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High catalytic activity of SBA-15-supported metallocene toward ethylene polymerization: The effect of the ordered porous structure of the support

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ABSTRACT

The catalytic activity of the $(n\text{BuCp})_2ZrCl_2$ metallocene supported on ordered SBA-15 mesoporous silica and on traditional amorphous silica toward the polymerization of ethylene is studied. High activity values were obtained with the SBA-15-supported catalyst (6953–8407 kg mol^{-1} Zr bar^{-1} h^{-1}), which were significantly higher than those presented by the catalyst supported on amorphous silica (959–4234 kg mol^{-1} Zr bar^{-1} h^{-1}). The highly ordered mesoporous structure of SBA-15 affords a more homogeneous distribution of the metallocene on the support surface and improves accessibility during metallocene activation and monomer insertion. Polyethylene (PE) synthesized with the SBA-15-supported catalyst retains the molecular weight distribution of the PE produced with the single-site homogeneous metallocene, making the SBA-15-supported catalyst a promising heterogeneous metallocene system.

1. Introduction

The heterogenization of metallocene catalyst precursors on preferably inorganic substrates is an essential aspect for the use of these polyolefin single-site catalysts in an industrial-scale process [1]. Different inorganic materials such as alumina, clays, magnesium chloride, zirconia, and zeolites have been investigated as supports for the immobilization of metallocenes [2–5]. Our research group has also made some significant contributions in the study of supported metallocenes, in which supporting materials such as porous and nonporous silica [6,7], porous metal oxides [8], silsesquioxane-modified silica [9,10], and more recently nanosized zeolites [11] have been studied in detail. Porous amorphous silica appears so far as the most widely used metallocene support because of their relatively large surface area and porosity, good mechanical properties, and stability under reaction and processing conditions. Relatively novel silica materials with an ordered mesoporous structure, such as MCM-41 and SBA-15, may provide improved catalytic performance for heterogeneous metallocenes compared to traditional amorphous silica. SBA-15 mesoporous silica consists of a highly ordered hexagonal porous structure and has a larger internal surface area, greater uniform pore size, and cylindrical pores with thicker walls than MCM-41 [12,13]. SBA-15 mesoporous silica, although promising as a metallocene catalyst support, has been relatively little studied for this purpose. Most of the studies using SBA-15-supported metallocenes are mainly focused on the effect of the SBA-15 structure on the morphology of the resultant polyolefin. Dong et al. [14,15] studied the preparation of polyethylene nanofibers via ethylene extrusion polymerization by using Cp_2ZrCl_2 metallocene catalyst precursor supported on SBA-15. The catalytic activity values obtained under atmospheric pressure on the SBA-15 supported metallocene was moderate (860–900 kg mol^{-1} Zr h^{-1} atm^{-1}). Turunen et al. [16] prepared heterogeneous zirconocenes by grafting SBA-15 with $ZrCl_4$ and subsequently with salts of cyclopentadiene (Cp) or indene (Ind), reporting only moderate activity for the SBA-15 supported zirconocenes (160–460 kg mol^{-1} Zr h^{-1} atm^{-1}) in a pressure range of 3.6–4.8 bar. Silveira et al. [17] studied the catalytic activity of a Cp_2ZrCl_2/$(n\text{BuCp})_2ZrCl_2$ metallocene mixture supported on SBA-15, MCM-41, MCM-22, and ITQ-2 mesoporous materials. The activity of the metallocene catalyst precursors and the molecular weight of the polyethylene product were shown to depend on the textural characteristics of the supports, namely grain size and pore diameter. Of the series of supported catalysts, metallocene mixtures fixed on SBA-15 presented the highest activity (3200 kg mol^{-1} Zr h^{-1} atm^{-1}), and this was attributed to the higher pore diameter of the SBA-15 support.

It is known that structurally ordered porous materials as supports for heterogeneous catalysts give better yields than amorphous porous materials. For example, replacement of amorphous silica–alumina by crystalline zeolite as support for hydrocraking catalysts afforded a notably improved performance of this industrial reaction [18]. The higher activity comes from greater strength

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and organization of the actives sites in the zeolites. Likewise, the use of ordered SBA-15 silica as a metallocene catalyst support could also to improve the catalytic activity of these systems with respect to the traditional catalyst supported on amorphous silica.

In this work we studied the effect of the structural properties of the support on the ethylene polymerization activity of the $(n\text{BuCp})_2ZrCl_2$ catalyst precursor supported on ordered SBA-15 silica as compared to that heterogeneized on traditional amorphous silica. High ethylene polymerization activity values for the SBA-15-supported metallocene are presented.

2. Experimental

2.1. Preparation of SBA-15 mesoporous silica

SBA-15 mesoporous silica was synthesized according to the procedure reported by Zhao et al. [19] using the gel composition of 6.96×10^{-4} P123:4.08 $\times 10^{-2}$ TEOS:0.24 HCl:1.67 H_2O. This synthesis solution was prepared by mixing appropriate amounts of amphiphilic triblock copolymer, Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_w = 5800, BASF); 2 M HCl solution, tetraethyl orthosilicate (TEOS 98%, Aldrich), and distilled water. The resulting solution was submitted to an aging period at 40 °C for 24 h with stirring. After that, the solution was added to Teflon-lined stainless steel autoclaves and hydrothermally treated at 100 °C for 48 h under static conditions. After crystallization the solid product was filtered, washed with distilled water, and dried overnight at 100 °C. The material was calcined in air at 550 °C for 8 h, at a heating rate of 1 °C/min to decompose the triblock copolymer and obtain a white powder (SBA-15).

2.2. Preparation of supported metallocene catalysts

All the operations described here were carried out in a nitrogen atmosphere using Schlenk's technique. Nitrogen was deoxygenated and dried by passing successively through columns of Cu catalyst (BASF) and activated molecular sieve (13X). Toluene was purified by refluxing and freshly distilled under nitrogen from a Na/benzophenone system.

Prior to catalyst fixation, the prepared SBA-15 silica and commercial amorphous silica (EP17G, Crosfield Catalysts) were activated at 450 °C for 6 hours under ultra-high vacuum conditions (10^{-6} Torr). The metallocene bis(*n*-butylcyclopentadienyl) zirconium dichloride ($(n\text{BuCp})_2ZrCl_2$) (Boulder) was directly supported on the activated silica supports and on methyaluminoxane (MAO)-treated supports.

Metallocene impregnation was carried out by contacting 1 g of the silica supports with 20 cm^3 of 0.5% $n(\text{BuCp})_2ZrCl_2$ toluene solution for 30 min at room temperature. The slurry was then filtered through a fritted disk. The resulting solids were washed six times with 10-cm^3 toluene aliquots and dried under vacuum for 4 h. For the MAO pretreatment of the support, 1 g of activated silica support was contacted at 60 °C for 3 h with 20 cm^3 of a 0.56 wt% MAO solution in toluene prepared from a 10% MAO solution (Witco). The bulk Zr and Al content in the supported catalysts was measured by inductively coupled plasma–atomic emission spectroscopy (ICP–AES).

2.3. Ethylene polymerization

Ethylene polymerization was carried out in a 450 mL stainless steel reactor (Parr), equipped with mechanical stirring and inlets for catalyst suspension, nitrogen, and the monomer. For each experiment 3×10^{-6} mol of supported metallocene catalyst were added to the reactor, using an amount of soluble MAO in an Al/Zr mole ratio of 1500. The polymerization was carried out at 60 °C for 30 min under an ethylene pressure of 2 bars. After this period the polymerization was stopped by quenching with acidified (HCl) ethanol. The polyethylene product was recovered by filtration, washed with ethanol, dried at 40 °C overnight, and then weighed to determine the catalytic activity. Polymerization was also carried out using the unsupported metallocene catalyst under identical reaction conditions.

2.4. Material characterization

SBA-15 mesoporous silica was analyzed by X-ray diffraction (XRD) within a 2θ range of 0.5–5°. Low angle XRD patterns were measured on a Siemens D 5000 diffractometer using CuKα radiation at a scanning speed of 0.2 °/min.

SBA-15 silica, amorphous silica, and the corresponding supported catalysts were examined by high resolution transmission electron microscopy (HRTEM) on a FEI-Tecnai G2 F20 S-Twin HRTEM microscope equipped with a Field Emission Gun (FEG) operating at an accelerating voltage of 120 kV. Specimens were prepared by transferring a small drop of sample-ethanol suspension to carbon-film-coated copper grids. Elemental analysis was done using energy dispersed X-ray spectrometry (EDX) attached to the microscope. The selected area electron diffraction (SAED) pattern was also obtained for SBA-15.

Textural characterization of silica supports and corresponding heterogeneous catalysts was done by N_2 adsorption at 77 K in a Micromeritics ASAP 2010 sorptometer. The specific apparent surface areas (S_g) were calculated using the BET equation, and the micropore volume (V_o) by the Dubinin–Radushkevich equation applied to the experimental data obtained from N_2 adsorption isotherms. The pore size distribution curves were obtained using the desorption branches of the N_2 adsorption isotherms and by the Barrett-Joyner–Halenda (BJH) method.

Molar masses and molar mass distributions of polyethylene products were obtained with a Waters (Alliance GPC 2000) GPC instrument equipped with three Styragel HT-type columns (HT3, HT5, and HT6E). 1,2,4-Trichlorobenzene was used as solvent at a flow rate of 1 cm^3/min and a temperature of 135 °C. The columns were calibrated with polystyrene standards. Polymer melting points (T_m), crystallization temperatures (T_c) and crystallinities (X_c) were determined by differential scanning calorimetry (DSC), using DSC 2920, TA Instruments, equipment calibrated with indium. Heating scans at 10 °C/min in the temperature range −10 to 170 °C were carried out. The heating cycle was performed twice, but only the results of the second scan are reported, because the former is influenced by the mechanical and thermal history of the samples.

3. Results and discussion

3.1. Preparation of supported metallocene catalysts

Structural characteristics of the silica supports are presented through HRTEM analysis (Fig. 1). The hexagonal array of uniform channels in the mesoporous structure of SBA-15 is clearly visible in the HRTEM image viewed along the [0 0 1] direction (Fig. 1a). When the electron beam is perpendicular to the pore axis (Fig. 1b), the SBA-15 mesopores can be observed as curved cylinders of relatively uniform size. HRTEM channel-spacing distribution of SBA-15 (Fig. 1c) shows that the distance between the centers of two adjacent cylindrical pores is 8.2 nm. Considering the thickness of the pore walls (2.1 nm), the effective pore diameter of SBA-15 silica is around 6.1 nm. The ordered structure of SBA-15 was also verified through its XRD pattern, which exhibited the