

Study of metallocene supported on porous and nonporous silica for the polymerization of ethylene

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Porous and nonporous silicas are good supports for the synthesis of coordinative heterogeneous catalysts for ethylene polymerization. The catalytic activity of nonporous Aerosil depends critically on the percentage of incorporated zirconium. The calcination of the support also affects the activity, showing the best results with nonporous silica at 1000°C, and with porous silica at 800°C.

Keywords: metallocene, zirconium, polymerization, silica support, ethylene

1. Introduction

Since the discovery of the so-called “Kaminsky–Sinn catalyst” for polymerizing olefins, there have been many attempts not only to investigate the polymerization mechanism, but also to develop more simplified catalysts for practical use [1,2]. Several kinds of homogeneous catalyst systems of metallocenes with methylaluminoxane (MAO) have been developed, with $\text{EtInd}_2\text{ZrCl}_2$ being one of the most widely studied [3–6]. At the same time, great efforts have been made to prepare different types of supports for heterogeneous catalysts based on metallocenes, in order to introduce the catalyst directly into the various processes currently in operation [7,8]. Supports like SiO_2 , Al_2O_3 , MgCl_2 , etc., have been used, all of them characterized by high activity and good control of the morphology of the final product [9].

Supported metal complexes offer distinct advantages over their homogeneous counterparts in transition-metal-catalysed organic transformations. The application of catalysts containing immobilized complexes to organic synthesis has been increasing recently. Much of the effort in this area has been directed at fixing organometallic fragments to organic polymers or to silica in order to understand other catalytic processes [10].

The deposition and anchoring of new and more active species on the surface of metal oxide supports has been extensively investigated with the aim of developing improved catalysts for the polymerization of olefins. In principle, supported catalyst systems can offer good efficiency since the metal ions are located only on the surface of the support. Because the support material is usually chemically innocuous, it need not be removed [11–13].

Studies related with the adsorption and other proper-

ties of the surface oxide adsorbents, particularly silica, are known to depend on the surface hydroxyl (silanol) groups. By varying the concentration of hydroxyl groups on the surface of oxide adsorbents using different methods, it is possible to change substantially the properties of that surface [14].

2. Experimental

Materials: Commercial toluene was purified by refluxing over metallic sodium, with benzophenone as indicator. Polymerization grade ethylene was deoxygenated and dried by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. ES-70 microspherical and EP-10 granular porous silica (Crossfield Catalyst), and nonporous Aerosil 200 [15] were used as supports. Prior to their use they were heated overnight at 150°C under vacuum, and then calcined at 500, 800 and 1000°C, and stored in a nitrogen atmosphere. Methylaluminoxane (MAO) and the catalysts $\text{EtInd}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrCl}_2$, all supplied by Witco, were used directly. All manipulations were carried out in an inert nitrogen atmosphere.

Preparation of the support catalyst: Two grams of calcined silica and different amounts of metallocene were suspended in 100 cm³ of toluene and stirred for 3 h at 130°C. The resulting solid was carefully washed with toluene ensuring the absence of homogeneous parts and then extracted, filtered and dried under vacuum at 60°C for 6 h. Their Zr content was measured by inductively coupled plasma (ICP) spectroscopy.

Polymerization: For the polymerization of ethylene, 250 cm³ of toluene, 14 cm³ of MAO (1.66 M) and between 200 and 900 mg of supported metallocene were

placed in a 0.5 ℓ glass reactor. Polymerization was normally carried out at 60°C for 30 min at an absolute monomer pressure of 1.6 bar.

Measurements: Supports and supported catalysts were characterized by the following physicochemical methods: the specific surface area and pore volume of silica samples and its catalysts were determined by the BET method using a Sorptomatic 1900 (Fisons Instrument), particle size distribution by laser ray diffraction (Mastersizer X), and Zr content by inductively coupled plasma spectroscopy.

3. Results and discussion

3.1. Catalyst characterization

Three different silicas were studied as supports for catalyst polymerization. It was necessary to carry out a careful study of the variation of some physicochemical properties with calcination temperature, since it is well known that the surface properties of the silicas change with thermal treatment, especially silanol groups, specific areas, etc.

Table 1 shows the characterization of the supports and catalysts produced with metallocenes for three calcination temperatures. As expected, decreasing values were obtained for the specific area of the catalysts as compared to the supports. It can be seen that the area also decreases with increasing calcination temperature both for the silicas and the catalysts, with a higher decrease observed always for ES-70. This can be a result of the disappearance of pores due to sintering. In Aerosil this is not so pronounced since it has no porosity.

3.2. Catalyst activity

In spite of the different ways in which the silicas can

be prepared and of their different structural characteristics, the average values of the hydroxyl group (α -OH) concentration proved to be similar [16]. According to this, for calcination at 500°C for example, α -OH is 1.8 OH/nm², which represents a maximum average theoretical value of 7% Zr in the impregnation, considering that the relation hydroxyl group–metallocene molecule is 1 : 1. Taking this into account, a study was made to correlate the type of support with the amount of Zr incorporated and with the catalytic activity. This correlation is shown in table 2.

For ES-70 and EP-10 the amount of Zr incorporated is not the predominant factor in the catalytic activity. For metallocene supported on Aerosil, however, the activity of the catalyst increased almost two-fold with the percentage of Zr. The nonporous structure of Aerosil is probably highly effective as an anchoring agent for the metallocene molecules because they can be well distributed on the surface and have internal spaces where large amounts of the Zr active centers can be stored during the preparation of the catalyst. On the other hand, ES-70 and EP-10 have pores that may hinder some active sites, making the activity remain constant at higher percentages of Zr.

For nonbridged metallocene catalysts (the last three in table 2), the activity is lower with all of them compared with the bridged one. This confirms the results that have been obtained in homogeneous polymerization studies [17].

3.3. Effect of the calcination temperature on the activity of the catalyst

No reports seem to have been published regarding the influence of the calcination temperature of different supports on the catalytic activity. The results for two catalysts, ES-70 and Aerosil, which are well characterized with respect to their physicochemical properties, are shown in table 3. It can be seen that the activity increases

Table 1
Characterization of supports and catalysts

	Specific area (m ² /g)			Pore volume (cm ³ /g)			Particle size (μ m)		
	500°C ^a	800°C	1000°C	500°C	800°C	1000°C	500°C	800°C	1000°C
<i>Support</i>									
ES-70	250	237	113	1.03	0.21	0.1	41	56	33
EP-10	278	–	–	1.35	–	–	117	–	–
Aerosil	200	183	148	–	–	–	0.012	–	0.014
<i>Catalyst</i>									
ES-70 EtInd ₂ ZrCl ₂	229	172	91	1.45	0.15	0.08	34	39	31
ES-70 Ind ₂ ZrCl ₂	231	–	–	1.39	–	–	45	–	–
EP-10 EtInd ₂ ZrCl ₂	267	–	–	1.63	–	–	100	–	–
EP-10 Ind ₂ ZrCl ₂	253	–	–	1.62	–	–	80	–	–
AER EtInd ₂ ZrCl ₂	150	141	115	–	–	–	–	–	–

^a Calcination temperatures of the supports.

Table 2
Effect of the support and the amount of Zr incorporated in the catalyst on the activity for ethylene polymerization ^a

Type of catalyst	Zr(%) in the catalyst	Productivity (kg-PE/(mol-Zr h))	Activity (kg-PE/(mol-Zr h pressure))
ES-70 EtInd ₂ ZrCl ₂	1.4	64	106
	2.4	65	108
	6.0	72	119
EP-10 EtInd ₂ ZrCl ₂	1.2	65	108
	6.1	64	107
AER EtInd ₂ ZrCl ₂	3.7	67	111
	6.0	122	204
ES-70 Ind ₂ ZrCl ₂	1.5	49	82
EP-10 Ind ₂ ZrCl ₂	1.3	58	96
AER Ind ₂ ZrCl ₂	6.0	118	197

^a Calcination temperature: 500°C; temperature of polymerization reaction: 60°C; time of polymerization reaction: 30 min; pressure of ethylene: 1.6 bar; Al/Zr: 200; zirconium in the reactor: 1.20×10^{-4} mol.

with calcination temperature up to 800°C for both systems. At higher temperatures the activity of ES-70 decreases while that of Aerosil continues increasing. This phenomenon may be due to a sintering process. As the calcination temperature increases, the activity would be expected to increase as a result of the elimination of vicinal silanol groups, meaning that there would be only one OH group per molecule of metallocene to form real active centers.

At temperatures above 800°C the porous support will suffer the greater loss of OH groups that generate active centers for the sintering of the pores. This is confirmed by the amount of Zr incorporated (4.7%). On the other hand, for the nonporous support the amount of Zr is higher (5.8%), leading to higher activity because the OH groups are located on the surface of the support. They are therefore more accessible, first to the metallocene molecules and then to the incoming ethylene molecules for polymerization.

3.4. Morphological aspects

As expected, the morphology of the final polymer formed is a “replica” of the original catalyst and subse-

quently of the support. Figure 1 shows the morphology for a polymer formed on spherical silica (ES-70). Aerosil particles are also spherical, but with a very small particle size, so the polymer formed loses the uniform structure. The results are similar to those obtained when homogeneous metallocene catalysts are used for the polymerization of ethylene.

4. Conclusions

The fixation of a metallocene to a silica support can be controlled up to about 7% zirconium content. For the metallocene supported on Aerosil the catalytic activity depends on the amount of zirconium incorporated in the support.

The nonporous nature of Aerosil allows all the fixed metallocene to act as active centers for ethylene polymerization. For porous supports (ES-70 and EP-10) some of the active sites can be trapped in pores, thereby decreasing their activity.

When treated at high temperatures, the porous supports undergo a greater decrease of OH groups than the nonporous supports, generating fewer active centers.

Table 3
The effect of the calcination temperature of the support on the catalytic activity for ethylene polymerization ^a

Catalyst	Zr(%) in the catalyst			Activity (kg-PE/(mol-Zr h pressure))		
	500°C ^b	800°C	1000°C	500°C ^b	800°C	1000°C
ES70 EtInd ₂ ZrCl ₂	6.0	6.4	4.7	119	180	143
AEREtInd ₂ ZrCl ₂	6.0	6.6	6.2	197	254	319

^a Time of polymerization: 30 min; temperature of polymerization: 60°C; Al/Zr: 200; pressure: 1.6 bar.

^b Calcination temperatures of the supports.

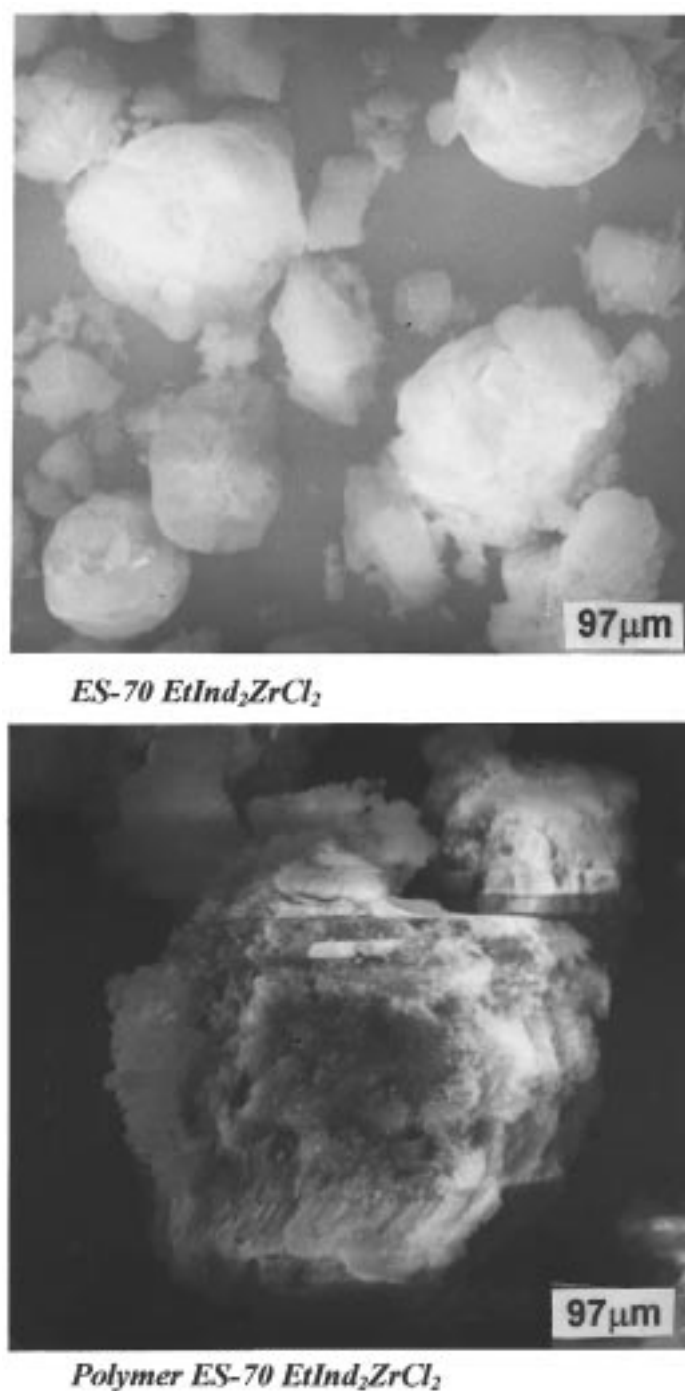


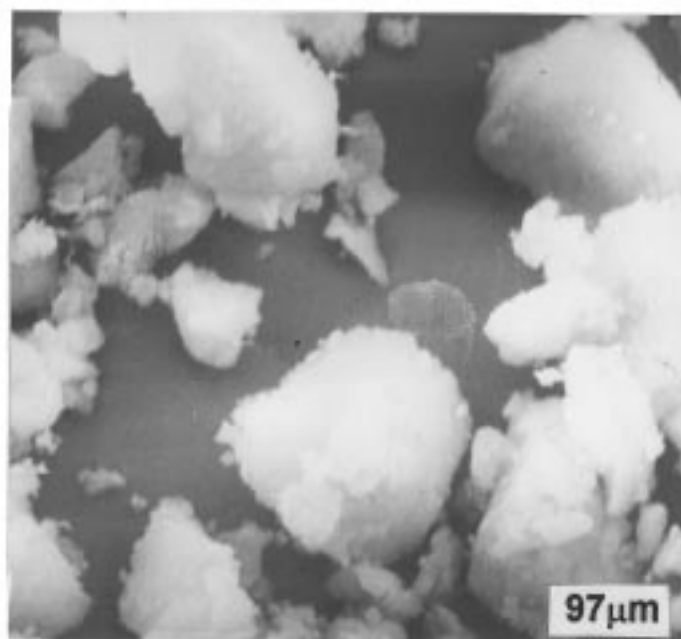
Figure 1. SEM micrographs of catalysts and polymers. (Continued on next page.)

The nonporous supports increased the incorporation of zirconium after heating up to 1000°C.

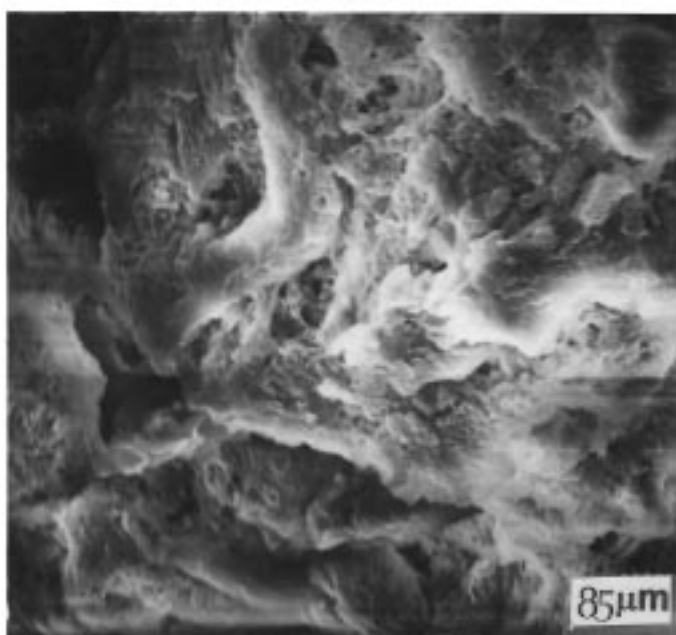
The microstructural characterization of supported catalysts and polymers shows a morphological correlation due to the fact that the active centers are spread over the surface of the support, so polymer chain growth occurs around it. With catalysts supported on nonporous

silica (Aerosil), the particle size is too small compared to the other supports, and the polymer shows a different morphology.

Modifying the surface of the silica changes the availability of active sites on which the polymer chain can grow and opens up new avenues of research of novel catalyst supports.



AER EtInd₂ZrCl₂



Polymer AER EtInd₂ZrCl₂

Figure 1. (Continued.)

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