Tris(pyrazolyl)borate imido vanadium (V) compound immobilized on inorganic supports and its use in ethylene polymerization

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Abstract

Tris(pyrazolyl)borate imido vanadium (V) was immobilized onto a series of inorganic supports: SiO_2, MAO-modified SiO_2 (4.5 and 23 wt.% Al/SiO_2), SiO_2–Al_2O_3, $MgCl_2$, MCM-41 and MgO. Immobilized metal content determined by XRF remained between 0.045 and 0.098 mmol V/g support. The highest metal content were observed in the case of supports bearing large surface area (SiO_2–Al_2O_3 and MCM-41). All the systems were shown to be active in ethylene polymerization in the presence of MAO or TiBA/MAO mixture (Al/V = 1000). Catalyst activity was shown to depend on the support nature, being between 8.1 and 88.0 kg PE/(mol V h). Best results were observed in the case of silica as support. Acid or basic supports afforded less active systems. In situ immobilization led to higher catalyst activity, even in the presence of common alkylaluminum co-catalyst (TiBA). Resulting polyethylenes showed M_w higher than 2.7×10^6 Da, suggesting the production of ultra-high molecular weight polymers.
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Keywords: Tris(pyrazolyl)borate imido vanadium; Supported catalysts; Polyethylene; UHMWPE

1. Introduction

Early transition metal compounds bearing a wide variety of ancillary ligands have been successfully used in the polymerization of ethylene and α-olefins over the past decade [1]. Although the most part of theses studies are focused on Group 4 metals, significant advances have been done in the synthesis of "well-defined" olefin polymerization catalysts containing Group 5 metals, and in special those based on high-valent vanadium species [2]. In the last years, we have been interested in exploring the chemistry of Groups 4 and 5 complexes bearing sterically hindered tris(pyrazolyl)borate ligands aiming at developing novel olefin polymerization catalysts [3]. In the specific case of vanadium (V) catalysts, our studies have demonstrated that compounds of general formula $\{Tp'\}V(NR)Cl_2$ (R: ^tBu, 2,6-$^iPr_2$-C_6H_3; Tp': HB (3-mesityl-pyrazolyl)$_2$(5-mesityl-pyrazolyl)$^-$ (Tp^{Ms*}), HB(3-mesityl-pyrazolyl)$_3^-$ (Tp^{Ms})) exhibit high catalyst activity for ethylene polymerization in the presence of

MAO or TiBA/MAO [4]. However, despite of the high activities, taking into account that most of the existing polymerization plants run slurry- or gas-phase processes with heterogeneous catalysts, such homogeneous ones must be heterogeneized by grafting on a support for the application in those processes. Furthermore, the heterogeneization of catalysts is necessary to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive polymer swelling, and to produce polymer particles of a desired regular morphology. Therefore, the immobilization of a soluble vanadium (V) catalyst on support seems to be extremely important in order to overcome some problems such as the loss of catalytic performance and reduction of molecular weight at high polymerization temperatures.

Several routes, employing different supports and grafting protocols, are described in the scientific and patent literature for the heterogeneization of metallocenes [5]. The nature of the surface species, as well as its activity, depends on the nature of the support and on its textural properties.

In the present paper, we report the immobilization of $\{Tp^{Ms*}\}V(N^tBu)Cl_2$ (**I**) on different inorganic supports namely SiO_2/MAO (23 wt.% Al/SiO_2), SiO_2/MAO (4.5 wt.% Al/SiO_2), SiO_2, SiO_2–Al_2O_3, $MgCl_2$, MCM-41

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and MgO and their use in the polymerization of ethylene using methylaluminoxane (MAO) and/or triisobutylaluminum (TiBA) as activators. The effect of nature of the support on the V grafted content, on catalyst activity in ethylene polymerization and on the polymer properties is discussed.

Ms = 2,4,6-trimethylphenyl

Structure **I**
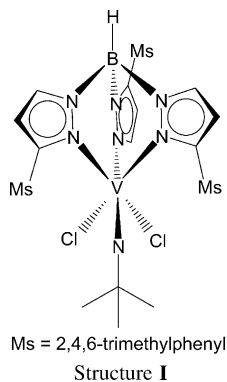
2. Experimental

2.1. Materials

All manipulations were carried out under Ar atmosphere using standard Schlenk techniques. Toluene and hexane were dried with Na/benzophenone, distilled and stored under argon. $\{Tp^{Ms*}\}V(N^tBu)Cl_2$ (**1**) compound was prepared according to literature procedure [4]. Silica Grace 948 ($255 m^2/g$), SiO_2–Al_2O_3 ($600 m^2/g$), MgO ($60 m^2/g$) and MCM-41 ($1027 m^2/g$) were activated under vacuum ($P < 10^{-4} mbar$) for 16 h at 100 °C. The supports were then cooled to room temperature under dynamic vacuum and stored under dried argon. MCM-41 was synthesized according to the literature [6]. The SiO_2/MAO (23.0 wt.% Al/SiO_2, Witco) and $MgCl_2$ (Tosoh) were 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 (5.21 wt.% toluene solution), and TiBA (Akzo, supplied by Ipiranga Petroquímica, 8.0 wt.% hexane solution) were used as received.

2.2. Preparation of SiO_2/MAO (4.5 wt.% Al/SiO_2)

MAO-modified silica was prepared by impregnating 1.0 g of thermally treated silica Grace 948 with a MAO toluene solution (0.9 ml, solution in toluene 5.1 wt.%) at room temperature for 3 h under stirring. The solvent was removed under vacuum and the solid was dried.

2.3. General procedure for preparation of supported catalysts

In a typical support catalyst procedure, $\{Tp^{Ms*}\}V(N^tBu)$ Cl_2 (**1**) toluene solution corresponding to 0.5 wt.% V/support was canulla-transferred at 50 °C onto inorganic support

(1.0 g) toluene slurry. After 4 h the mixture was allowed to cool to room temperature and stirred for 20 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), then with hexane, and finally dried under vacuum for 24 h. In the case of SiO_2/MAO (23.0 wt.% Al/SiO_2) the employed vanadium amounts were 0.05 and 0.5 wt.% V/SiO_2.

2.4. Catalyst characterization

2.4.1. X-Ray fluorescence spectroscopy (XRF)

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.

2.4.2. Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA)

SEM and EPMA experiments were carried on a JEOL JXA-8900L WD/ED combined microanalyzer. The catalysts were initially fixed on a carbon tape and then coated with carbon by conventional sputtering techniques. The employed accelerating voltage was 20 kV and current ca. $3 × 10^{-8}$ A for EPMA and ca. $1 × 10^{-10}$ A for SEM.

2.5. Polymerization reactions

Ethylene homopolymerizations were performed in 350 ml of hexane in a 1L Pyrex glass reactor connected to a constant temperature circulator and equipped with mechanical stirrer and inlets for argon and the monomer. MAO or MAO/TiBA were used as cocatalyst in an Al/V = 1000. For each experiment, a mass of catalyst system corresponding to 10^{-5} mol/l of V was suspended in 10 ml of hexane and transferred into the reactor under argon. The polymerizations were performed at atmospheric pressure of ethylene at 30 °C temperature for 1 h. Acidified (HCl) ethanol was used to quench the process, and the reaction products were separated by filtration, washed with distilled water, and finally dried under reduced pressure at 60 °C.

In some cases, polymerization reactions were carried out in a 100 ml glass reactor connected to a constant temperature circulator and equipped with magnetic stirrer. The procedure used for these polymerization reactions was the same as described above.

2.6. Polyethylene characterization

Polymer melting temperatures (T_m) were determined on a thermal analysis instruments DSC-2010 calibrated with indium, using a heating rate of 10 °C/min in the temperature range of 40–180 °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. For GPC analysis, 2 mg of polyethylene was dissolved in 4 ml of 1,2,4-trichlorobenzene (TCB) in the oven at 180 °C for 1 h. Molar masses and molar mass distributions were investigated with a Waters GPCV 2000 high-temperature GPC instrument, equipped with viscometrical detector and four columns (107, 107, 106E, 140). TCB was used as solvent at a flow rate of 1 ml/min. The analyses were performed at 140 °C. The columns were calibrated with standard narrow molar mass distribution polystyrenes and with linear low density polyethylenes and polypropylenes.

3. Results and discussion

As long as we know, supported $Tp^{Ms*}V(N^{t}Bu)Cl_2$ (**1**) catalysts have not been developed. In an exploratory research, this complex was grafted onto a series of inorganic supports varying the surface area and the nature of immobilization sites (acid and basic supports). Studies concerning the immobilization of the compound $Tp^{Ms*}V(N^{t}Bu)Cl_2$ (**1**) onto different inorganic supports aims at determining the best supports for the development of a supported catalyst for ethylene polymerization. Thus, compound **1** was immobilized onto a series of inorganic supports, namely SiO_2, MAO-modified SiO_2, SiO_2–Al_2O_3, MCM-41, MgO and $MgCl_2$. The resulting grafted systems were evaluated in terms of V grafted content and of catalyst activity in ethylene homopolymerization. The V content on the inorganic supports remained between 0.054 and 0.098 mmol V/g support, being dependent of the nature of the support (Table 1).

Table 1
Resulting V content in the supported catalysts

Support	mmol V/g support	V/support (wt.%)
SiO_2	0.054	0.28
SiO_2/MAO (4.5 wt.%)	0.081	0.41
SiO_2/MAO (23.0 wt.%)	0.074	0.28
SiO_2–Al_2O_3	0.098	0.50
MgO	0.045	0.22
MCM-41	0.097	0.47

The surface of silica consists of a layer of silanol groups (Si–OH) and physically adsorbed water. Most of the water is removed upon drying at 100–110 °C range, generating a totally (110 °C) or partially hydroxylated silica (above 110 °C) [7]. The number of silanol groups depends on the thermal treatment, varying from ca. 5.0 OH nm^{-2} (110 °C) to 1.5 OH nm^{-2} (450 °C) [8]. Grafting surface reaction takes place by elimination of one or more of the original organometallic ligands (such as halide or alkoxides, for instance) in a 1:1 ratio with hydrogen atom from silanol groups on the support. In the present study, silica was treated at 100 °C, since at this thermal treatment temperature, its surface bears a larger number of silanol groups. Thus, such surface is more prone to react to bulky V derivatives. Similar reactions take place when MAO is reacted with thermally pretreated silica, evolving methane. In the case of MAO-modified silica bearing 4.5 wt.% Al/SiO_2, there are still available silanol groups, since silica saturation level for MAO is around 8–10 wt.% Al/SiO_2 [9]. Therefore, in this case, the immobilization can take place both on silanol and on MAO groups (Scheme 1). On the other hand, in the case of the commercial silica (23.0 wt.% Al/SiO_2), the only available fixation sites are

Ms = 2,4,6-trimethylphenyl

L = tert-butyl imido
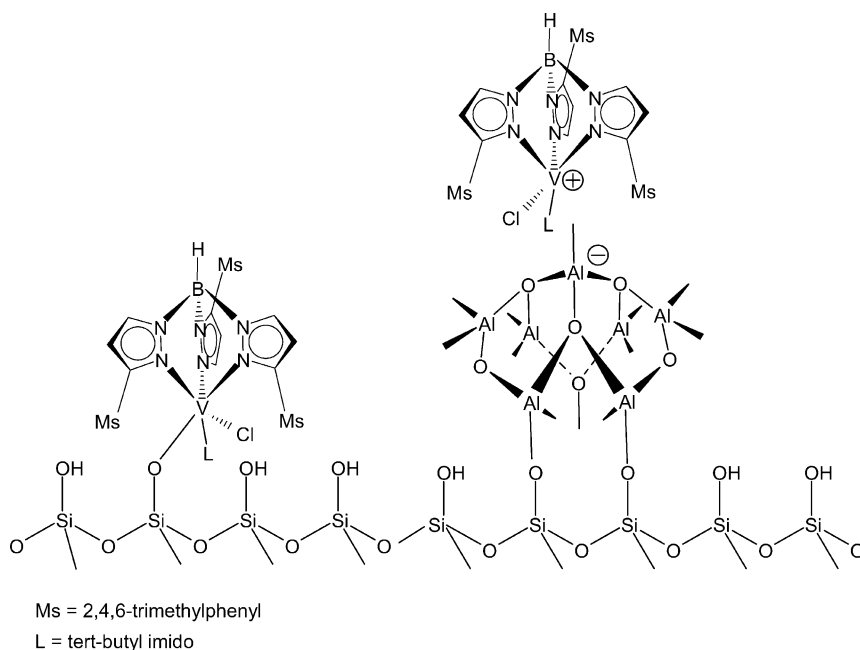
Scheme 1.

those from MAO, because in this case there are not available silanol groups [10].

The immobilization of **1** on SiO_2 and on MAO-modified silicas containing these two Al amounts aimed at verifying the influence of MAO content on the immobilized vanadium content, on the catalyst activity and on the characteristics of the resulting polyethylenes. The analysis by XRF showed that the grafted amount of compound **1** on the MAO-modified silicas (4.5 and 23.0 wt.% Al/SiO_2) is higher than that obtained using bare SiO_2 as support, suggesting that the vanadium compound is more prone to react on MAO immobilized groups. Similar behavior has been reported in the case of supported zirconocene catalysts [11]. It is worth noting that the V contents in SiO_2 and SiO_2/MAO (4.5 wt.% Al/SiO_2) supports are not exactly comparable to commercial SiO_2/MAO (23.0 wt.% Al/SiO_2) (0.074 mmol V/SiO_2) since the preparation method, textural properties and the nature of the surface species might be different. In a previous study [9], we determined BET surface area and average power diameter of silica Grace 948. None of these values changed after Cp_2ZrCl_2 grafting, suggesting the zirconocene immobilization did not block the pores. Taking into account that compound **1** presents a much higher steric hindrance, it is very likely that the grafting reaction might have taken place at the uttermost external surface.

The surface of $SiO_2–Al_2O_3$ is characterized by strong Brönsted and Lewis acid sites. The former are constituted of hydroxyl groups bound in bridge between an aluminum atom and a silicon atom. The Lewis acid sites correspond to three-coordinated aluminum atoms formed by dehydration along the thermal treatment [12]. Comparing this support to the other ones, $SiO_2–Al_2O_3$ afforded the highest vanadium content (0.098 mmol V/SiO_2). This value might be in part attributed to the fact that this support presents one of the highest specific area (ca. 600 m^2/g) when compared to the other ones.

MCM-41 is a mesoporous (2–50 nm) solid and shows a regularly ordered pore arrangement and a very narrow pore-size distribution. This is an aluminosilicate material and the incorporation of aluminum into silica structures is known to form acid sites in the framework. However, independent of the aluminum content in the framework, MCM-41 materials show only weak acidity [13]. This support, as well as the $SiO_2–Al_2O_3$, afforded high V content when compared to the other ones. As mentioned above, this behavior can be partially explained in terms of its high specific area (1027 m^2/g).

In case of MgO, the Mg^{2+} and O^{2-} ions are five-fold coordinated. This surface is neutral, and there is no need to postulate the presence of additional ions to account for the necessary charge balance. Nonetheless, protons are usually present in surface –OH groups, observed by infrared spectroscopy and formed by dissociative adsorption of water. The O^{2-} ions and –OH groups on the MgO surface are basic, and the chemistry of the surface of MgO is dominated by its basicity [14]. This support showed lower vanadium contents, partially due to its low specific area.

Table 2
Catalyst activity of the resulting supported systems and PE melting temperature of Pe[a]

Entry	Catalyst	Cocatalyst	Activity (kg PE/(mol V h))	T_m (°C)
1	**1**/SiO_2	MAO	73.8	137
2	**1**/SiO_2/MAO (4.5 wt.%)	MAO	26.2	136
3	**1**/MCM-41	MAO	17.4	138
4	**1**/SiO_2/MAO (23.0 wt.%)	MAO	13.6	138
5	**1**/$SiO_2–Al_2O_3$	MAO	10.2	139
6	**1**/MgO	MAO	8.1	139
7	**1**/SiO_2	TiBA/MAO	88.8	140
8	**1**/SiO_2/MAO (4.5 wt.%)	TiBA/MAO	21.2	132
9	**1**/MCM-41	TiBA/MAO	27.0	76 137
10	**1**/SiO_2/MAO (23.0 wt.%)	TiBA/MAO	25.3	139
11	**1**/$SiO_2–Al_2O_3$	TiBA/MAO	11.4	136
12	**1**/MgO	TiBA/MAO	9.8	139
13	**1** (homogeneous)	MAO	922.4	139

[a] Polymerization conditions: glass reactor (1 l); hexane (350 ml); $P = 1$ atm; reaction time: 1 h; $T = 30$ °C; Al/V = 1000; TiBA/MAO: 1:1.

It is worth mentioning that the results concerning vanadium content in $MgCl_2$ support demonstrated that the amount of catalytic precursor present in this surface is negligible considering the detection limit of XRF, suggesting that the presence of bulk ligands coordinated to the vanadium center impinges an extremely weak electrostatic interaction among the Mg orbital of surface with free electrons from Cl ligands from the vanadium compound. Taking into account this aspect, the complex **1** might be easily removed from the surface during washing step with solvent.

The resulting supported catalyst systems were evaluated in ethylene polymerization, carried out in hexane at 30 °C, and using MAO or TiBA/MAO as cocatalyst (Al/V = 1000) (Table 2). The choice of the temperature (30 °C) resides in previous study, in which maximum catalyst activity was observed, producing polyethylene in the range of 2230–2790 kg PE/(mol V h) [4].

All the supported systems were shown to be active in ethylene polymerization. Catalyst activity was shown to be dependent of support nature, being comprised between 8.1 and 88.0 kg PE/(mol V h). It is worth mentioning that MAO is very soluble in aromatic solvents (up to 30%), but it has very low solubility in aliphatic solvents (only 3 or 4%) [15]. The main problem concerning the use of an aliphatic hydrocarbon solvent as polymerization milieu is low solubility of the catalyst components due to the low polarity of the solvent [16]. The introduction of triisobutylaluminum (TiBA) in the polymerization milieu increases the solvent polarity, enhancing MAO solubility and the formation and stabilization of the active species [17]. Therefore, for comparative reasons, polymerization reactions were carried out in hexane

using MAO as cocatalyst, and then with a co-catalyst mixture TiBA/MAO (Table 2).

For the polymerization reactions using MAO as cocatalyst, the highest catalyst activity was observed for the system $\mathbf{1}$/SiO$_2$. It is worth remarking that this activity is nine times higher than that showed by $\mathbf{1}$/MgO system (8.1 kg PE/(mol V h)) (compare Entry 1 to Entry 6), in spite of both catalyst systems bearing similar vanadium content (0.054 mmol V/g for $\mathbf{1}$/SiO$_2$ and 0.045 mmol V/g for $\mathbf{1}$/MgO). The basic nature of MgO support might not favor the generation of active surface species.

In the polymerization reactions carried out with a co-catalyst mixture TiBA:MAO (1:1) an increase in the catalyst activity was observed for $\mathbf{1}$/SiO$_2$, $\mathbf{1}$/SiO$_2$/MAO (23.0 wt.% Al/SiO$_2$) and $\mathbf{1}$/MCM-41. On the other hand, no significant variation in catalyst activity was observed for the other systems.

Comparing catalyst activity of the homogeneous system with the supported ones, a reduction is clearly observed in the latter. For instance, the most active supported system ($\mathbf{1}$/SiO$_2$–73.8 kg PE/(mol V h)) is still 12 less active than the homogeneous one (922.4 kg PE/(mol V h)). This reduction
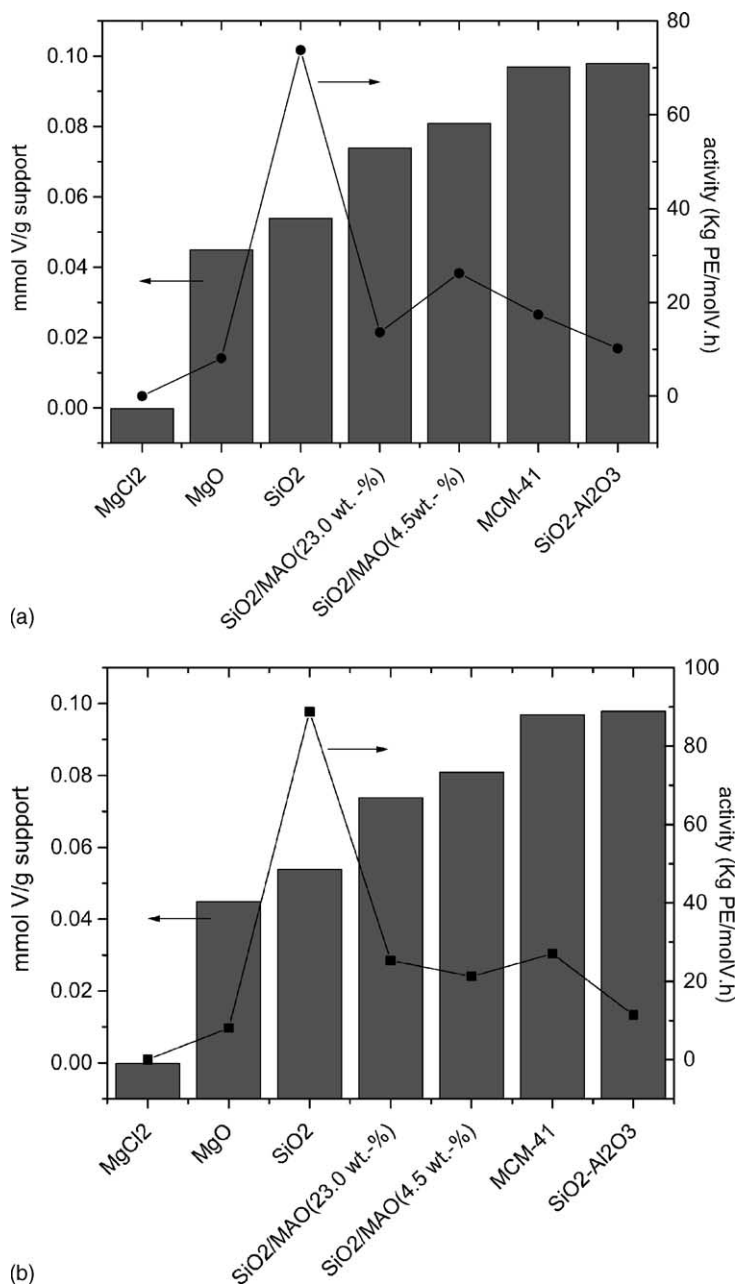

Fig. 1. Correlation between the nature of support and the resulting V content in the supported systems and catalyst activities in ethylene polymerization using: (a) MAO and (b) TiBA/MAO (1:1), as cocatalyst.

might be due to the decreasing of the number of active species generated on the support surface. Similar results have been reported in the case of supported zirconocenes, where only ca. 1% of the supported species are believed to be active [18].

Fig. 1 presents a correlation between catalyst activity, nature of the support and V amount present in the supported systems using MAO and TiBA/MAO as cocatalyst. Comparing the catalyst activity results with V amount present in the different supported systems, it was observed that high V content does not imply in high catalyst activity. This can be explained in terms of a high concentration of V species on the support which might favor bimolecular deactivation reactions as reported in the case of supported zirconocene catalysts [19].

For $1/SiO_2$ and $1/SiO_2/MAO$ (4.5 wt.% Al/SiO_2) systems, it was observed that the presence of MAO on silica surface affords an increase in the V content on the support and a decrease in catalyst activity. Comparing the activities results obtained for $1/SiO_2$, $1/SiO_2–Al_2O_3$, $1/MCM$-41 and $1/MgO$ in presence of MAO or TiBA/MAO, it was observed that when the complex 1 is grafted onto $SiO_2–Al_2O_3$ or MgO catalyst activity is much lower than that obtained using $1/SiO_2$ system (Table 2). The $1/MCM$-41 system showed higher activity than $1/MgO$ and $1/SiO_2–Al_2O_3$, however, this value is still much lower than that obtained with $1/SiO_2$. Taking into account the acid nature of $SiO_2–Al_2O_3$, weak acid of MCM-41 and the MgO basicity, these results suggest that the most inert character of the silica surface favors the formation of active species for the present V derivative.

The spatial distribution of V on the catalyst grain was evaluated by electron probe microanalysis (EPMA), by detecting its characteristic X-ray emission. The resulting element distribution maps in the catalyst particle of $1/SiO_2/MAO$ (4.5 wt.% Al/SiO_2), $1/SiO_2/MA0$ (23.0 wt.% Al/SiO_2) and $1/SiO_2–Al_2O_3$ are shown in Fig. 2. Low metal content corresponds to the darker region, while higher metal content, to the brighter one.

According to EPMA spectrum (Fig. 2a), in the case of $1/SiO_2/MAO$ (4.5 wt.% Al/SiO_2) there are zones of higher V concentration, suggesting a non-uniform metal distribution along the catalyst grain. A roughly better distribution can be observed in the case of $1/SiO_2/MA0$ (23.0 wt.% Al/SiO_2) system (Fig. 2b). Comparing spectra from those two systems, there is a higher V content in the former, in agreement with XRF results, which showed that metal content is higher in the $1/SiO_2/MAO$ (4.5 wt.% Al/SiO_2) supported system.

A very uniform metal distribution was observed in the case of $1/SiO_2–Al_2O_3$ (Fig. 2c). It is worth noting that according to XRF measurements, the supported systems resulting from the immobilization of 1 onto SiO_2/MAO (4.5 wt.% Al/SiO_2) and onto $SiO_2–Al_2O_3$ bear roughly comparable V content. Nevertheless, the latter exhibits a much lower catalyst activity. Therefore, taking into account EPMA results, it seems that the lower catalyst activity observed for the $1/SiO_2–Al_2O_3$ was not due to the a non-uniform V
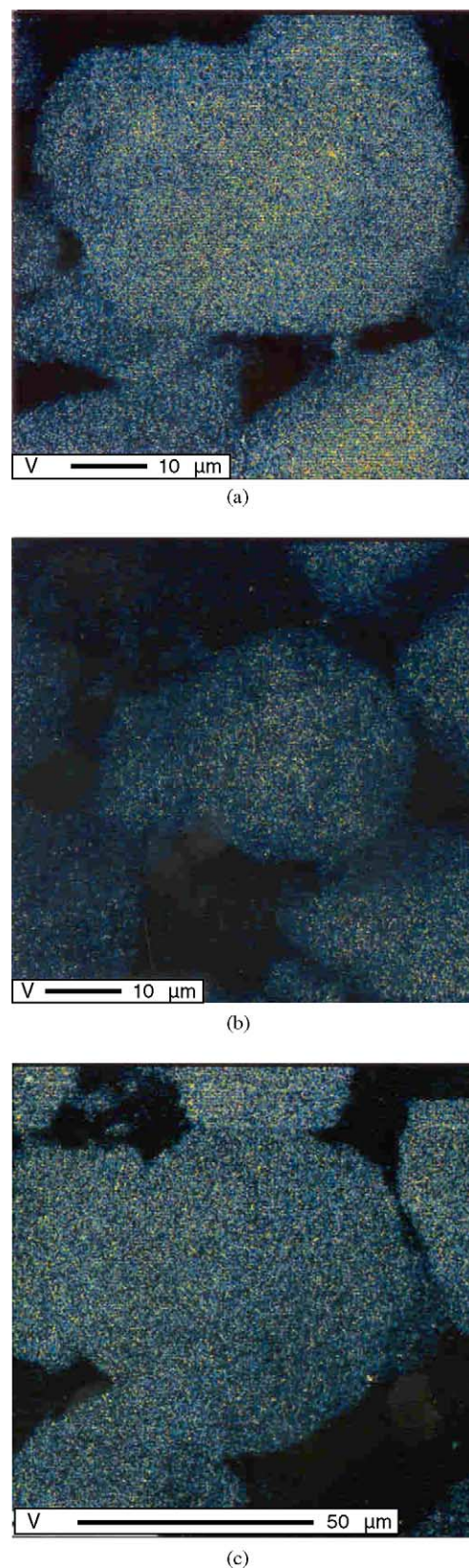

Fig. 2. Element distribution map of V in the resulting supported catalysts: (a) $1/SiO_2/MAO$ (4.5 wt.%); (b) $1/SiO_2/MAO$ (23.0 wt.%) and (c) $1/SiO_2–Al_2O_3$.
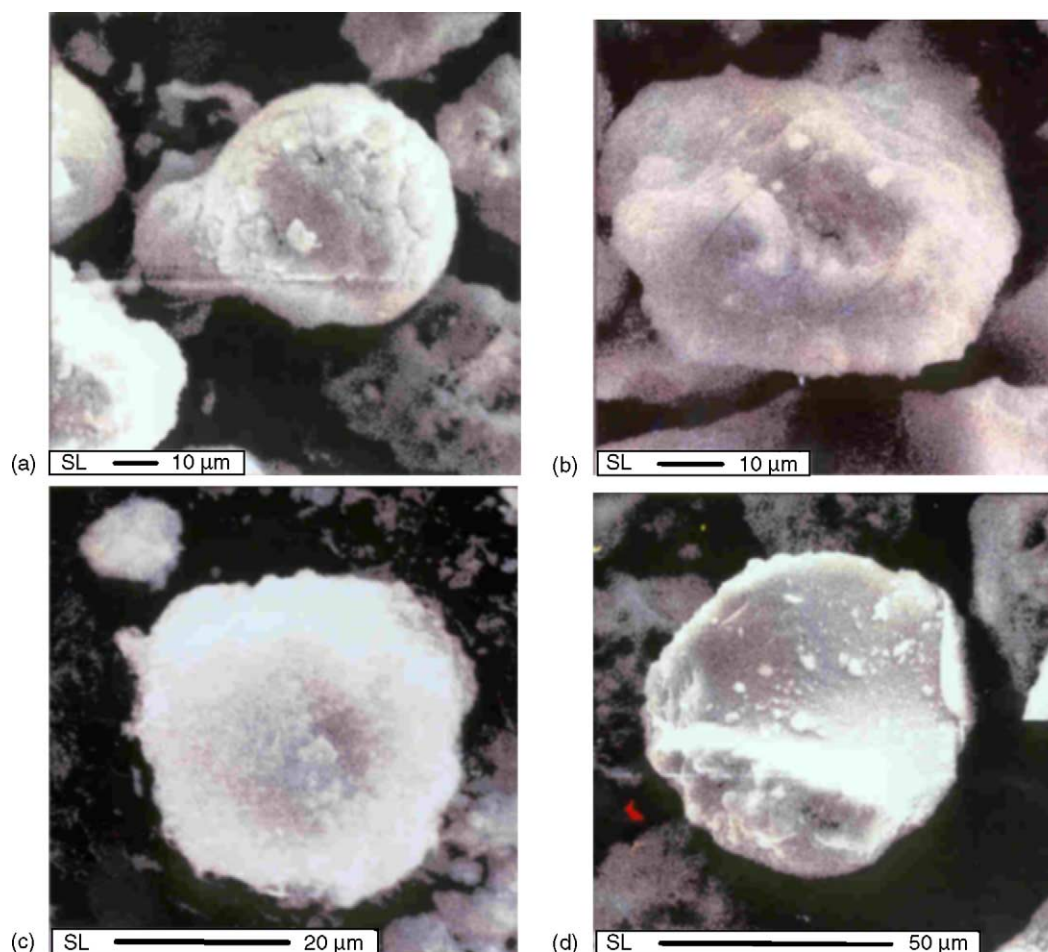
Fig. 3. SEM photographs of resulting catalysts. (Top) (a) **1**/SiO$_2$/MAO (4.5 wt.%) (left) and (b) **1**/SiO$_2$/MAO (23.0 wt.%) (right). (Bottom) (c) **1**/MgO (left) and (d) **1**/SiO$_2$–Al$_2$O$_3$ (right).

distribution (which could induce to bimolecular deactivation reactions), but probably due to the intrinsic acid nature of this support.

The supported catalysts were further analyzed by scanning electron microscopy (SEM). According to Fig. 3, the spherical particle morphology is roughly maintained.

The effect of V on the catalyst was evaluated in the case of **1**/SiO$_2$/MAO (23.0 wt.% Al/SiO$_2$). A supported catalyst bearing 0.05 V/support (wt.% V/SiO$_2$), i.e. five times lower than the value obtained previously (see Table 1) was prepared. The behavior of this supported catalyst in ethylene polymerization is shown in the Table 3.

According to Table 3 and comparing these results with data in Table 1, the system **1**/SiO$_2$/MAO (23.0 wt.% Al/SiO$_2$) containing 0.05% in weight of V/g support showed a catalyst activity which is five times higher (64.4 kg PE/(mol V h)) than that exhibited by **1**/SiO$_2$/MAO (23.0 wt.% Al/SiO$_2$) containing 0.28 % in weight of V/g support (13.6 kg PE/(mol V h)). This behavior might be explained in terms of better distribution of **1** on the support surface hindering bimolecular deactivation reactions. This trend was also observed when a TiBA/MAO (1:1)

co-catalyst mixture was used. In this case, the activity was three times higher than that shown in Table 1 (Entries 15 and 10). It is worth noting that as previously observed, TiBA/MAO (1:1) co-catalyst mixture led to higher activity than that verified in the case of only MAO.

The "in situ" metallocene supporting has been reported as an approach to produce immobilized polymerization catalysts, without the necessity of previous grafting step. This approach has been claimed to be less time-demanding and to produce more active systems [20]. In the present study, **1** was "in situ" immobilized onto commercial SiO$_2$/MAO

Table 3
Catalyst activity and PE melting temperature of PE using **1**/SiO$_2$/MAO (23.0 wt.% of Al/SiO$_2$)[a,b] catalyst system

Entry	Cocatalyst	Activity (kg PE/(mol V h))	T_m (°C)
14	MAO	64.4	135
			139
15	TiBA/MAO	74.8	138

[a] 0.05 wt.% V/support.
[b] Polymerization conditions: glass reactor (100 ml); hexane (80 ml); $P = 1$ atm, reaction time = 1 h; $T = 30\,°C$, Al/V = 1000.

Table 4
Results of polymerization reactions "in situ" with ethylene using 1/SiO$_2$/MAO (23 wt.% of Al/SiO$_2$)[a,b] system

Entry	Cocatalyst	Activity (kg PE/(mol V h))	T_m (°C)
16	MAO	352.3	131
17	TiBA	105.0	133

[a] 0.05 wt.% V/SiO$_2$.

[b] Polymerization conditions: glass reactor (100 ml); hexane (75 ml), $P = 1$ atm; 30 °C; Al/V = 1000; catalyst pre-contact with support : 30 min, reaction time = 30 min.

Table 5
Molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the resulting polyethylenes

Catalyst system	M_w	M_w/M_n
1/SiO$_2$	2856215	3.2
1/SiO$_2$/MAO (4.5 wt.%)	3856036	7.3
1/SiO$_2$/MAO (23.0 wt.%)	5452894	3.5
1/MgO	2773364	6.8
1/MCM-41	4001479	2.9

(23.0 wt.% Al/SiO$_2$) employing 0.05 wt.% V/SiO$_2$. This concentration was chosen considering that it is much lower than that present in Table 1. Therefore, all the V present in solution might have immobilization sites available on the support. Under these conditions, catalyst solution and support slurry were directly added to the reactor under ethylene flow, establishing a pre-contact, followed by the co-catalyst addition. The results are shown in Table 4.

Comparing Entry 16 (Table 4) and Entry 13 (Table 3) it was observed that the polymerization reaction carried out "in situ" showed activity five times higher (352.3 kg PE/(mol V h)) than that when the catalyst was first supported and then introduced for ethylene polymerization (64.4 kg PE/(mol V h)). This result can be attributed to MAO availability on the support which might favor catalyst stability along the polymerizarion reaction. Besides, ethylene might also stabilize the active centers, and therefore catalyst activity increases. On the other hand, in the absence of ethylene in the milieu (as in the case of grafting reaction during the immobilization of the complex on the support), part of active centers formed might become unstable, and consequently inactive.

It is worth noting that polymerization reaction using only TiBA as cocatalyst showed that this resulting supported catalysts is active in the absence of external MAO. For comparative reasons, the same reaction was performed using SiO$_2$ as support, and the resulting catalyst system was not shown to be active in ethylene polymerization. Thus, it seems that the MAO present on the support might act as co-catalyst, generating active species during the polymerization reaction [21].

Polyethylenes produced by the supported systems were characterized by differential scanning calorimetry (DSC). DSC curves of the PE showed melting temperatures (T_m) in the range of 132 and 140 °C. DSC curve corresponding to the PE produced by 1/SiO$_2$/MAO (23.0 wt.% Al/SiO$_2$) is shown in Fig. 4. In the case of the PE produced by 1/MCM-41 with MAO/TiBA co-catalyst mixture, the presence of two peaks was observed, suggesting probably the existence of two different catalyst species on the support (Fig. 4), or resulting from the use of two distinct cocatalyst. Some spectroscopic measurements are under investigation in order to get more details of the species nature on that support.

Some polyethylenes were characterized by GPC. According to Table 5, all polymers exhibited $M_w > 1.5 \times 10^6$ Da, suggesting the production of ultra-high molecular weight polyethylene (UHMWPE). In the case of 1/SiO$_2$/MAO (4.5 wt.% Al/SiO$_2$), the high polydispersity index suggests the possibility of the presence of two surface species: one

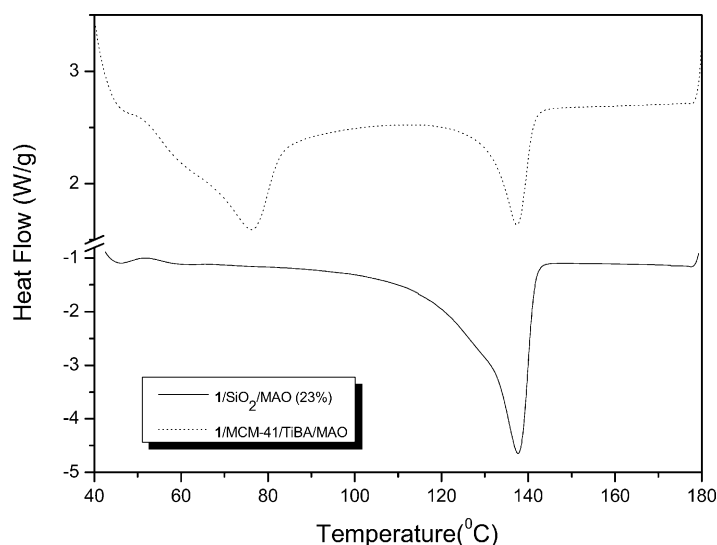Fig. 4. DSC curves corresponding to the PE produced by 1/SiO$_2$/MAO (23.0 wt.%) and 1/MCM-41 in the polymerization reaction using a mixture of TiBA/MAO cocatalysts.

generated by the direct reaction with silanol surface groups and another produced on MAO-moieties. On the other hand, in the case of MCM-41, in spite of the potential of two different kinds of crystallites as shown by thermogram in Fig. 4, the polydispersity remained narrow.

According to Table 5, no trend could be established between polymers produced by homogeneous and supported systems. It is worth mentioning that in the case of metallocene catalysts, supported systems usually afford polymers with higher molecular weight. Conversely, in the present study, PE obtained with homogeneous catalysts exhibited higher M_v.

4. Conclusions

The immobilization of $Tp^{Ms*}V(N^tBu)Cl_2$ onto inorganic supports afford supported catalysts which were active for ethylene polymerization in the presence of MAO or TiBA/MAO cocatalyst. Grafted metal content and catalyst activity was dependent on the nature and on the texture of the support, higher V content being observed in the case of high surface area supports. Higher catalyst activity was observed in the case of SiO_2, which exhibits a much inert character. Acid or basic supports afforded less active catalysts systems.

In situ immobilization procedures were shown to be a potential approach for the development of supported systems. Catalyst activity was shown to be higher than that presented by the catalysts prepared by the grafting method.

The M_w determination of the resulting polyethylenes suggested theproduction of ultra-high molecular weight polymers.

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