Polymerization of ethylene by the tris(pyrazolyl)borate titanium(IV) compound immobilized on MAO-modified silicas

Marcelo P. Gil [a], João H. Z. dos Santos [b], Osvaldo L. Casagrande, Jr. [b],*

[a] *Instituto de Química de Araraquara, UNESP C.P. 355, Araraquara, SP 14800-900, Brazil*
[b] *Laboratory of Molecular Catalysis, Instituto de Química, UFRGS, Av. Bento Gonçalves 9500, Porto Alegre, RS 91509-900, Brazil*

Abstract

The immobilization of soluble catalyst $\{Tp^{Ms^*}\}TiCl_3$ ($Tp^{Ms^*}HB(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})^-$) on silica and MAO-modified silicas containing 4.0, 8.0 and 23.0 wt.% Al/SiO_2 yields active supported catalysts for ethylene polymerization. Among the supported catalysts studied by XRF spectroscopy, higher titanium content was obtained using MAO-modified silica containing 8.0 wt.% Al/SiO_2 as support. For the ethylene polymerization reactions carried out in hexane at 60 °C using a combination of triisobutylaluminum (TiBA) and methylaluminoxane (MAO) (1:1), the activities varied between 24.4 and 113.5 kg of PE/mol [Ti] h. The highest activity is reached using MAO-modified silica containing 4.0 wt.% Al/SiO_2 as support. The viscosity-average molecular weights ($\bar{M}_v$) of the PE's produced with the supported catalysts varying from 1.44 to 9.94 × 10^5 g/mol with melting temperatures in the range of 125–140 °C. The use of other Lewis acid cocatalysts, including TiBA, diethylaluminum chloride (DEAC), and trimethylaluminum (TMA) resulted also in the formation of active catalysts for ethylene polymerization. However, the activities are lower than that one using a combination of TiBA and MAO. The viscosity-average molecular weights ($\bar{M}_v$) of PE's are influenced by varying the cocatalysts as well as the Al/Ti molar ratio. The supported catalyst generated in situ under ethylene atmosphere is roughly four times more active than supported one containing 4.0 wt.% Al/SiO_2.
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1. Introduction

The chemistry of the non-metallocene catalysts has grown considerably over the past decade, largely due to the remarkable variety of non-cyclopentadienyl ligands available and their high-performance in olefin polymerization [1]. Many contributions have thus been made concerning this topic, especially using Group 4 metals [2]. Among them, the most part is related to the titanium compounds containing a wide variety of ancillary ligands including those based on tris(pyrazolyl)borate [3]. Tris(pyrazolyl)borate ligands have been widely used in coordination and organometallic chemistry as stabilizing groups in high-oxidation state transition metal complexes considering their strong electron donor ability [4]. In the recent years, we have been interested in exploring the chemistry of Group 4 complexes that contain-ing sterically hindered tris(pyrazolyl)borate ligands aiming at designing novel olefin polymerization catalysts. Our studies have demonstrated that the presence of mesityl substituents at the 3 (5) position of pyrazolyl rings establishes the formation of highly-active catalyst species for ethylene polymerization [5]. For instance, the $\{Tp^{Ms^*}\}TiCl_3$ compound ($Tp^{Ms^*}HB(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})^-$) exhibits activities as high as 9.0×10^3 kg of PE/mol [Ti] h atm with the production of essentially linear polyethylene. However, in spite of these interesting properties, supporting the soluble catalysts on inorganic material are desirable to provide "drop-in" catalysts suitable for the slurry or gas-phase polymerization existing technologies. In this context, several non-metallocene homogeneous catalysts have been immobilized on supports and their performance has been investigated in olefin polymerization [6]. Silica has been used as support due to its high surface area and porosity, good mechanical properties, and stability under processing conditions [7]. Additionally, alternative silica-based supports have been prepared by reaction of

* Corresponding author. Tel.: +55-51-3316-7220;
fax: +55-51-3316-7304.
E-mail address: osvaldo@iq.ufrgs.br (O.L. Casagrande Jr.).

thermally treated silica with methylaluminoxane (MAO) [8].

Herein, we report the preparation of supported catalysts by the immobilization of tris(pyrazolyl)borate titanium complex on silica and on MAO-modified silicas, and their use in slurry ethylene polymerization. The effects of the Al content on the MAO-modified silicas, of the nature of cocatalyst, and of the polymerization temperature on the activity and on polymer properties were evaluated.

2. Experimental

2.1. Materials

All manipulations were carried out under Ar atmosphere using standard Schlenk tube techniques. Toluene and hexane were dried with Na/benzophenone, distilled and stored under argon. $\{Tp^{Ms^*}\}TiCl_3$ (**1**) was prepared according to literature procedures [5a]. Silica Grace 948 ($255\,m^2/g$) was activated under vacuum ($P < 10^{-4}$ mbar) for 16 h at $100\,°C$. The support was then cooled to room temperature under dynamic vacuum and stored under dried argon. The SiO_2/MAO (23 wt.% Al/SiO_2, WITCO) was used as received. Ethylene (White Martins) and argon were deoxygenated and dried through columns of BTS (BASF) and activate molecular sieve (3 Å) prior to use. MAO (Witco, 5.21 wt.% toluene solution), TiBA (Akzo, gently supplied by Ipiranga Petroquímica, 8.0 wt.% hexane solution), DEAC (Aldrich, 1.8 M, 25 wt.% toluene solution) were used as received. TMA was purchase from Witco and a solution was prepared prior to use (4.62 wt.% toluene solution).

2.2. Preparation of SiO₂/MAO (4 and 8 wt.% Al/SiO₂) [8]

MAO-modified silica was prepared by impregnating 1.0 g of thermally treated silica Grace 948 with a MAO toluene solution corresponding to 4 and 8 wt.% Al/SiO_2 at room temperature for 3 h under stirring. The solvent was removed under vacuum and the solid was dried. The resulting solids were named SiO_2/MAO (4%) and SiO_2/MAO (8%), respectively.

2.3. General procedure for preparation of supported catalysts

In a typical supported catalyst procedure $\{Tp^{Ms^*}\}TiCl_3$ (**1**) toluene solution corresponding to 1 wt.% Ti/support was canulla-transferred into silica toluene slurry, at room temperature, during 3 h. The slurry was then filtered through a fritted disk. The resulting solids were washed several times (ca. 5×10 ml) with toluene at $50\,°C$ (until resulting in a colorless eluate), and dried under vacuum for 24 h.

In the case of SiO_2 the mixture was stirred for 5 h, at $50\,°C$, then allowed to cool to room temperature and stirred for 65 h.

2.4. Catalyst characterization

Metal contents on the resulting supported catalysts 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. UV-Vis analysis were performed in a Shimadzu spectrophotometer in the range 400–800 nm wavelength range using an experimental apparatus similar to that described by Coevoet [9].

2.5. Polymerization reactions

Ethylene polymerization experiments were carried out in a 120 ml double-walled glass reactor equipped with magnetic stirring and thermocouple with continuous feed of ethylene at 1.1 atm. Under argon atmosphere were introduced sequentially the proper amounts of hexane or toluene, and cocatalyst solution, and then the system was saturated with ethylene. After complete saturation with ethylene and thermal equilibration of the system, the polymerization reactions were started by adding solution of $\{Tp^{Ms^*}\}TiCl_3$ to the reactor. The total volume of the reaction mixtures was 80 ml for all polymerizations. The polymerization reaction was stopped by the addition of 1 ml of methanol. The polymer was washed with acidic ethanol, then water and ethanol, and dried in a vacuum oven at $60\,°C$ for 12 h. On the basis of the results of multiple runs, we estimate the accuracy of the productivities to $\pm 8\%$.

2.6. Polyethylene characterization

Polymer melting points (T_m) and crystallinities (X_c) were determined on a Thermal Analysis Instruments DSC-2010 calibrated with indium, using a heating rate of $10\,°C/min$ in the temperature range 40–200 °C. The heating cycle was performed twice, but only the results of the second cycle are reported, since the former is influenced by the mechanical and thermal history of the samples. The viscosity-average molecular weight ($\bar{M}_v$) was determined by viscosimetry (intrinsic viscosity $[\eta]$ measured in decaline at $135\,°C$) on a modified Ostwald capillary viscometer, at concentrations of 0.1 dl/g.

3. Results and discussion

3.1. Preparation of the supported catalysts

It is well known that the number of silanol groups on the silica surface depends on the thermal treatment, varying from ca. 5.0 OH nm^{-2} ($110\,°C$) to 1.5 OH nm^{-2} ($450\,°C$) [10–12]. In the present, study silica was preheated at $100\,°C$ since at this thermal treatment temperature its surface bears

Table 1
Titanium content immobilized on silica and MAO-modified silicas

Catalyst	Support	Ti/support (μmol)	Ti/support (wt.%)
S1	SiO_2	109	0.52
S2	SiO_2/MAO (4%)	167	0.80
S3	SiO_2/MAO (8%)	182	0.87
S4	SiO_2/MAO (23%)	101	0.48

a larger number of silanol groups rendering more likely the immobilization of titanium species on the support. Then, the reaction between silica and $\{Tp^{Ms^*}\}TiCl_3$ (**1**) (1 wt.% Ti/support) was initially performed in toluene at 50 °C for 5 h. The resulting metal content on the support was negligible according to the XRF measurements, being inferior to the technique detection limit. Thus, a modified procedure was adopted wherein the toluene solution containing **1** and silica, after being stirred at 50 °C for 5 h, was allowed to cool to room temperature and then further stirred for 65 h. In this case, the analysis of supported catalysts (**S1**) by XRF showed that the titanium content on the silica was 0.52 wt.% Ti/SiO₂ (Table 1).

For metallocene catalysts, studies have revealed that the silica chemically modified with MAO allow to impregnate a higher amount of catalytic species on the surface resulting in a more active supported catalysts in comparison with that using bare silica [13]. Taking into account this fact we decided to immobilize the titanium complex on MAO-modified silicas containing 4.0, 8.0 and 23.0 wt.% Al/SiO₂. The supported catalysts (**S2**–**S4**) were prepared by reaction of $\{Tp^{Ms^*}\}TiCl_3$ (**1**) (1 wt.% Ti/support) with MAO-modified silica in toluene at room temperature for 3 h. Table 1 shows the resulting titanium content determined by XRF expressed in terms of wt.% Ti/SiO₂. The titanium content on the MAO-modified silicas varied from 0.48 to 0.87 wt.% Ti/support, being the highest value attained for the MAO-modified silica containing 8.0 wt.% Al/SiO₂.

Table 1 shows the dependence of the titanium amount on the Al content present on the silica surface. Comparing titanium contents among **S1**–**S3** systems, it was observed that as the Al content increases, from 0.0 to 8.0 wt.% Al/SiO₂, more titanium species are adsorbed on the support suggesting that **1** bound preferably to the MAO present on the surface. According to Table 1, in the case of commercial MAO-modified silica, in spite of bearing higher Al content, lower grafted Ti species was observed. Similar results were reported for grafted $(nBuCp)_2ZrCl_2$ [14], in which lower metal content was observed in the case of MAO-modified commercial silica in comparison to those results noticed for silica modified with lower Al contents.

3.2. Ethylene polymerization using the supported catalysts S1–S4

The ethylene polymerization behavior of the supported catalyst **S1**–**S4** were investigated in hexane at 60 °C using a combination of triisobutylaluminum (TiBA) and MAO (1:1) keeping constant the Al/Ti molar ratio of 300. The results are summarized in Table 2. The supported catalysts **S1**–**S4** displayed activity varying from 24.4 to 113.5 kg of PE/mol [Ti] h. In addition, higher activity was obtained using the supported catalysts **S2** containing 4.0 wt.% Al/SiO₂ (entry 2, 113.5 kg of PE/mol [Ti] h). Catalysts prepared with supports containing more than 4.0 wt.% Al/SiO₂ showed decreasing activity. For instance, the activity found for **S4** which contain 23.0 wt.% Al/SiO₂ is almost five times lower than that found for **S2** (compare entries 2 and 4). Comparing Ti contents for both **S2** and **S3**, the metal content in both systems does not differ very much, while catalytic activities do. It seems that lower Al content on silica surface affords more stable catalytic species. This argument is better visualized correlating the Ti contents and type of supports with the activities as shown in Fig. 1.

Comparing the supported catalysts **S2** and **S3**, it was observed that although the latter shows higher amount of Ti species on the surface, its activity is lower than that displayed by **S2** suggesting in this case that the Ti species might be more uniformly distributed. Experiments with electron probe microanalysis are under investigation.

The lower activity of supported catalyst **S1** compared to those displayed using **S2** and **S3** can be probably attributed to the formation of inactive catalytic species. In this case, we could suggest that the titanium compound **1** reacts with hydroxyl on silica surface to form a stable $Si-\{Tp^{Ms^*}\}Ti(O-Si\equiv)_xCl_y$ compound which is just partially converted to a catalytic species upon reacting with external cocatalyst. Similar results have been reported in the literature, where zirconocenes supported on MAO-modified

Table 2
Ethylene polymerization results using the supported catalysts (**S1**–**S4**)[a]

Entry	Supported catalyst	[Ti] (μmol)	Polymer yield (g)	Activity[b]	T_m (°C)	χ (%)	$[\eta]$ (dl/g)	$\bar{M}_v$ ($\times 10^{-5}$)[c]
1	**S1**	16.0	0.13	24.4	125	15	1.92	1.44
2	**S2**	15.9	0.60	113.5	140	34	6.99	9.94
3	**S3**	15.8	0.40	75.8	139	36	4.71	5.52
4	**S4**	15.4	0.13	24.7	131	27	1.22	0.73

[a] Polymerization conditions: glass reactor (100 ml), hexane = 60 ml, 60 °C, TiBA/MAO (1:1), Al/Ti = 300, polymerization time = 20 min.
[b] kg of PE/mol [Ti] h.
[c] Calculated from the experimental intrinsic viscosities ($[\eta]$, decaline at 135 °C) according to the $[\eta] = k(\bar{M}_v)^\alpha$ with $k = 6.7 \times 10^{-4}$ dl/g and $\alpha = 0.67$.
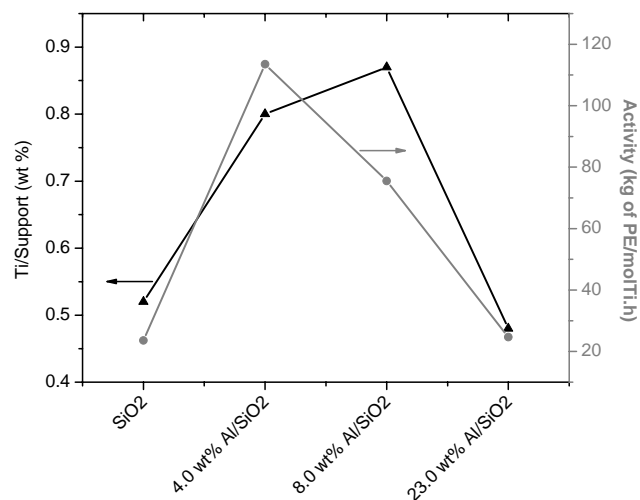
Fig. 1. Correlation between nature of the support, Ti content (wt.%), and catalytic activity in the ethylene polymerization performed at 60 °C, and using TiBA/MAO (1:1) as cocatalysts.

Fig. 2. DSC curves of the polyethylenes obtained with the supported catalysts **S1**–**S4** in hexane at 60 °C using external TiBA/MAO (1:1) as cocatalysts (Al/Ti = 300).

silica afford more active catalyst systems [15]. Besides, Haag et al. observed that catalyst activity loss is more intense as grafted MAO content increased from 2.1 to 8.6 wt.% Al/SiO$_2$ [13].

The polyethylenes (PE's) produced by **S1**–**S4** were found to exhibit melt transitions (T_m's) between 125 and 140 °C (Fig. 2), with crystallinities varying from 15 to 36%. The lowest T_m showed by the PE produced with **S1** is attributed to the dissimilar catalytic species formed on bare silica surface as discussed previously. Increasing the Al content from 4.0 to 8.0 wt.% Al/SiO$_2$ does not change significantly the T_m values as can be visualized in Fig. 2.

The viscosity-average molecular weights ($\bar{M}_v$) of the PE's produced with the supported catalysts are in the range of $1.44–9.94 \times 10^5$ g/mol. The lower ($\bar{M}_v$) obtained for the PE's produced with **S1** and **S4** (entries 1 and 4) is attributed to low catalytic activity of these systems. Furthermore, the influence of the Al content on surface on polymer molecular weight is also verified comparing the ($\bar{M}_v$) values of the PE's
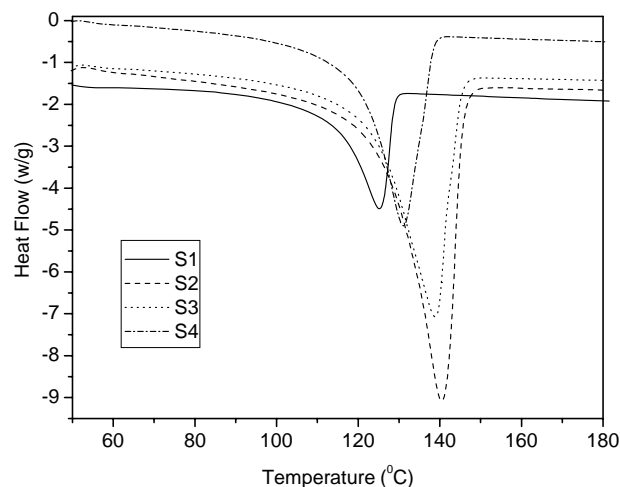
produced with **S2**–**S3**. For instance, the viscosity-average molecular weight drops from $\bar{M}_v = 9.94 \times 10^5$ g/mol when the polymerization reaction was carried out employing **S2** to $\bar{M}_v = 5.52 \times 10^5$ g/mol using **S3**. The decrease of the molecular weight can be rationalized assuming the predominant chain transfer process to AlMe$_3$ (present in MAO solution) as demonstrated in previously polymerization studies involving the catalyst precursor **1** in homogeneous medium [5a].

3.3. Effects of the polymerization condition using the supported catalyst S2

Based on the preliminary ethylene polymerization studies involving the supported catalysts **S1**–**S4**, we decided to carry out some additional studies using **S2** in order to evaluate the influence of some polymerization parameters namely temperature, Al/Ti molar ratio, and nature of cocatalyst on the activity and on the polymer properties. The polymerization results are summarized in Table 3.

Table 3
Effect of conditions on polymerization by supported catalyst **S2**[a]

Entry	Cocatalyst	Al/Ti	T (°C)	[Ti] (μmol)	Polymer yield (g)	Activity[b]	T_m (°C)	χ (%)	[η] (dl/g)	$\bar{M}_v$ ($\times 10^{-5}$)[c]
2	TiBA/MAO	300	60	15.9	0.60	113.5	140	34	6.99	9.94
5	MAO	300	60	16.6	0.40	72.2	139	32	7.25	10.50
6	TiBA	300	60	15.9	0.14	26.4	126	13	3.77	3.96
7	DEAC	300	60	15.6	0.09	17.4	124	8.4	2.04	1.58
8	TMA	300	60	15.8	0.08	15.2	124	6.4	2.87	2.63
9	TiBA/MAO	300	30	18.4	0.55	89.8	139	32	9.23	15.06
10	TiBA/MAO	100	60	15.6	0.20	38.4	128	36	_[d]	_[d]
11	TiBA/MAO	500	60	16.1	0.37	69.0	131	51	4.38	6.75
12	TiBA/MAO	1000	60	16.2	0.18	33.3	128	23	1.75	1.26

[a] Polymerization conditions: glass reactor (100 ml), hexane = 60 ml, polymerization time = 20 min.

[b] kg of PE/mol [Ti] h.

[c] Calculated from the experimental intrinsic viscosities ([η], decaline at 135 °C) according to the [η] = $k(\bar{M}_v)^\alpha$ with $k = 6.7 \times 10^{-4}$ dl/g and $\alpha = 0.67$.

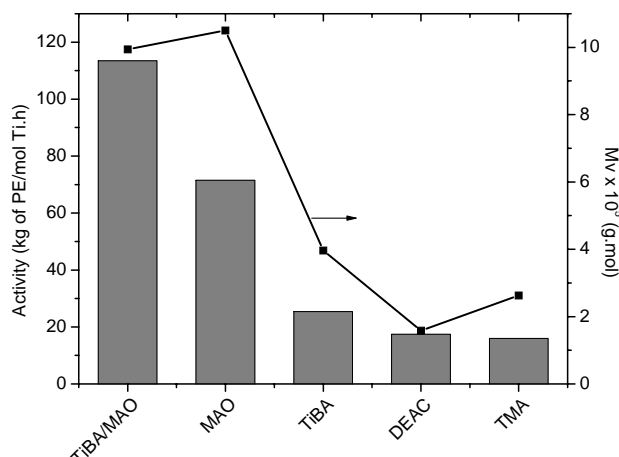[d] PE sample insoluble in decaline at 135 °C.

Fig. 3. Dependence of the activity and of the viscosity-average molecular weight on the type of cocatalysts in the ethylene polymerization using supported catalysts **S2** in hexane at 60 °C using Al/Ti = 300.

Varying the cocatalyst to a constant Al/Ti molar ratio of 300, higher activity was reached using a combination of TiBA/MAO (1:1) (entry 2, 113.5 kg of PE/mol [Ti] h,). The use of other Lewis acid cocatalysts, including tri-isobutylaluminum, diethylaluminum chloride (DEAC), and trimethylaluminum (TMA) resulted also in active ethylene polymerization catalysts. However, their activities were lower than those achieved using MAO or TiBA/MAO (Fig. 3). For instance, the polymerization reaction using MAO showed activity of 72.2 kg of PE/mol [Ti] h while that employing TMA was only 15.2 kg of PE/mol [Ti] h. In the polymerization reaction carried out in the absence of external cocatalyst no production of polyethylene was observed indicating that the MAO present on the silica surface is not enough to generate, stabilizes, and alkylate the surface species.

The molecular weight of the polymers are strongly influenced by the type of cocatalyst employed in the polymerization reaction as can be better visualized in Fig. 3. Assuming that the predominant chain-transfer process for $\{Tp^{Ms^*}\}TiCl_3$ is related to chain transfer to aluminum, [5a] the wide range of the viscosity-average molecular weights ($\bar{M}_v$) found for the PE's are directly associated to the capacity of the cocatalyst acts as transfer agent. In this context, lower viscosity-average molecular weights were obtained by using TMA and DEAC cocatalysts (entries 7 and 8) while polyethylenes with higher viscosity-average molecular weights were found in the presence of MAO. For instance, the viscosity-average molecular weight of the PE drops from $\bar{M}_v = 10.50 \times 10^5$ g/mol when the polymerization reaction was performed using MAO to $\bar{M}_v = 1.58 \times 10^5$ g/mol employing DEAC as cocatalyst.

The activity of the **S2**/TiBA/MAO system is dependent on the Al/Ti molar ratio. Polymerization runs varying the Al/Ti ratio from 300:1 to 1000:1 revealed that the system is active at an Al/Ti ratio as low as 100:1 (38.4 kg of PE/mol [Ti] h). Maximum activity was attained using Al/Ti molar ratio of

300:1 (113.5 kg of PE/mol [Ti] h). Increasing the aluminum concentration (500 and 1000:1) resulted in lower activities. For instance, the polymerization reaction using an Al/Ti ratio of 1000:1 displayed an activity of 33.3 kg of PE/mol [Ti] h (entry 12). This effect is probably due to the coordination of $AlMe_3$, present in the MAO, to the active species disfavoring monomer coordination [16].

3.4. UV-Vis spectroscopic study of the $\{Tp^{Ms^*}\}TiCl_3/MAO$

The UV-Vis spectroscopy has become an important tool for olefin polymerization catalysts considering the useful informations that this technique provides on the metal complex electronic structure [9,16,17]. Furthermore, this spectroscopic method was found to be very effective for the observation of the successive elementary steps yielding cationic active species produced during the polymerization reaction. In this context, and objecting to get some insight into the stability of the catalytic species originated from reaction of $\{Tp^{Ms^*}\}TiCl_3$ with MAO we have performed an UV-Vis spectroscopic study in toluene at 25 °C.

As shown in Fig. 4, the absorption spectrum of the $\{Tp^{Ms^*}\}TiCl_3$ recorded under argon atmosphere does not show any characteristic UV-Vis absorption maximum between 400 and 800 nm. Addition of MAO (Al/Ti = 300) to the toluene solution of the Ti complex results immediately in the appearance of a low intensity peak (solid line) suggesting that a decomposition process of the titanium compound took place. On the other hand, if the interaction between $\{Tp^{Ms^*}\}TiCl_3$ and MAO is performed under ethylene atmosphere it is observed the formation of one new absorption band (dot line) centered at 465 nm which can be attributed to the structural and electronic modifications on the titanium compound after reaction with MAO in accord to the data observed in the case of zirconocenes [9]. The same profile curve (dash dot line) obtained using hexene-1
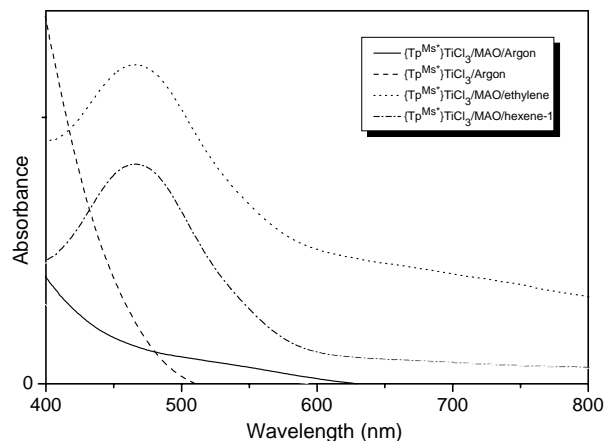

Fig. 4. UV-Vis absorption spectra of $\{Tp^{Ms^*}\}TiCl_3$ and $\{Tp^{Ms^*}\}TiCl_3/$ MAO catalytic system in toluene at 25 °C. ([Ti] = 5 μmol; Al/Ti = 300; [Hex] = 0.38 M).

Table 4
Ethylene polymerization results over in situ supported catalyst[a]

Entry	Solvent	Cocatalyst	[Ti] (μmol)	Polymer yield (g)	Activity[b]	T_m (°C)	χ (%)	$[\eta]$ (dl/g)	$\bar{M}_v$ ($\times 10^{-5}$)[c]
13	Hexane	TiBA/MAO	3.3	0.43	388.5	134	40	2.51	2.16
14	Toluene	MAO	3.5	0.50	433.5	137	35	7.77	11.65

[a] Polymerization conditions: glass reactor (100 ml), 0.1% of Ti on MAO-modified silica (4.0 wt.% Al/SiO$_2$), solvent = 60 ml, 60 °C, Al/Ti = 300, polymerization time = 20 min.
[b] kg of PE/mol [Ti] h.
[c] Calculated from the experimental intrinsic viscosities ($[\eta]$, decaline at 135 °C) according to the $[\eta] = k(\bar{M}_v)^{\alpha}$ with $k = 6.7 \times 10^{-4}$ dl/g and $\alpha = 0.67$.

instead of ethylene in the experiment carried out under argon atmosphere suggest for both case the formation of the same catalytic species.

3.5. Ethylene polymerization employing in situ supported catalyst

Considering the instability of the catalytic species formed by interaction {Tp$^{Ms^*}$}TiCl$_3$ and MAO in the absence of monomer, we decided to perform some polymerization reactions using supported catalyst generated in situ by reacting directly in the reactor {Tp$^{Ms^*}$}TiCl$_3$ with MAO-modified silica containing 4.0 wt.% Al/SiO$_2$ under ethylene atmosphere, similarly to the methodology introduced by Soares et al. [18]. Thus, to a Pyrex glass reactor thermally equilibrated at 60 °C containing 50 ml of hexane or toluene were introduced under ethylene atmosphere the proper amounts of MAO-modified silica and toluene solution of {Tp$^{Ms^*}$}TiCl$_3$ corresponding to 0.1 wt.% Ti/support. The slurry suspension was stirred for 20 min and then the polymerization reaction was started by the addition of external cocatalyst. The polymerization results are presented in Table 4.

The polymerization reactions using in situ supported catalyst carried out in hexane or toluene exhibited similar activities of 388.5 and 433.5 kg of PE/mol [Ti] h, respectively. These values are almost four times higher than that displayed using the supported catalyst **S2** (113.5 kg of PE/mol [Ti] h, entry 2). These data are in accord with the UV-Vis spectroscopy results suggesting that the most part of the titanium species are deactivated during the grafting process after reaction with MAO.

The difference found for the polymer molecular weight regarding the entries 13 and 14, it is explained by the presence of TiBA in the reaction for the entry 13, which acts in addition to TMA present in the MAO, as agent of chain transfer, resulting in a lower polymer molecular weight.

4. Conclusion

The grafting of soluble-catalyst {Tp$^{Ms^*}$}TiCl$_3$ (**1**) on silica and MAO-modified silicas afforded supported catalysts which are active for ethylene polymerization. The titanium content on the support increases as the Al content increases

up to 8.0 wt.% Al/SiO$_2$ suggesting that **1** preferably binds to the MAO present on the surface. The ethylene polymerization activities of the supported catalysts **S1**–**S3** are influenced by Al content on the support. The lower activity of **S1** compared to those displayed by **S2**–**S3** suggest the formation of more stable titanium species generated by reaction of **1** with hydroxyl groups on silica. Taking into account the similar Ti content for both **S2** and **S3**, the higher activity showed by **S2** can be attributed to the formation of more stable catalytic species. Considering the predominant chain-transfer process to aluminum, the viscosity-average molecular weights ($\bar{M}_v$) of the PE's are strongly influenced by the Al content on the surface as well as the nature of cocatalyst. Lower $\bar{M}_v$ can be achieved using either high Al/Ti molar ratio or DEAC as cocatalyst. Higher activities obtained with the supported catalyst generated in situ under ethylene atmosphere are in agreement to the UV-Vis spectroscopic studies where it has been verified that catalytic species formed from the reaction of titanium compound with alkylaluminum are not stable under argon atmosphere. Further investigations into the reactivity of the supported catalyst generated in situ under ethylene atmosphere will be the subject of a future report.

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