Supported dichlorobis(3-hydroxi-2-methyl-4-pyrone)Ti(IV) catalysts: Evaluation on ethylene polymerization

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Abstract

Dichlorobis(3-hydroxi-2-methyl-4-pyrone)Ti(IV) complex was grafted on different inorganic supports, namely different kinds of SiO_2, MAO-modified silica, MCM-41, Al_2O_3, ZrO_2 and MgO. The resulting supported catalysts were shown to be active in ethylene polymerization using methylaluminoxane (MAO) as cocatalyst, most of them being even more active that the homogeneous complex. The highest catalyst activities were observed for the Ti complex supported on SiO_2 948 activated at 450 °C, MCM-41 and Al_2O_3.
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1. Introduction

The production of polyolefins in recent years is continuously growing. Polyolefins are indispensable materials with certain social impact in countless beneficial ways. Worldwide production volume of polyolefins has grown to more than 80,000,000 tonnes/year and is predicted to rise continuously at a high rate. Intense research has been carried on olefin polymerization catalysis, in order to develop new catalytic systems capable of producing new materials, as well as developing more economic and versatile processes.

Since the 1980s, metallocene catalysts have become increasingly important for α-olefin polymerization. The metallocene/methylaluminoxane (MAO) system combines high activity with the possibility of tailoring polymer properties [1]. Depending on the metallocene substituent pattern and symmetry, these catalysts permit a strong control of regio- and stereoregularities and of molecular weight distribution of homopolymers, as well as the synthesis of copolymers with a uniform comonomer distribution. The rapid market penetration of metallocene-based polyethylenes (PE) is due to its high-value attributes, such as greater stiffness and impact strength, greater stretch and puncture resistance and improved sealability. Moreover, polymer properties such as temperature resistance, hardness, impact strength, and transparency can be precisely controlled through the metallocene structure [1].

More recently, new generations of non-metallocene catalysts have been proposed in the literature [2]. The aim is to develop new systems (the so-called *post-metallocene catalysts*), which besides not being covered by patents, are capable to afford further improvements in polymer product properties and production flexibility. While metallocene catalysts are very versatile, the new non-metallocene single-site catalysts provide several advantages, among them their chemical synthesis being much more straightforward in many cases than that of the metallocene. New non-metallocene complexes bearing ancillary ligands such as amido, alkoxo, tris(pyrazolyl)borate, diketimine and related polydentate ligands have appeared as a new trend in this field of research [3–7].

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Non-metallocene catalyts based on bidentate alcoxide ligands have been proposed in the literature [8–11]. Relatively simple catalytic systems containing alcoxide ligands based on 3-hydroxi-2-methyl-4-pirona have been reported as active for the ethylene polymerization. Sobota and co-workers have synthesized and evaluated the catalysts of the complex diclorobis(3-hydroxi-2-methyl-4-pirona)Ti(IV) in the ethylene polymerization, having shown that this ligand can be used as a good alternative to the cyclopentadienyl ring [12]. Recently, we have synthesized the complex diclorobis(3-hydroxi-2-methyl-4-pirona)Zr(IV) which, in the presence of methylaluminoxane (MAO) or triisobuthylaluminum (TIBA), showed to be active for the ethylene polymerization, producing polymers with high molecular weight. The complex has also revealed to be active when supported on silica or MAO-modified silica [13].

However, these new polymerization catalysts, whether metallocene or non-metallocene, are soluble systems. A solution polymerization process requires separation of the polymer and removal, recovery and purification of the solvent. A gas phase process is lower in cost and energy consumption in comparison with the solution process. As most of the existing polymerization plants run a slurry- and gas-phase process with heterogeneous catalysts, the homogeneous catalysts must be heterogenized on a support in order to apply those processes. In addition the heterogenization of the polymerization catalysts is necessary to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive swelling of polymers, and to produce polymer particles of a desired regular morphology.

Many routes for the preparation of supported metallocenes have been reported in the literature [14,15]. Silica, chemically-modified or not, is the most employed support. Nevertheless, other supports such as modified montmorillonite [16], diamond black powder [17], sulfated metal oxides [18], MCM-41 (Mobil Composition of Matter) [19] or polymers [20,21] have also been investigated. These procedures afford different catalysts which, in turn, produce polyolefins with different properties.

In the present work we investigated the catalytic activity of the complex diclorobis(3-hidroxi-2-methyl-4-pirona)Ti(IV) grafted on different inorganic carriers, namely SiO_2, MAO-modified silica, MCM-41, MgO, Al_2O_3 and ZrO_2. The choice of these supports is based on the fact that they present different textures (surface area and pore diameter), as well as surface sites bearing different acid/base characteristics.

The resulting systems were evaluated in ethylene polymerization, having methylaluminoxane (MAO) as cocatalyst.

2. Experimental

2.1. General procedures

All the experiments were performed under inert atmosphere using the Schlenk technique. Toluene was dried by usual methods existing on literature and stored under dried argon. The titanium complex was synthesized accordingly to the literature [12].

The supports were activated under vacuum ($P < 10^{-4}$ mbar) for 16 h. The activation temperature for SiO_2 2133 (PQ Corporation, surface area: $350 \, m^2 \, g^{-1}$; pore diameter: 272 Å), SiO_2 956 (Grace, surface area: $350 \, m^2 \, g^{-1}$; pore diameter: 272 Å) and ZrO_2 (Riedel, surface area: $20 \, m^2 \, g^{-1}$) was 110 °C, for SiO_2 948 (Grace, surface area: $255 \, m^2 \, g^{-1}$; pore diameter: 248 Å) was 110° and 450 °C, while MCM-41 (surface area: $1,100 \, m^2 \, g^{-1}$), MgO (Riedel, surface area: $60 \, m^2 \, g^{-1}$) and Al_2O_3 (Inlab, surface area: $110 \, m^2 \, g^{-1}$) the activation temperature was 450 °C. These activated supports were stored under argon atmosphere. MAO-supported silica (SMAO, 23 wt.% Al, Witco) was used without treatment. MCM-41 was synthesized according to the literature [22]. MAO (10.0 wt.% toluene solution) was purchased from Witco.

2.2. Preparation of supported catalysts

The supported catalysts were prepared by the grafting method. In a typical experiment, for instance, an initial toluene solution of the synthesized titanium complex [dichlorobis(3-hidroxy-2-methyl-4-pirone)titanium(IV)] corresponding to 0.5 wt.% Ti/support was added to the pretreated support (1.0 g) and the resulting slurry was stirred for 1 h at 80 °C, and then filtered through a fritted disk. The resulting solids were washed with 15 aliquots ($2.0 \, cm^3$) of toluene and dried under vacuum for 4 h.

2.3. Characterization of supported catalysts

Titanium loadings on different supports were determined by X-ray fluorescence spectroscopy (XRF) using a Rigaku (RIX 3100) wavelength dispersive XRF spectrometer tube operated at 50 kV and 70 mA, bearing a LiF 200 crystal and a scintillation counter. Samples were pressed as homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems.

Specific surface area was determined by the BET method from N_2 adsorption data at 77 K using a Gemini 2375 (Micrometrics). The samples were outgassed at 333 K for 6 h before measuring the nitrogen adsorption.

The catalyst morphology was identified through scanning electron microscopy (SEM), using a JEOL JSM 5800 equipment. The catalysts were fixed on a carbon tape and then coated with gold by conventional sputtering techniques.

2.4. Polymerization reactions

Ethylene homopolymerizations were performed using a $0.3 \, dm^3$ of toluene or hexane in a Pyrex glass reactor connected to a constant temperature circulator, with an internal temperature indicator, equipped with mechanical stirring and inlets for argon and the monomer. MAO was used as co-

catalysts in an Al/Ti = 1000. For each experiment, a mass of catalyst system corresponding to 3×10^{-6} mol of Ti was suspended in toluene and transferred into the reactor under argon. The polymerization reactions were carried out under 1.6 bar of ethylene pressure, at 40 °C for 1 h. Acidified (HCl) ethanol was used to quench the process, and reaction products were separated by filtration, washed with distilled water, and dried under reduced pressure, at room temperature for 48 h.

2.5. Leaching test

A mass of Ti/SiO$_2$ supported catalyst (SiO$_2$ activated at 110 °C) corresponding to 3×10^{-6} mol of Ti was suspended in 0.3 dm^3 of toluene with MAO (Al/Ti = 1000) under argon. The system was stirred for 1 h at 40 °C and then filtered through a fritted disk. The filtered solution was transferred into the reactor under argon. The polymerization reactions were carried out under 1.6 bar of ethylene pressure, at 40 °C for 1 h. Acidified (HCl) ethanol was used to quench the process.

2.6. Polymer characterization

The melting points (T_m) and crystallinities (Xc) of the polymers were determined using a differential scanning calorimeter (Perkin-Elmer, DSC-4), at a heating and cooling rate of 10 °C min^{-1} in the temperature range of 30–160 °C. The heating cycle was performed twice, but only the results of the last scan were considered.

Molar masses were measured with capillary viscometer. The measurements carried out at 135 °C, using decahidronaftalene as solvent. Intrinsic viscosities were calculated by the following equation:

$$[\eta] = \frac{(\eta_{sp}/C)}{\exp(k_M[\eta]C)}$$

where C is the solution concentration (g/dL), $k_M = 0.32$ (Martin equation constant) and η_{sp} is the specific viscosity. The viscosity-average molecular weight can be calculated according to the Kuhn-Mark-Houwink-Sakurada equation:

$$[\eta] = KM_v^{\alpha}$$

where $K = 6.7 \times 10^{-4}$ dL g^{-1} and $\alpha = 0.67$ are the constants for polyethylene on decahidronaftalene at 135 °C [23].

Moreover, molar masses and molar distributions were measured by high temperature gel permeation (GPC) using a 150C Waters instrument, equipped with a differential refractometer and HT Styragel columns (HT3, HT4 or HT6). 1,2,4-trichlorobenzene was used as mobile phase at 140 °C.

Polymeric morphology was measured by SEM as described above for the catalyst characterization.

3. Results and discussion

The [dichlorobis(3-hidroxy-2-methyl-4-pirone)titanium (IV)] complex was grafted on different inorganic supports, bearing different texture properties and surface characteristics. The resulting metal content determined by XRF and surface area for some catalysts are reported in Table 1.

According to Table 1, the grafted content depends on the nature of the support, varying from 0.1 to 0.5 wt.%. For the evaluated silicas, considering that the initial solution concentration was that corresponding to 0.5 wt.% Ti/SiO$_2$, all the metal complex present in solution seems to be immobilized, independently of the surface area (230, 255 and 350 m^2 g^{-1}, for SiO$_2$ 956, SiO$_2$ 948 and SiO$_2$ 2133, respectively). Taking into account, the initial grafting solution presented the complex concentration corresponding to 0.5 wt.% Ti/SiO$_2$, it is very likely that the surface saturation might not be reached for the observed values. Further experiments concerning adsorption isotherm determination should be done in order to verify the maximum catalyst loading available for such supports treated under such conditions. It is worth noting that in the case of SiO$_2$ 948, pre-treated at different temperatures (110 and 450 °C), lower grafted content was observed in the case of treatment at higher temperature. This fact can be attributed to the lower silanol density which is roughly reduced from 5.0 to 1.5 OH nm^{-2}, from 110 to 450 °C [24].

Table 1
Grafted Ti content on different supported catalysts and BET results

Support	Ti/support (wt.%)	Support surface area (m^2/g)	Catalyst surface area (m^2/g)	Support average pore diameter (Å)	Catalyst average pore diameter (Å)
SiO$_2$ 956	0.5	230	193	284	105
SiO$_2$ 2133	0.5	n.d.	n.d.	n.d.	n.d.
SiO$_2$ 948[a]	0.5	n.d.	n.d.	n.d.	n.d.
SiO$_2$ 948[b]	0.4	255	240	248	190
SMAO	0.2	n.d.	n.d.	n.d.	n.d.
MCM-41	0.4	1100	743	27	26
Al$_2$O$_3$	0.1	180	165	74	73
ZrO$_2$	0.5	20	4	100	88
MgO	0.4	n.d.	n.d.	n.d.	n.d.

n.d.: not determinate.
[a] Activated at 110 °C.
[b] Activated at 450 °C.

Comparing the grafted content between systems using bare silica and MAO-modified one, lower metal content was observed in the latter. This fact is contrarily to that which is usually observed in the case of supported metallocenes, in which higher grafted contents were achieved in the case of MAO-modified silicas [25–27].

A leaching test was carried out in order to check if MAO cocatalyst would removed supported catalyst from the support surface to the solution. In the case of silica-supported system, no activity was observed in the supernatant liquid.

In spite of the high surface area of MCM-41 ($1100\,m^2\,g^{-1}$), the incorporated metal content was smaller than those observed in the case of silica treated a $110\,^{\circ}C$. A relatively high metal immobilization was obtained for the supports such as ZrO_2 and MgO, which surface area is very low: 20 and $60\,m^2\,g^{-1}$, respectively. Nevertheless, such supports bear a more basic surface nature, which seems to favor this surface reaction. On the other hand, for Al_2O_3, which bears both acid and basic Lewis center (amphoteric character), the metal loading was much lower [28].

Fig. 1 shows the catalyst activity of the resulting supported catalysts in the polymerization of ethylene. The catalytic systems showed moderate activity, in accordance with observations done on other similar complexes based on ligands bearing alkoxide donors [2]. In general, the activity of supported metallocene catalysts is reduced in comparison to those of homogeneous systems. Many reasons have been attributed to this reduction in activity, such as the generation of only 1.0% of the total grafted content as active species [29] and steric effect of the support surface, which plays the role of a huge ligand. However, according to Fig. 1, the supported non-metallocene complex dichlorobis(3-hidroxy-2-methyl-4-pirone)titanium(IV) showed catalytic activities higher than those observed in the case of homogeneous system for almost all the tested supports. This behavior can be partially explained by the generation of more stable immobilized on support surfaces, probably by keeping them apart from each other, hindering bimolecular deactivation of the catalytic complex.

According to Fig. 1, no direct trend between grafted metal content (Table 1) and catalyst activity (Fig. 1) could be estab-
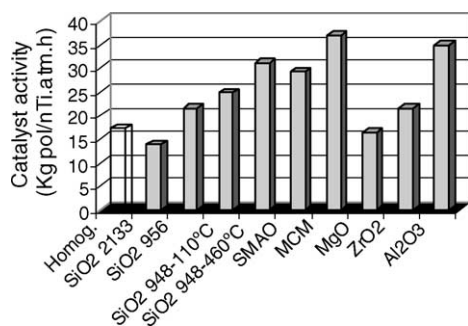
Table 2
Viscosity ($[\eta]$) and viscosity-average molecular weight (M_v) results of polymers obtained with supported catalysts

Support	$[\eta]$ (dL/g)	M_v (g mol^{-1})
–	2.83	257.665
SiO$_2$ 956	3.68	381.421
SiO$_2$ 2133	3.16	304.576
SiO$_2$ 948[a]	1.58	108.026
SMAO	3.68	382.061
MCM-41	1.29	80.752
Al$_2$O$_3$	1.13	65.491
ZrO$_2$	0.89	46.585

[a] Activated at $450\,^{\circ}C$.

lished. The highest catalyst activities were observed for the Ti complex supported on silica 948 activated at $450\,^{\circ}C$, MCM-41 and alumina. Silica 948 and MCM-41 presents higher surface area than the other supports (250 and $1000\,m^2\,g^{-1}$, respectively), which can be contributing to more spaced active catalytic species. An increase in activity in the case of silica 948 treated at $450\,^{\circ}C$ confirms this possibility, since in this case, the lower amount of surface silanol groups, might have generated more spaced catalyst species. High activity was also observed in the case of alumina suggesting that for these systems the presence of acid or basic sites might favor or stabilize somehow the catalyst species. Basic supports such as MgO and ZrO_2 did not afford very active species.

The resulting polymers showed melting temperature (T_m) typical of high-density polyethylene ($130–132\,^{\circ}C$). The polymers obtained with supported catalyst on MgO were not soluble in decahydronafatalene at $135\,^{\circ}C$. For the others the viscosity-average molecular weight (M_v) are shown in Table 2.

Polyethylene with high viscosity-average molecular weight (M_v) were obtained with the supported catalysts on SiO$_2$ 2133, SiO$_2$ 956 and SMAO suggesting a stable nature on the support. The polymers synthesised with supported
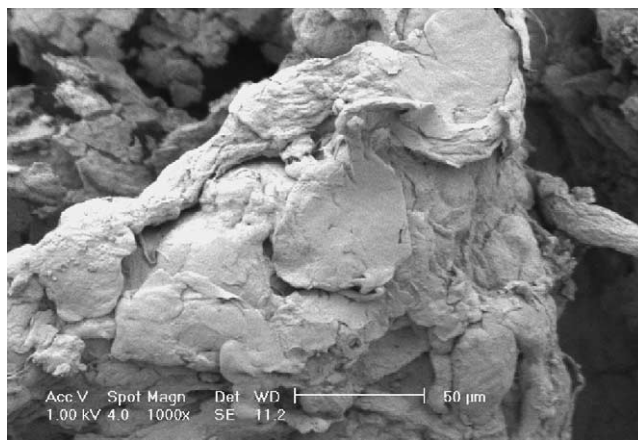

Fig. 1. Catalyst activity of the resulting supported catalysts in ethylene polymerization. [Ti] = 3×10^{-6} mol (toluene); MAO (Al/Ti = 1000); $T = 40\,^{\circ}C$.

Fig. 2. Micrography of PE obtained homogeneous catalyst, using toluene, Al/Ti=1000 (MAO), $T = 40\,^{\circ}C$. Amplification of 1000×.
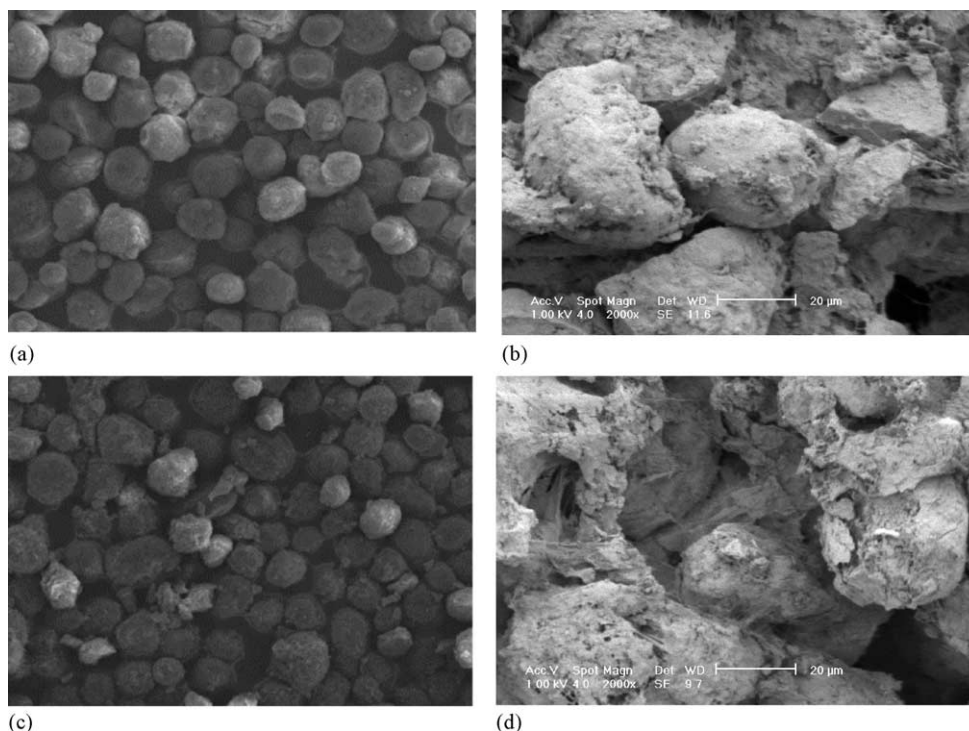
Fig. 3. Micrography of supports and PE obtained with supported catalysts. (a) SiO_2 (200×); (b) PE obtained with supported catalysts grafted on SiO_2 (2000×); (c) SMAO (200×); (d) PE obtained with supported catalysts grafted on SMAO (2000×).

catalysts on MCM, Al_2O_3 and ZrO_2 exhibited lower M_v. Attempts to characterize the polymers were unsuccessful. Most of them were not soluble in 1,2,4 trichlorobenzene at 140 °C. Only the polymers obtained with supported catalyst on SiO_2 2133, SiO_2 948 (activated at 110 °C) and MgO, were able to be characterized by GPC. Those catalysts produced polyethylene with high molecular weight (Mw) and narrow polydispersity (Mw/Mn). The Mw for such systems were 346,000, 344,000 and 224,000 g mol^{-1}, with polydispersity of 3.1, 2.1 and 2.0, respectively. The narrow polydispersity suggest a single site nature on the support.

The morphology of the polymers obtained by both homogeneous and some supported catalysts were examined by SEM. According to Fig. 2, the polymer obtained with homogenous catalyst did not have defined morphology. On the other hand, the polymers made using supported catalysts grafted on SiO_2 and SMAO showed morphology similar to the corresponding supports, indicating that the polymer grain growth around support particle and higher morphology control when compared to polyethylene synthesized with homogeneous catalyst (Fig. 3).

supported catalysts which were active in ethylene polymerization. For different silicas, the grafted titanium content seems to be independent of the surface area and pore diameter. The others systems, MCM-41, MgO and ZrO_2, showed a relatively high metal fixation, whereas for Al_2O_3 the metal loading was lower. These results denote the dependence on the nature of the support for Ti grafted content. Nevertheless, the Ti grafted content is not directly related to catalytic activity.

Comparing the supported catalysts and the homogeneous system, in almost all the tested supports, the former exhibited a higher catalytic activity than the latter. The highest catalyst activities were observed for the catalyst supported on silica 948 activated at 450 °C, MCM-41 and alumina. The supported catalytic systems SiO_2 2133, SiO_2 948 and MgO produced polyethylene with high molecular weight (Mw) and narrow polydispersity (Mw/Mn). The polymers which were made by using supported catalysts grafted on SiO_2 and SMAO showed morphology similar to the corresponding supports, indicating that the polymer replicates the support particle and there is a higher morphology control when compared to polyethylene synthesized with homogeneous catalyst.

4. Conclusions

Grafting [dichlorobis(3-hidroxy-2-methyl-4-pirone)titanium(IV)] complex onto different inorganic supports, bearing different texture properties and surface properties, afforded

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