

Metallocene Immobilized within Silica by a Sol-gel Method: Investigation of the Support Structure

INTRODUCTION

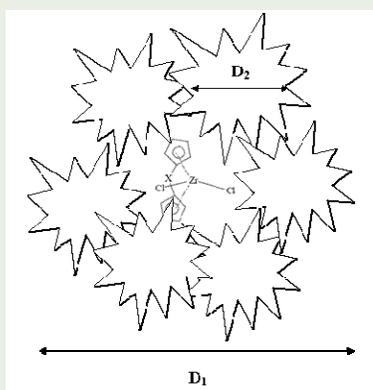
Several methods have been proposed in the literature dealing with the supporting methodology for metallocene catalysts. As a matter of fact, silica has largely been the most employed material for grafting metallocenes in the studies. In a different approach, we have proposed the immobilization of zirconocenes into silica matrix concomitant to the oxide synthesis obtained by non-hydrolytic sol-gel method. The resulting catalysts were shown to be active for ethylene polymerization with similar activities to those found to zirconocene on commercial SiO₂. As an extension of this previous work, the present study deals with the immobilization of different metallocene structures within the silica by the proposed method and characterization of the resulting silica by SAXS. In addition, the catalysts were evaluated in ethylene polymerization in an attempt to obtain some correlation with the silica structural parameters.

SAXS MEASUREMENTS

A typical SAXS profile for the supported metallocenes is shown in Figure 1, presenting 2 regions: D₁ for q < q_b and D₂ for q > q_b. A characteristic length (ξ), corresponding to the spatial scale of the primary particles (see Scheme 1), was estimated as ξ = 2π/q_b.

The scattering intensity profile for q < q_b shows characteristics of the particle with dimension higher than ξ (D₁ region). Conversely, the characteristics of the particle with dimension lower than ξ are found in the region of scattering profile where q > q_b (D₂ region). Therefore, information about the influence of the metallocene in the silica structure could be found in this region considering that the organometallic complex is trapped within the interstices formed by the primary particle agglomeration. Scheme 1 represents the particle structure and the dimensions related to the SAXS scattered profile.

Table 1 shows the results of data fitting for each region. α₁ values were found to be between 3-4, relating to surface fractal structures. However, no clear trend can be established between α₁ values and the metallocene structures. On the other hand, the α₂ values could be correlated to ligand-metal-ligand angle which is a steric hindrance measurement of the metallocene structure as shown in Figure 2. In addition the dimension of ξ was estimated around 16 nm independently of the metallocene structure. This results suggest a deep location of the metallocene inside the oxide network.



Scheme 1: Sketch of the aggregation of primary silica particles of silica.

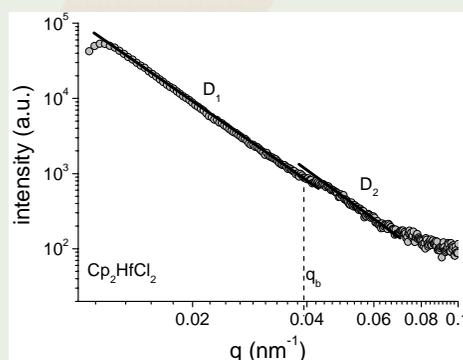


Figure 1: Typical scattering profile found to supported metallocene (Cp₂HfCl₂/SiO₂).

Table 1: Fractal dimensions α₁ (D₁) and α₂ (D₂).

Entry	Catalyst	α ₁	α ₂	ξ (nm)	R _g (nm)
1	Cp ₂ ZrCl ₂ /SiO ₂	3.2	3.5	15.7	9.5
2	Cp ₂ TiCl ₂ /SiO ₂	3.3	3.5	15.7	9.8
3	Cp ₂ HfCl ₂ /SiO ₂	3.4	3.3	15.7	9.2
4	Et(Ind) ₂ ZrCl ₂ /SiO ₂	3.4	3.1	15.7	9.3
5	Et(IndH ₄) ₂ ZrCl ₂ /SiO ₂	3.1	2.1	15.3	9.6
6	(nBuCp) ₂ ZrCl ₂ /SiO ₂	3.1	-	-	10.6
7	(fBuCp) ₂ ZrCl ₂ /SiO ₂	3.4	3.2	16.1	10.0
8	(fBuCp) ₂ ZrCl ₂ /SiO ₂	3.1	3.0	15.7	9.8
9	Cp ₂ ZrCl ₂ /SiO ₂ ^b	-	-	-	-
10	Cp ₂ TiCl ₂ /SiO ₂	-	-	-	-
11	Cp ₂ HfCl ₂ /SiO ₂	-	-	-	-
12	Et(Ind) ₂ ZrCl ₂ /SiO ₂	-	-	-	-

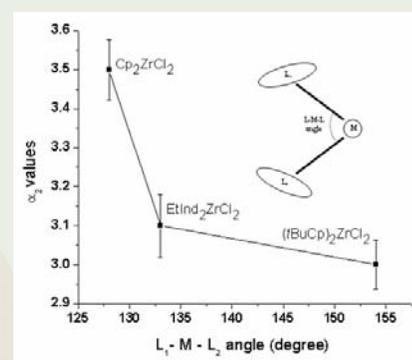


Figure 2: Relationship between fractal dimension and the metallocene bit angle.

POLYMERIZATIONS

Catalyst activity in the ethylene polymerization is shown in Table 2 as well as the metallocene content (wt. % M, M = Zr, Ti or Hf). In a general way, all catalysts showed a poor activity with exception of those systems containing Cp₂ZrCl₂, Cp₂HfCl₂, and (nBuCp)₂ZrCl₂. In addition, it was not found any evident correlation between activity and fractal dimension as well. The reduction in the catalytic activity could be attributed to restrictions of monomer access to the active sites hindering the chain propagation due to an inadequate particle fragmentation during the early moments of the polymerization (see Figure 3). This could be attributed to the deep location of the metallocene complex into the oxide matrix. In this sense, a huge shell of oxide matrix around the metallocene hinders the breakup of the particle leading to a poor activity. In an attempt to solve the described diffusional problems, new catalysts were synthesized with higher metallocene content (c.a. 1.5 w.% Zr). Increasing the load of metallocene allows the catalysts to breakup adequately during the early moments of the polymerization avoiding monomer accessibility problems to the active sites.

Table 2: Catalyst activities in ethylene Polymerization.

Entry	Catalyst	Metallocene content (wt.% M)	Activity (kg _{pol} /mol _h) ^a
1	Cp ₂ ZrCl ₂ /SiO ₂	0.50 ± 0.048	2300
2	Cp ₂ TiCl ₂ /SiO ₂	0.30 ± 0.0039	Traces
3	Cp ₂ HfCl ₂ /SiO ₂	0.44 ± 0.0033	100
4	Et(Ind) ₂ ZrCl ₂ /SiO ₂	0.27 ± 0.0064	Traces
5	Et(IndH ₄) ₂ ZrCl ₂ /SiO ₂	0.27 ± 0.032	Traces
6	(nBuCp) ₂ ZrCl ₂ /SiO ₂	0.35 ± 0.017	3600
7	(fBuCp) ₂ ZrCl ₂ /SiO ₂	0.30 ± 0.011	Traces
8	(fBuCp) ₂ ZrCl ₂ /SiO ₂	0.19 ± 0.027	Traces
9	Cp ₂ ZrCl ₂ /SiO ₂ ^b	0.71 ± 0.058	200
10	Cp ₂ TiCl ₂ /SiO ₂	1.36 ± 0.037	700
11	Cp ₂ HfCl ₂ /SiO ₂	1.45 ± 0.042	1000
12	Et(Ind) ₂ ZrCl ₂ /SiO ₂	1.43 ± 0.065	800

a- Polymerization conditions: 1.6 bar of ethylene, Al(MAO)/M = 1000, 60°C, toluene, 30 min.

b- Catalyst particles with diameter 53-100 μm.

Activities of the homogeneous metallocenes under same polymerization conditions: Cp₂TiCl₂: 1150 kg_{pol}/mol_h; Cp₂HfCl₂: 1750 kg_{pol}/mol_h; and Et(Ind)₂ZrCl₂: 3000 kg_{pol}/mol_h.

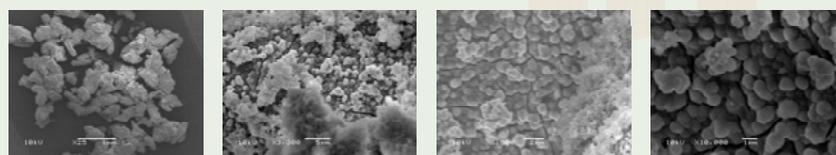


Figure 3: Micrographics of polymer particle obtained in the ethylene polymerization with Cp₂ZrCl₂/SiO₂ of diameter between 53-100 μm (entry 10 in Table 2). Magnification: 25× (a), 3300× (b), 6500× (c) and 10000× (d).

FINAL REMARKS

The immobilization of metallocenes within a silica matrix using a non-hydrolytic sol-gel route shows that the silica particle was formed by the aggregation of the primary structures with a diameter of about 16 nm. The aggregation process seems to be affected by the metallocene structure which suggests that the organometallic complex is surrounded by primary particles having a deeper location in the oxide matrix. Some metallocenes, which in homogeneous systems are less active, showed a negligible activity when entrapped within the oxide matrix by the proposed method. This result seems to be related to problems of catalyst fragmentation leading to monomer mass transfer limitations along the partially fragmented particle. In order to solve this problem, the amount of metallocene in the catalyst should be increased.

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