the co-catalyst (MAO) using an Al/Zr molar ratio of 500, and the remaining 10 mL was used to add the supported catalyst in a mass corresponding to 1.5 μmol of Zr. The polymerization was performed at 60 °C for 0.5 h under 2.8 bar of ethylene. The polymerization was quenched with acidified ethanol (HCl 5 wt%). The resulting polymer was filtered, washed with distilled water and ethanol, and dried under reduced pressure at 40 °C.

The immobilized catalysts were labeled with the support abbreviation used for heterogenization preceded by the letter "C" to differentiate them from its hybrid support. For instance, CMS indicates that hybrid silica containing methyl groups was used to support the metallocene Cp$_2$ZrCl$_2$.

2.5. Supported catalyst and polymer characterization

Scanning Electron Microscopy (SEM) was performed using a JEOL model JSM 6060 operated at 10 kV. The samples were deposited on double-sided carbon tape, fixed onto an SEM stub and coated with gold. Transmission Electron Microscopy (TEM) images were obtained with a JEOL JEM 1200 EXII operated at 120 kV. The hybrid silica was suspended in acetone, and a drop of the supernatant was deposited on the grid. Fourier Transform Infrared Spectroscopy (FT-IR) was performed on a Shimadzu FT-IR spectrophotometer model 8300 (32 scans with a resolution of 4 cm^{-1}). The samples were analyzed as pellets with an approximate thickness and diameter of 2 mm and 5 mm, respectively. The sample mass dilution was performed with KBr. The zirconium content of the supported catalysts was determined by Rutherford