



## Effect of the silica texture on the structure of supported metallocene catalysts

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### ABSTRACT

A series of hybrid supported catalysts was prepared by sequentially grafting  $\text{Cp}_2\text{ZrCl}_2$  and  $(n\text{BuCp})_2\text{ZrCl}_2$  (1:3 ratio) onto synthesized xerogel, aerogel, commercial silicas, MCM-41 and leached chrysotile. The supported catalysts were characterized by Rutherford backscattering spectrometry, matrix assisted laser desorption ionization time of flight mass spectroscopy, atomic force microscopy, extended X-ray absorption fine structure spectroscopy and nitrogen adsorption. The grafted metal content was between 0.15 and 0.84 wt.% Zr/SiO<sub>2</sub>. All the systems were shown to be active in ethylene polymerization with methylaluminoxane as the cocatalyst. The catalyst activity and molecular weight were shown to depend on the effect impinged by the textural characteristic of the supports on the structure of the supported catalyst species. The highest activity in ethylene polymerization (ca. 5300 kgPE molZr<sup>-1</sup> h<sup>-1</sup>) was reached with the supported catalyst using commercial silicas with narrow pore diameter and volume distribution. Polymers with higher molecular weight, characterized by gel permeation chromatography and differential scanning calorimetry, were associated with the reduction in the interatomic Zr–O distance, which was shown to be dependent on the support properties.

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### 1. Introduction

Supported metallocenes have been investigated in the last 20 years. Many routes of immobilization have been proposed, affording different catalyst activity or polymer properties [1]. The performance of an immobilized metallocene may be changed in comparison to the homogeneous counterpart due to electronic and steric effects attributed to the support. Most of the supported metallocenes have exhibited lower catalytic activities. Furthermore, polymer properties usually differ from those produced with the homogeneous complexes [1–3]. According to the literature, the reduction in catalytic activity has been attributed to: (i) deactivation of the metallocene complexes during the grafting reaction, (ii) inaccessibility of the metallocene complexes to the cocatalyst (methylaluminoxane, MAO) hindering its activation, (iii) generation of active sites with lower propagation rates due to interactions with the support surface, and (iv) restrictions of the monomer access to the active sites hindering the chain propagation [4]. Generally, polymers produced with supported metallocenes have a higher average molecular weight due to a reduction in the rate

of termination reactions [4–7]. Conversely, polymers with lower crystalline fractions have been produced with supported metallocene [8]. Changes in the stereoregularity and stereospecificity of the active sites generated by supporting a metallocene have also been reported [1]. Furthermore, a decrease in the insertion of long chain branches for supported metallocenes has been observed [5–7].

In spite of having been investigated for a long time, the field of supported metallocenes still attracts much attention. Silica has been the most investigated and proposed support. Recent research has dealt with other alternatives such as: the development of supported catalysts on tubular mesoporous aluminas capable of producing polyethylene nano-fibers [9], immobilization on nanosilicas [10], aluminophosphinates [11] and polymers [12], metallocenes encapsulated on silica produced by sol–gel [13], grafting on sulphonic-acid modified SBA [14] or MgCl<sub>2</sub>-based supports [15], to mention a few. Such examples suggest that the support may play an important role in the development of a supported catalyst.

In previous work, we reported the effect of grafting  $\text{Cp}_2\text{ZrCl}_2$  and  $(n\text{BuCp})_2\text{ZrCl}_2$  on the same support (silica), at different order and molecular ratios, on the catalyst activity and on the polymer properties. The best catalyst system was that resulting from grafting  $\text{Cp}_2\text{ZrCl}_2$  followed by  $(n\text{BuCp})_2\text{ZrCl}_2$  in a 1:3 ratio [16,17]. In a subsequent paper, both catalysts were grafted on silica supports

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produced by sol–gel (xerogel and aerogel) and precipitation methods. The catalyst activity and molecular weight were shown to depend on the textural characteristic of the silicas, namely grain size and pore diameter [18].

In the present study, we comparatively investigated the effect of the microstructure of different silica-based supports on the structure of the resulting grafted metallocene species. Different silica supports were employed: amorphous (commercial silicas, synthesized xerogel and aerogel silicas), crystalline (silica MCM-41) and fiber-like (from leached chrysotile) silicas.  $\text{Cp}_2\text{ZrCl}_2$  and  $(n\text{BuCp})_2\text{ZrCl}_2$  were grafted onto the supports in a 1:3 ratio. The resulting catalysts were characterized by Rutherford backscattering spectrometry (RBS), matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF-MS), atomic force microscopy (AFM), extended X-ray absorption structure (EXAFS) spectroscopy and nitrogen adsorption. The hybrid-supported catalysts were evaluated in ethylene polymerization with MAO as the cocatalyst. The polymers were characterized by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC).

## 2. Experimental

### 2.1. Materials

All chemicals were manipulated under inert atmosphere using the Schlenk technique. All supports were activated under vacuum ( $P < 10^{-5}$  bar) for 16 h at 450 °C.  $(n\text{BuCp})_2\text{ZrCl}_2$  (Aldrich),  $\text{Cp}_2\text{ZrCl}_2$  (Aldrich),  $\text{Si}(\text{OEt})_4$  (Merck),  $\text{SiCl}_4$  (Merck),  $\text{ZrCl}_4$  (Aldrich) and MAO (Witco, 10.0 wt.% toluene solution) were used without further purification. Ethylene and argon (White Martins) were passed through a molecular sieve (13 Å) prior to use. Toluene was purified by refluxing with sodium, followed by distillation under nitrogen just before use.

### 2.2. Preparation of the silica-based supports

#### 2.2.1. Synthesis of xerogel silica by the hydrolytic acid route [19–20]

Tetraethylorthosilicate ( $\text{Si}(\text{OEt})_4$ ) and  $\text{HNO}_3$  (0.3 M) were poured together into a glass reactor and vigorously stirred at room temperature. The  $\text{H}_2\text{O}:\text{Si}(\text{OEt})_4$  volume ratio was kept under 2. Initially, the mixture was separated into two phases. When the mixture was stirred, an emulsion was formed and water was dispersed as droplets. After 3–10 min, a homogeneous solution was formed. In the following days, the viscosity increased and a solid transparent monolith was obtained. The resulting xerogel (6.30 g) was washed with acetone and dried at 140 °C for three days.

#### 2.2.2. Synthesis of aerogel silica

Aerogel silica was synthesized by the sol–gel method under supercritical conditions at CENERG (France). The experimental conditions are described elsewhere [21].

#### 2.2.3. Chrysotile leaching

Natural chrysotile (ca. 30 g) was mixed with (1 L) of a hydrochloric acid solution ( $5.0 \text{ mol L}^{-1}$ ), according to the leaching procedure described in literature [22]. This suspension was stirred for 48 h at 626 °C yielding 15.0 g of product. The resulting leached chrysotile was abundantly washed with deionized water and dried.

### 2.3. Synthesis of supported hybrid catalysts

A  $\text{Cp}_2\text{ZrCl}_2$  toluene solution corresponding to 0.25 wt.%  $\text{Zr}/\text{SiO}_2$  was added to ca. 1.0 g of pre-activated silica and stirred for 30 min at room temperature. The solvent was removed under vacuum

through a fritted disk. A  $(n\text{BuCp})_2\text{ZrCl}_2$  toluene solution corresponding to 0.75 wt.%  $\text{Zr}/\text{SiO}_2$  was added and the resulting slurry was stirred for 30 min at room temperature, and then filtered through a fritted disk. The resulting solids were washed with  $15 \times 2.0 \text{ cm}^3$  of toluene and dried under vacuum for 4 h.

The procedure above was used for all of the silicas used in this work (Grace 956, 955 and 948, xerogel silica by the hydrolytic route and aerogel silica, MCM-41, and leached Chrysotile). These silicas generated the heterogeneous catalytic systems after grafting, respectively: G56, G55, G48, HYD, AER, M41 and ICR.

### 2.4. Characterization of supported catalysts

#### 2.4.1. Rutherford backscattering spectrometry (RBS)

The zirconium loadings in the catalysts were determined by RBS, using  $\text{He}^+$  beams of 2.0 MeV incidence, on homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems. The method is based on the determination of the number and energy of the detected particles which are elastically scattered in the Coulombic field of the atomic nuclei in the target. In this study, the  $\text{Zr}/\text{Si}$  atomic ratio was determined by the heights of the signals corresponding to each of the elements in the spectra and converted to wt.%  $\text{Zr}/\text{SiO}_2$ . For an introduction to the method and applications of this technique the reader is referred elsewhere [23].

#### 2.4.2. Fourier transform infrared spectroscopy (FT-IR)

Samples were analyzed as pellets, diluted in KBr, by absorbance FTIR, using a BOMEM FTIR spectrophotometer (MB-102) at 25 °C by coadding 32 scans at a resolution of  $4 \text{ cm}^{-1}$ . The measurements were restricted to the  $4000\text{--}2500 \text{ cm}^{-1}$  region.

#### 2.4.3. Nitrogen adsorption–desorption isotherms

Samples were previously degassed ( $10^{-2}$  mbar) at 120 °C (silica) or at 85 °C (supported catalysts) for 8 h. Adsorption–desorption nitrogen isotherms were measured at  $-196$  °C in a Gemini 2375 (Micromeritics). Specific surface areas ( $S_{\text{BET}}$ ) were determined by the Brunauer–Emmett–Teller equation ( $P/P_0 = 0.05\text{--}0.35$ ). The mesopore size and distribution were calculated by the Barrett–Joyner–Halenda (BJH method) using the Halsey standards. Desorption branch was used.

#### 2.4.4. Atomic force microscopy (AFM)

Images of silica and supported catalyst surfaces were obtained using an atomic force microscope, Nanoscope IIIa<sup>®</sup>, manufactured by Digital Instruments Co., using the contact mode technique with probes of silicon nitride. WS M 4.0 software from Nanotec Electronic S.L. [24] was used for the image treatment. Samples were compressed in the form of tablets and fragments of roughly  $16 \text{ mm}^2$  which were employed for the analysis.

#### 2.4.5. Extended X-ray absorption fine structure (EXAFS)

EXAFS measurements were performed around the Zr K edge ( $E = 17,998 \text{ eV}$ ) using the Si(220) channel-cut monochromator at the XAFS 1 beamline (LNLS, Campinas, Brazil). The spectra were collected in the fluorescence mode using one ionization chamber filled with argon and a Si(Li) detector. In order to perform EXAFS experiments, the powder of the supported metallocenes was compacted into a pellet and covered with Kapton<sup>®</sup> tape. All the manipulations were performed in a dry box to avoid the occurrence of oxidation reactions. The EXAFS spectra were acquired from 17,900 up to 18,900 eV with a 3 eV step. Several scans were averaged in order to improve the signal to noise ratio.

The IFEFFIT analysis package [25] and the Winxas program [26] were used for the EXAFS data analysis. The EXAFS signal between 1.0 and  $10.0 \text{ \AA}^{-1}$  was Fourier-transformed with a  $k^1$  weighting and

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