



Zirconium alkoxide complexes as catalysts for ethylene polymerization

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Abstract

The complexation of 2-hydroxy-1,4-naphtho-quinone and 3-hydroxy-2-methyl-4-pyrone with zirconium tetrachloride yielded complexes containing bidentate alkoxide ligands. In the presence of MAO or TIBA these complexes were found to be active for ethylene polymerization, producing polymers with high molecular weight. Both catalytic systems were also shown to be active when supported on silica or on MAO-modified silica.

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1. Introduction

In despite of almost a half of century has passed since Ziegler revealed that using transition metal salts as catalysts high density polyethylenes could be obtained and Natta demonstrated that the same type of catalysts produced isotactic polymers from α -olefins, efforts are still being done to obtain new active and selective families of olefins polymerization catalysts [1]. Such efforts have resulted mainly in remarkable advances in catalyst systems for olefin polymerization based on metallocenes. With these catalyst systems, polymer properties such as polymer molecular weight, molecular weight distribution, comonomer incorporation and stereochemistry can be controlled by the suitable choice of the coordination sphere around the metal center (see, e.g. [2]). In spite of industrial and academic research having been carried for the development of new metallocenes bearing different ligands and of new polymer properties, much effort has also been done in the uncovering of new olefin polymerization catalysts. Therefore, new non-metallocene complexes bearing ancillary ligands such as amido, alkoxo,

and related polydentate ligands have appeared as a new trend in this field of research (see, e.g. [3]).

Among the new uncovered complexes those bearing terminal oxygen donors have showed activity in α -olefin polymerization. In the case of alkoxide ligands, they ought to have some characteristic to afford active catalysts for olefin polymerization, namely, metal center must be in high oxidation state, mononuclearity and structural rigidity around the metal center. Besides, there must be two reducible unsaturated ligands, one in the *cis* position to the other [4].

Schaverien and co-workers reported a study using various chelating phenoxide complexes of titanium and zirconium, which were active in α -olefin oligomerization and polymerization, butadiene polymerization and terminal acetylene cyclotrimerization in the presence of methylaluminoxane (MAO) as cocatalyst [5]. Ethylene-bridged bis(alkoxide) complexes were also studied in the copolymerization of ethylene with styrene [6,7]. Ethylene and propylene homopolymerization as well as in copolymerization through complexes containing salicylaldehyde derivative as ligands are active in producing high molecular weight polyethylene with broad molecular weight distribution [4]. The activity of new catalytic systems based on acetylacetonate group 4 complexes for the polymerization of propylene has been reported. The titanium complex was found to be active for the polymerization of propylene producing elastomers, whereas

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for the less active zirconium complex highly stereoregular polypropylene was obtained [8]. Recently, Sobota and co-workers reported the synthesis and crystal structure of new titanium complex with 3-hydroxy-2-methyl-4-pyrone as ligand [9]. This complex has been shown to be active catalyst for ethylene polymerization with the appropriate activator.

We have shown that the complex bis(3-hydroxy-2-methyl-4-pyrone)tin(II) is active as a catalyst in polyesterification reaction [10].

In the present paper we report the synthesis and catalytic activity of two zirconium complexes bearing 2-hydroxy-1,4-naphtho-quinone and 3-hydroxy-2-methyl-4-pyrone as ligands. To our knowledge this is the first example of this kind of complexes tested for ethylene polymerization. Both catalysts were also grafted on silica and on MAO-modified silica and evaluated in ethylene polymerization.

2. Experimental

2.1. General procedures

All experiments were performed under argon atmosphere using Schlenk-type glassware. Tetrahydrofuran (THF) and hexane were distilled from sodium and benzophenone. Dichloromethane was dried by refluxing over phosphorus pentoxide and toluene was deoxygenated and dried by standard techniques before use. The ligands, 3-hydroxy-2-methyl-4-pyrone and 2-hydroxy-1,4-naphthoquinone (Aldrich), sodium methoxide (Vetec) and $ZrCl_4$ (Merck) were used without further purification. Grace 948 silica ($255\text{ m}^2\text{ g}^{-1}$) was activated under vacuum ($<10^{-4}$ mbar) for 16 h at 450°C . The support was then cooled at room temperature under dynamic vacuum and stored under dried argon. MAO (Witco, 10.0 wt.% toluene solution, 1.7 Al as trimethylaluminum (TMA) (average molar mass 900 g mol^{-1}), and triisobutylaluminum (TIBA) (9.2% w/v in hexane) were employed as received. Ethylene and argon were deoxygenated and dried through columns of activated molecular sieve (13 \AA) prior to use.

2.2. Synthesis of dichlorobis(2-hydroxy-1,4-naphthoquinone)zirconium(IV) (I)

Sodium methoxide (0.31 g, 5.74 mmol) was added to a solution of 2-hydroxy-1,4-naphthoquinone (1.00 g, 5.75 mmol) using THF (50 ml) as solvent and immediately the yellow light solution became red. This solution was stirred during 20 min at room temperature, and then the solvent was evaporated and a red solid was obtained, which was dissolved in CH_2Cl_2 (50 ml) and cooled to -20°C . It was added dropwise to a stirred, cooled (-20°C) solution of $ZrCl_4$ (0.67 g, 2.89 mmol) in CH_2Cl_2 (80 ml). The deep red mixture was allowed to warm slowly to room temperature and stirred during 18 h. The crude product was dissolved in dichloromethane, filtered and precipitated in hexane as a

red solid. The precipitate was removed by filtration, washed with hexane ($2 \times 20\text{ ml}$) and dried under vacuum during 12 h resulting in a deep red powder (0.59 g, 40%). $^1\text{H NMR}$ (DMSO): δ 7.99–7.56 (m, 4H, aromatics), 7.32 (s, 1H, CH).

2.3. Synthesis of dichlorobis(3-hydroxy-2-methyl-4-pyrone)zirconium(IV) (2)

The ligand 3-hydroxy-2-methyl-4-pyrone (1.00 g, 7.94 mmol) in solution of THF was added dropwise to a stirred solution of $ZrCl_4$ (0.92 g, 3.96 mmol) in THF. The mixture was stirred at room temperature for 30 min, then filtered and washed with diethyl ether ($3 \times 5\text{ ml}$). The product was dissolved in CH_2Cl_2 (10 ml) and it was solubilized with ultra sound during 20 min. After hexane (40 ml) was added to give a white precipitate, which was filtered, washed with hexane ($3 \times 5\text{ ml}$) and dried under vacuum. The yield of complex was 1.33 g (82%). $^1\text{H NMR}$ (DMSO) δ 8.48 (d, Ha, $J_{6,8}\text{ Hz}$), 6.82 (d, Hb $J_{6,8}\text{ Hz}$), 2.35 (s, 6H, CH_3). $^{13}\text{C NMR}$ (DMSO) δ 179.64 (C=O, C_4), 158.09 (C6), 153.36 (C3), 152.19 (C2), 110.24 (C5), 14.78 (CH_3 , C_7); IR (KBr): 1609 ($\nu_{C=C}$), 1557, 1478, 1274 (ν_{C-O}), 1203 (ν_{C-O}) cm^{-1} ; λ_{max} (hexane): 247 nm. Elemental analysis calcd (%) for $C_{12}H_{10}O_6Cl_2Zr$ (412.34): C 34.93%, H 2.43%, found C 34.96%, H 2.92%.

2.4. Complex characterization

The NMR complexes were prepared in $DMSO-d_6$ and recorded on a Varian Inova 300 spectrometer. The IR spectroscopy data was determined on a Michelson Series FT-IR spectrometer using KBr. UV spectra were done in a special cell with inert atmosphere, using hexane as solvent and recorded on a UV-Vis spectrophotometer UV-1601PC Shimadzu. Elemental analysis (C, H and N) was made with a Fisons EA 1108 microanalyzer.

2.5. Preparation of supported catalysts

Supported catalysts were prepared by the grafting method reported elsewhere [11]. In a typical preparation, a 1 or 2 toluene solution (concentration corresponding to 1.5 wt.% Zr/SiO_2) was added to 1.0 g of pretreated silica Grace 948. The slurry was stirred for 1 h at 80°C , then filtered and washed with toluene ($12 \times 2.0\text{ l}$). The resulting solid was dried under vacuum for 4 h.

2.6. Characterization of the supported catalyst

Zirconium loadings in catalysts were determined by RBS using He^+ beams of 2.0 MeV incident on homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems. During analysis the base pressure in the chamber is kept in the 10^{-7} mbar range using membrane (to prevent oil contamination of the sample) and turbodrag molecular pump. The method is based on the determination of the

number and the energy of the detected particles which are elastically scattered in the Coulombic field of the atomic nuclei in the target. In this study, the Zr/Si atomic ratio was determined from the heights of the signals corresponding to each of the elements in the spectra and converted to wt.% Zr/SiO₂. For an introduction to the method and applications of this technique the reader is referred elsewhere [12].

2.7. Polymerization

Ethylene polymerizations were performed in 0.31 of toluene in a 1.01 Pyrex glass reactor connected to a constant temperature circulator, equipped with a mechanical stirrer, and inlets for argon and the monomer. MAO or TIBA were used as cocatalyst in an Al/Zr molar ratio of 2500. For each experiment, 1×10^{-5} mol of Zr catalyst was suspended in toluene or hexane and transferred into the reactor under argon. The polymerizations were performed at 1.6 bar pressure of ethylene at 60 °C for 60 min. The reagents were introduced in the reactor in the following order: solvent, cocatalyst, ethylene and catalyst. Acidified (HCl) ethanol was used to quench the processes, and reaction products were separated by filtration, washed with distilled water, and finally dried under reduced pressure at room temperature.

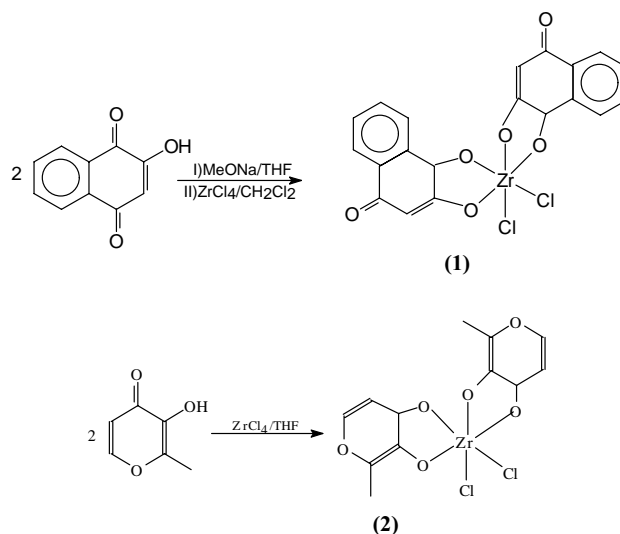
2.8. Polymer characterization

Polymer melting points (T_m) were determined in a Polymer Laboratories differential scanning calorimeter calibrated with Indium, using a heating rate of 10 °C min⁻¹ in the temperature range 30–160 °C. The heating cycle was performed twice, but only the results of the second scan are reported. Molar masses and molar mass distributions were investigated with a Waters high-temperature GPC instrument, CV plus system, Model 150C, equipped with optic differential refractometer and three Styragel HT type columns (HT3, HT4 and HT6) with exclusion limit 1×10^7 for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of 11 min⁻¹. The analyses were performed at 140 °C. The columns were calibrated with standard narrow molar mass distribution polystyrenes and then universally with linear low density polyethylenes and polypropylenes.

The ¹³C NMR spectra were recorded at 120 °C using a Varian 300 spectrometer operating at 75 MHz. Sample solutions of the polymer were prepared in *o*-dichlorobenzene and benzene-*d*₆ (20 v/v). Spectra were taken with a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s.

3. Results and discussion

The tetravalent zirconium complexes **1** and **2** were easily prepared from addition of ligands to ZrCl₄ (Scheme 1). The resulting complexes are thin powders insoluble in most of common organic solvents, which rendered difficult their purification and characterization.



Scheme 1.

In spite of the difficult characterization of dichlorobis(2-hydroxy-1,4-naphthoquinone)zirconium(IV) (**1**), it was possible to observe in the ¹H NMR spectra (see Section 2), the resonance signal related to aromatic protons (7.99–7.56 ppm) and methyne (7.33 ppm) groups. Dichlorobis(3-hydroxy-2-methyl-4-pyrone)zirconium(IV) (**2**) complex was characterized by ¹H, ¹³C NMR, IR, UV spectroscopy and elemental analysis (see Section 2). The elemental analysis of compound **2** indicates that two organic molecules were incorporated per ZrCl₂ fragment. Fig. 1 shows the ¹H NMR spectra of the ligand (a) and the zirconium complex **2** (b). We can observe the disappearance of hydrogen resonance signal of the ligand hydroxyl group at 8.83 ppm (Fig. 1a) in the complex spectrum (Fig. 1b) and a shift in the resonance signs to higher frequencies in relation to free ligand. The protons in the complex are deshielded in comparison with the ligand due to coordination of carbonyl and hydroxyl oxygen to the metal center. ¹³C NMR spectra (Fig. 2a and b) show that resonance signals of carbons attached to oxygen atoms shift to higher field in relation to free organic ligand. This shift also suggests their coordination to metallic center. The IR spectra for complex **2** showed the disappearance of OH bond band and a shift of C=O bond band to lower frequencies when the complexes are formed due to the decrease of double bond character of this group. Fig. 3a and b show UV spectra of the ligand and of the complex **2**. A clear hypsochromic shift of the complex band related to the ligand (from λ_{max} 273 to 247 nm). This effect can be attributed to the decrease of the double bonds conjugation in the complex with respect to the ligand, due to the engagement of the carbonyl group in the coordination to Zr. The results obtained from ¹H, ¹³C NMR, IR, UV spectroscopy and elemental analysis indicate that the coordination occurs by both oxygen, forming a 5-membered chelate ring for compound **2**. The similarity of molecular

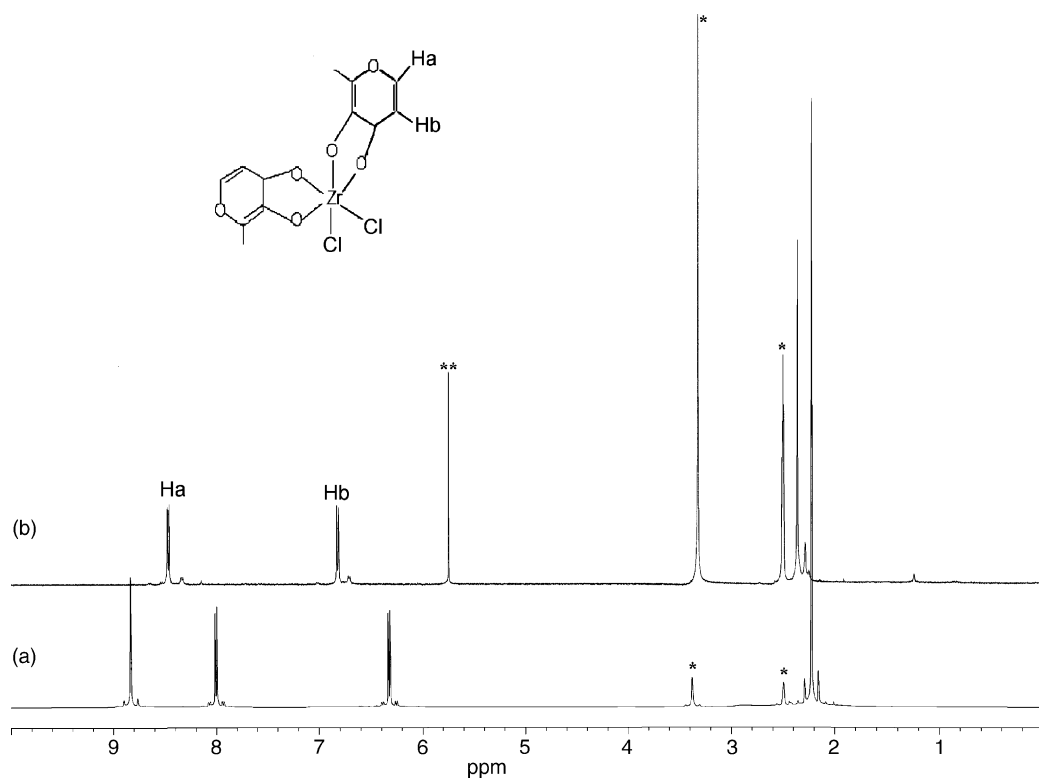


Fig. 1. (a) 3-Hydroxy-2-methyl-4-pyrone ^1H NMR and (b) dichlorobis(3-hydroxy-2-methyl-4-pyrone)zirconium(IV) ^1H NMR. (*) DMSO; (**) CH_2Cl_2 .

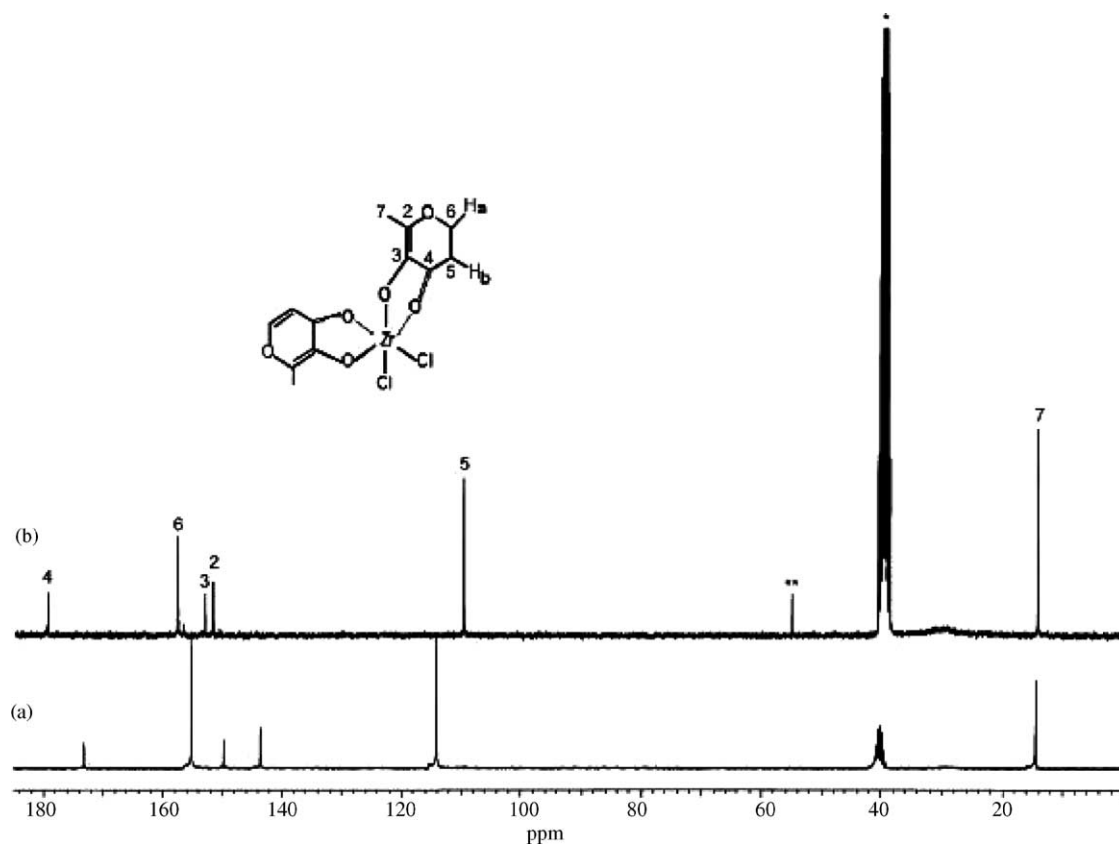


Fig. 2. ^{13}C NMR spectra of (a) 3-hydroxy-2-methyl-4-pyrone and (b) dichlorobis(3-hydroxy-2-methyl-4-pyrone)zirconium(IV). (*) DMSO; (**) CH_2Cl_2 .

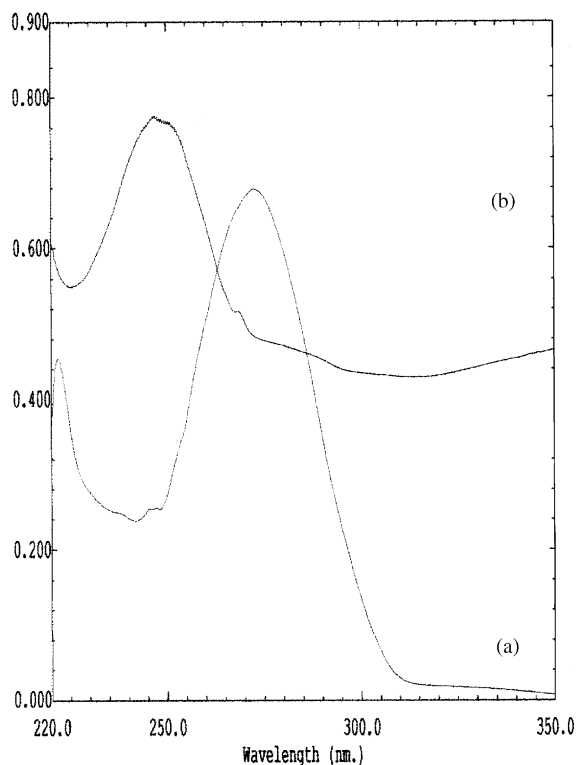


Fig. 3. UV spectra in hexane of (a) 3-hydroxy-2-methyl-4-pyrone, λ_{\max} 273 nm, (b) dichlorobis(3-hydroxy-2-methyl-4-pyrone)zirconium(IV), λ_{\max} 247 nm.

structure of compounds **1** and **2** suggests that complex **1** might also be coordinated by both oxygen.

Catalytic activity of complexes **1** and **2** was evaluated in ethylene homopolymerization. According to Table 1, complex **2** was much more active than **1**. Homopolymerization by catalyst **2** was also performed in hexane, since the catalyst showed a better solubility in this solvent than in toluene. Nevertheless, this condition afforded lower catalytic activities than in toluene. Reactions performed in hexane, using

Table 1
Catalyst activity of **1** and **2**, homogeneous and supported catalysts and properties of the resulting polymers

Catalyst system	Catalytic activity ($\text{kg mol}^{-1} \text{Zr h}^{-1} \text{atm}^{-1}$)	T_m ($^{\circ}\text{C}$)	X_c (%)
1	4.3	132.6	9
1 /SiO ₂	3.2	–	–
1 /MAO/SiO ₂	7.1	135.0/125.3	3
2	180	135.0	41
2 /SiO ₂	16	133.5	10
2 /MAO/SiO ₂	19	128.3	7
2 ^a	35	–	–
2 ^b	40	135.1	18

Polymerization conditions as follows: $T = 60^{\circ}\text{C}$; $[\text{Zr}] = 10^{-5} \text{mol l}^{-1}$; cocatalyst: MAO; Al/Zr = 2500; solvent: toluene; ethylene pressure: 1.6 atm; reaction time: 60 min. X_c : crystallinity.

^a Hexane used as solvent.

^b TIBA used as cocatalyst in hexane.

Table 2
Resulting metal content of the supported catalysts

Catalyst system	Zr/SiO ₂ (wt.%)
1 /SiO ₂	0.45
1 /MAO/SiO ₂	0.54
2 /SiO ₂	0.42
2 /MAO/SiO ₂	0.90

MAO as cocatalyst led to a reduction in activity, in comparison to that performed in toluene. One reason for the reduction in catalyst activity might be attributed to the very low solubility of MAO in aliphatic solvents (ca. 3–4%). Ethylene polymerization with catalyst **2** using TIBA as cocatalyst in hexane showed an increase of catalytic activity compared with the system MAO/hexane, but a decrease with respect to the system MAO/toluene. In the case of TIBA as cocatalysts, the reduction in activity might be attributed to the lower alkylating properties, besides the lower steric effect played by this cocatalyst.

Both complexes were also supported on carriers since the applicability of these polymerization catalysts depends in part of their capability of being supported on inorganic carriers allowing *drop in* technology in the present heterogeneous Ziegler-Natta plants. Table 2 reports the grafted metal content determined by RBS. On silica, both complexes afforded supported catalysts with comparable metal loading. It is worth mentioning that these grafted Zr contents are close to those achieved with some classes of zirconocenes, immobilized under the same experimental conditions [13,14]. Grafting onto MAO-modified silica afforded higher metal loading particularly in the case of **2**/MAO/SiO₂. Similar behavior has already been reported in the literature in the case of zirconocene catalysts supported on SiO₂ and on MAO-modified silica [15].

According to Table 1, comparing homogeneous and supported catalysts, the former exhibit a much higher catalytic activity than the latter. This fact is usually observed with supported catalysts and it has been attributed to the generation of some inactive species during surface reaction and to the steric effect of silica, which plays the role of a huge ligand. Among the resulting supported catalysts, those prepared from **2** were shown to be more active in ethylene polymerization.

Both catalytic systems showed to be active when supported on silica or MAO-modified silica. For system **1** immobilization on silica did not lead to a reduction in catalyst activity. In the case of the MAO-modified silica, we observe an increase in catalytic activity, probably due to the generation of different surface species, which are more stable or active. Similar behavior was already reported in the literature for systems supported on silica and MAO-silica [15].

Table 1 also presents the resulting polymer melting temperature (T_m) and crystallinity (X_c). Polyethylene produced by complex **1** has a low melting point (132.6) and crystallinity (9%) for a linear polyethylene but the product was

too insoluble to be studied by NMR and GPC. Polymer produced by catalyst **1**/SiO₂ does not show a melting point, but ¹³C NMR proved the presence of linear PE. Catalyst **1**/MAO/SiO₂ presented a bimodal DSC curve and very low crystallinity (3%). All the products obtained with catalyst **1** were too insoluble for GPC analysis. This insolubility suggests very high molecular weights or the presence of residual of catalyst system. In effect, this catalyst shows a very high insolubility in mostly all solvents which makes it difficult to be separated from the polymer. It is worth noting that when the catalyst activity was low, the percentage of oxides from silica or MAO and also the presence of insoluble catalyst in the polymer became relatively important in the final product and could make it not completely soluble in GPC solvent.

The homogeneous complex **2** gave high activities of linear polyethylene (signal at 1.25 ppm in ¹H NMR and at 30.0 ppm in ¹³C NMR) with an expected melting point (135 °C) and crystallinity (41%) for this type of product. GPC showed a molecular weight of $M_w = 161,800 \text{ g mol}^{-1}$ and a straight polydispersity (1.9).

Catalyst **2** supported on SiO₂ and on MAO/SiO₂ gave products with lower melting points (133.5 and 128.3 °C) and crystallinities (10 and 7%), respectively, but too insoluble to be either studied by NMR nor GPC.

The polyethylene formed in the presence of MAO in hexane does not show a melting point in the PE region. However, when TIBA was used as cocatalyst, polymer was obtained a product with a high melting point (135.1 °C). This result is very interesting from industrial point of view, taking into account that TIBA is less expensive than MAO. Further studies have been carried out in order to evaluate the effect of some experimental variables on catalytic activity and polymer properties, as well as in α -olefin copolymerization.

4. Conclusions

Zirconium(IV) complexes with bidentate alkoxide ligands are easy to prepare. These complexes were shown to be active in ethylene polymerization, producing polyethylene probably of high molecular weight, taking into account that some of them were not soluble for GPC analysis.

The products that could be studied by NMR showed no branching, but in certain cases melting points and crystallinities were too low for pure linear PE. It is possible that in the cases where catalytic activities were low there exist a considerable amount of residual catalytic system in the final product. Catalyst **2** was active in ethylene polymerization

even when TIBA was used as cocatalyst instead of MAO showing the potentiality of these systems.

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