Ethylene polymerization using tris(pyrazolyl)borate vanadium (V) catalysts in situ supported on MAO-modified silica

Adriana C.A. Casagrande, Patrícia S. dos Anjos, Douglas Gamba,
Osvaldo L. Casagrande Jr., João H.Z. dos Santos *

Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500, 91501-970 Porto Alegre, RS, Brazil

Abstract

The catalyst precursors $Tp^{Ms*}V(L)Cl_2$ [**1**, L = N^{t}Bu; **2**, L = O; Tp^{Ms*} = (3-mesityl-pyrazolyl)$_2$(5-mesityl-pyrazolyl)] were in situ supported onto SiO_2 and onto methylaluminoxane (SMAO-4) and trimethylaluminum (STMA-3) modified silicas using 0.02 wt.% V/support. All catalyst systems were shown to be active in ethylene polymerization, with activities lying between 1000 and 1900 kg of PE/mol [V] h atm. Similar activities were found by employing different types of cocatalysts (MAO, TMA, and IPRA) in the in situ polymerization reaction using **1**/SMAO-4. Furthermore, the systems were shown to be stable at different [Al]/[V] molar ratios and polymerization temperatures. Polyethylenes were characterized by differential scanning calorimetry (DSC). The impossibility of dissolving them in a common solvent for GPC analysis suggests that such polymers might present very high molecular weights.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Pirazolyl; In situ supported catalysts; MAO; Silica; Polymerization

1. Introduction

The immobilization of soluble olefin polymerization catalysts onto inorganic supports is essential for industrial applications since such heterogenized catalysts can provide catalysts suitable for the existing slurry or gas-phase polymerization technologies [1]. Furthermore, the heterogenization of catalysts is necessary to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive polymer swelling, and to produce polymer particles with a desired regular morphology. For this purpose, several classes of metallocene and non-metallocene homogeneous catalysts have been immobilized on supports, and their performance has been investigated in olefin polymerization [1]. Our studies in this area have shown that the immobilization of non-metallocene catalyst precursors $Tp^{Ms*}V(N^tBu)Cl_2$ [2] and $Tp^{Ms*}TiCl_3$ [3] onto inorganic supports (SiO_2, MAO-modified SiO_2, $SiO_2–Al_2O_3$, $MgCl_2$, MCM-41, and MgO) affords active species for ethylene polymerization. However, these catalyst systems display low activities as compared to the results obtained with the homogeneous counterpart, which may be attributed to the instability of the catalyst species formed by the interaction of such catalysts with MAO in the absence of monomer. In order to overcome this problem, preliminary studies using $Tp^{Ms*}TiCl_3$ in situ supported on MAO-modified SiO_2 (SMAO) have showed that this procedure allows activities 4-fold higher than those found when such systems were ex-situ immobilized on SMAO [3]. The in situ immobilization of the precatalyst onto silica-supported MAO within the polymerization reactor, followed by the introduction of an alkylaluminum complex and monomer, has been introduced by Soares and co-workers [4]. It has been demonstrated that this approach eliminates the necessity of a supporting step before polymerization, therefore demanding less time and affording more active systems. As in the case of ex situ supporting procedures, in the case of an in situ one, the employed support remains entrapped into the polymer matrix. In the present paper, we report the potentiality of using in situ immobilization methodology for the generation of a supported polymerization catalyst system based on the combination of $Tp^{Ms*}V(L)Cl_2$ (**1**, L = N^{t}Bu; **2**, L = O) with two silica-based supports, namely: SiO_2, SiO_2/MAO (4.0 wt.% Al/SiO_2), and SiO_2/TMA (3.0 wt.% Al/SiO_2). The effect of the nature of the cocatalyst, the [Al]/[V] molar ratio,

---

* Corresponding author. Tel.: +55 51 3316 7238; fax: +55 51 3316 7304.
  E-mail address: jhzds@iq.ufrgs.br (J.H.Z. dos Santos).

and the polymerization temperature on the activity and on polymer properties are discussed.

2. Experimental

2.1. Materials

All manipulations were carried out under an Ar atmosphere using standard Schlenck tube techniques. Toluene and hexane were dried with Na/benzophenone, distilled, and stored under argon. $Tp^{Ms*}V(L)Cl_2$ (**1**, L = N^{t}Bu; **2**, L = O) compounds were prepared according to literature procedure [5]. Silica Grace 948 ($255 m^2 g^{-1}$) was activated under vacuum ($P < 10^{-4}$ mbar) for 16 h at 100 °C. Ethylene (White Martins) and argon were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieve (3 Å) prior to use. Metilaluminoxane, MAO (Eurecen, 5.21 wt.% toluene solution), trimethylaluminum (TMA), and isoprenylaluminum (IPRA) (Akzo, gently supplied by Ipiranga Petroquímica, 8.0 wt.% hexane solution) were used as received.

2.2. Preparation of SiO$_2$/MAO (4.0 wt.% Al/SiO$_2$)

MAO-modified silica was prepared by impregnating 1.0 g of previously thermally activated silica with a MAO toluene solution (0.9 mL) at room temperature for 3 h under stirring. The solvent was removed under vacuum and the solid was dried. The resulting solid was named SMAO-4 [6].

2.3. Preparation of SiO$_2$/TMA (3.0 wt.% Al/SiO$_2$)

TMA-modified silica was prepared by impregnating 1.0 g of thermally treated silica Grace 948 with a TMA toluene solution (1.6 mL) at room temperature for 3 h under stirring. The solvent was removed under vacuum and the solid was dried. The resulting solid was named STMA-3.

2.4. In situ supported non-metallocene catalyst

$Tp^{Ms*}V(N^tBu)Cl_2$ (**1**) or $Tp^{Ms*}V(O)Cl_2$ (**2**) was directly added to support within the polymerization reactor in presence of cocatalyst.

2.5. General procedure for in situ polymerization reactions with ethylene

The experiments were performed in a Fisher–Porter bottle (100 mL) equipped with a magnetic stirrer bar and a stainless steel pressure head fitted with inlet and outlet needle valves, a septum-capped ball valve for injections, and a pressure gauge. Under ethylene atmosphere, the proper amount of hexane was introduced. This was followed by the addition of support and catalyst precursor **1** or **2** toluene solution corresponding to 0.02 wt.% V/support. After 30 min under stirring, the cocatalyst was added to start the polymerization. The volume of the reaction mixture was 70 mL for all polymerization runs. The total pressure (3 atm) was kept constant by a continuous feed

of ethylene. The polymerization runs were stopped by introducing 1 mL of methanol. The polymers were washed with acidic ethanol, then with ethanol and water, and dried in a vacuum oven at 60 °C for 12 h.

2.6. Catalyst characterization

2.6.1. X-ray fluorescence spectroscopy

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.

2.6.2. Inductively coupled plasma optical emission spectroscopy (ICP OES)

An inductively coupled plasma optical emission (ICP OES) spectrometer from Perkin-Elmer (Optima^{TM} 2000 DV) was used for V measurement in the catalysts. A Scott spray chamber and a GemCone® nebulizer composed the sample introduction system. Catalyst digestion was done with H_2SO_4 and HNO_3 ($H_2SO_4/HNO_3 = 3/1$) in a Teflon® capped vessel. The mixture was heated at 160 °C for 8 h in a heating block (Tecnal, Brazil). Samples and blanks were analyzed in duplicate.

2.7. 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 $10 °C min^{-1}$ 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. Microcalorimetric DSC analyses were also performed using micro DSC III (Seteram), capable of operation in either temperature scanning or isothermal modes. Typically, 2 mg of polymer samples were employed. Molar masses and molar mass distributions were investigated at 413 K with a Waters CV Plus 150 °C high-temperature GPC instrument equipped with viscometrical detector, differential optical refractometer, and 3 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 $1 cm^3 min^{-1}$. The columns were calibrated with standard narrow molar mass distribution polystyrenes and with linear low density polyethylenes and polypropylenes.

3. Results and discussion

3.1. Ethylene polymerization using in situ supported catalysts: activity trends

The in situ immobilization procedure takes into account that the catalyst species are directly generated on the support through combination of these two counterparts: homogeneous catalyst

Table 1
V content on SiO_{20}- and MAO-modified SiO_2 determined by XRF and ICP OES

Support	V content (wt.%/support)	Al/V
1/SiO₂	0.040[a]	
1/SMAO-4	0.039[a]	195
2/SiO₂	0.050[b]	
2/SMAO-4	0.029[b]	260

[a] XRF.
[b] ICP OES.

and support. Nevertheless, the generation of the immobilized species depends on the availability of anchoring sites on the support. In a previous study, we observed that the grafted content for catalyst **1** on silica or on MAO-modified silica lay between 0.28 and 0.41 wt.% V/support [2]. Thus, in the present study, we used a very low amount (0.05 wt.% V/g support) of **1** and **2** complexes in order to guarantee that all the catalyst would be potentially immobilized on the support surface. In a preliminary study, these complexes were combined with the supports, directly within the reactor, under ethylene atmosphere to ensure catalyst stability. After 30 min, the solid catalyst was filtered through a fritted disk and washed several times with toluene, then with hexane, and finally dried under vacuum. Metal grafted content was determined by XRF and ICP OES. Table 1 presents the V content and Al/V ratio in the resulting catalysts.

According to Table 1, grafted V content lies between 0.029 and 0.050 wt.% V/support. In the case of complex **1**, similar V content was observed for both SiO_2 or SMAO-4 supports. Besides, in these systems, practically all the V present in solution (corresponding to 0.05 wt.%) was immobilized on the support, suggesting the availability of anchoring sites and a strong interaction between the catalyst and support surface. It is worth noting that the silica was treated at 100 °C. This temperature affords a totally hydroxylated surface bearing ca. 5.0 OH nm^{-2} [7]. Thus, the immobilization of **1** on the surface is more probable since there is a larger number of silanol groups. In the case of SMAO-4, there are still available silanol groups, since the silica saturation level for MAO is around 8–10 wt.% Al/SiO₂ [8]. Therefore, in this case, the immobilization can take place on both the silanol and MAO groups. Thus, comparing the results obtained with SiO_2 and SMAO-4 for complex **1** (Table 1), it seems that the consumption of silanol groups during silica chemical modification with MAO does not affect the immobilized

vanadium content on these supports. In the case of complex **2**, similar grafted content is observed in the case of SiO_2. Nevertheless, in the case of SMAO-4, the final metal content is roughly 42% lower that that observed in the case of **1** grafted on this support.

In Table 1, Al/V ratio was also shown. These values suggest that there is a low Al/V ratio already in the starting catalyst, which might influence the catalyst activity.

After this preliminary study, complexes **1** and **2** were in situ immobilized using SiO_2, SMAO-4, and STMA-3 as supports employing catalyst concentration corresponding to 0.02 V (wt.%/support). This concentration was low enough to guarantee that all V complex in the solution might react on the support surface. The in situ immobilized catalysts were evaluated in ethylene polymerization having MAO or TMA as the cocatalyst, as shown in Table 2. Data are expressed in terms of activity and productivity.

According to Table 2, all the systems were shown to be active when ethylene polymerization reactions were carried out with in situ immobilization of complex **1**. For the polymerization reactions using MAO as the cocatalyst, **1**/SMAO-4 showed a catalyst activity which is two times higher than that exhibited by **1**/SiO₂ (compare entries 2 and 1), suggesting that, despite the two supports bearing roughly comparable V content, the stability or activity of **1** with SMAO-4 is higher than that resulting from the interaction with bare SiO_2.

For **1**/SMAO-4 in the presence of TMA as the cocatalyst, the activity is ca. 30% lower for the latter (entries 2 and 3). It is worth noting that in previous studies using complex **1**, in spite of being active in the presence of common alkylaluminum (triisobutylaluminum), the activity significantly decreased (reduction of 58%) when compared to that obtained with MAO [5a]. Thus, as proposed in the literature in the case of in situ supported systems using MAO-modified silica, the MAO from the support might ensure the stability of the catalyst species, affording higher catalyst activity [4c].

When complex **1** was immobilized onto STMA-3 using MAO as the external cocatalyst, this system showed a similar activity compared to that of system **1**/SMAO-4, under the same conditions (entries 2 and 4). This result should be associated with the fact that the TMA immobilization onto the silica surface might generate MAO moieties, in analogy to its formation by in situ hydrolysis of TMA into the MCM-41 mesoporous [9].

Table 2
Ethylene polymerization results using $Tp^{Ms*}V(N^tBu)Cl_2$ (**1**) and $Tp^{Ms*}V(O)Cl_2$ (**2**) catalysts in situ supported on SiO_2, SMAO-4 and on STMA-3[a]

Entry	Catalyst	Cocatalyst	Activity (kg PE/mol [V] h atm)	Productivity (g PE/g cat.)	T_m (°C)
1	**1**/SiO₂	MAO	1000	326	118/129 (sh)
2	**1**/SMAO-4	MAO	1900	624	124/132 (sh)
3	**1**/SMAO-4	TMA	1342	440	124
4	**1**/STMA-3	MAO	1704	560	122/133 (sh)
5	**1**[c]	MAO	1126	369	141
6	**2**/SiO₂	MAO	1880	670	126/134
7	**2**/SMAO-4	MAO	1535	550	127 (sh)/134
8	**2**[c]	MAO	460	165	135

[a] Polymerization conditions: Fischer–Porter reactor, 100 mL; hexane, 70 mL; $P_{C_2H_4}$, 3.0 atm; T, 30 °C, pre-contact of catalyst and support, 30 min; polymerization time, 5 min; [Al]/[V], 400, 0.02% in weight of V/g support; [V], 1×10^{-6} mol V; sh, shoulder.

R = mesityl
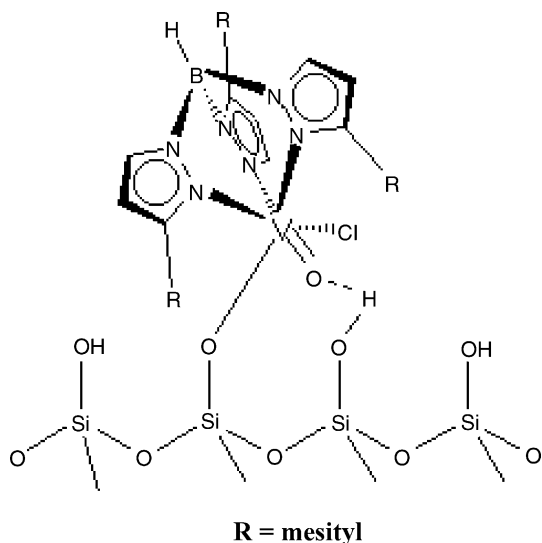
Scheme 1.

The in situ immobilization of complex **2** onto silica showed activity of 1880 kg of PE/mol [V] h atm, which was four times higher than that found in homogeneous medium (460 kg of PE/mol [V] h atm). In this case, the increase in activity after immobilization onto silica, under ethylene atmosphere, might be due to the more favorable interaction of complex **2** with the silanol groups, which could hinder the reaction of oxo ligand with the residual TMA present in MAO, therefore engendering better catalyst stability. On the other hand, we cannot neglect the possible interaction of the oxo ligand with acid centers, through of hydrogen bondings, also affording a better catalytic stability (Scheme 1).

In the case of MAO-modified silica, catalyst activity of complex **2** in situ supported system was comparable to that observed in the case of bare silica, suggesting that MAO did not contribute in additional stability for this system.

It should be pointed out that for the in situ polymerization using SiO$_2$ as support, the presence of oxo ligand (complex **2**) instead of N^{t}Bu group (complex **1**) determines an increase of the catalytic activity by factor of 2. For instance, the activity of **1**/SiO$_2$ was 1000 kg PE/mol [V] h atm (entry 1), while that obtained with **2**/SiO$_2$ was 1880 kg PE/mol [V] h atm (entry 6). This difference in activity should be related to the smallest steric effect played by the oxo ligand, when compared to N^{t}Bu group, which in turn should lead to a better interaction of **2** with the support.

Higher activities found for the supported catalysts related to the nonsupported ones (homogeneous phase) suggest that the supports might be favoring the formation of more stable active species as well as hindering the bimolecular deactivation reactions. Similar behavior was observed in the case of supported dichlorobis(3-hydroxi-2-methyl-4-pyrone)Ti(IV) derivatives [10].

Polyethylenes produced by the in situ supported systems were characterized by differential scanning calorimetry (DSC). DSC curves of the PE showed melting temperatures (T_m) in the range of 118 and 134 °C, probably suggesting the existence of different catalyst species, which produce polyethylenes with different
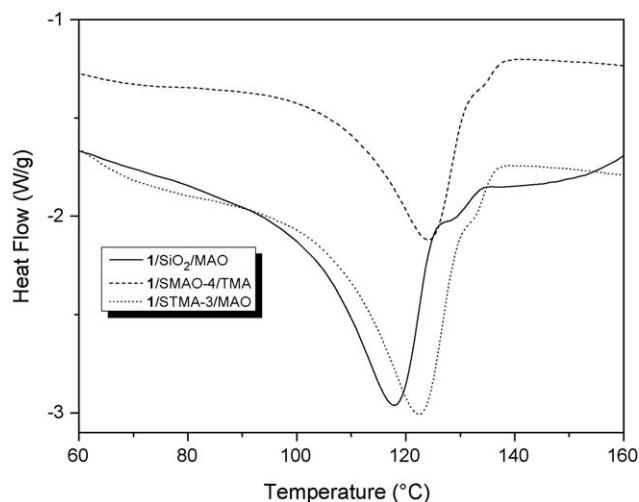

Fig. 1. DSC curves of polyethylenes obtained with **1** in situ immobilized onto different supports.

melting temperatures (Fig. 1). The polyethylenes produced by the homogeneous system showed only one peak and the values are 135 and 140 °C for **2** and **1**, respectively.

Microcalorimetric analysis was carried out for **1**/STMA-3 system, and the curve showed two peaks with practically the same amplitude and small differences in crystallization temperature: 91 °C (higher crystallinity) and 87 °C (lower crystallinity) (Fig. 2). The presence of two peaks also suggests the formation of different types of polymer, which may be produced in different catalyst sites. All attempts to carry out GPC analysis failed since such polymers were insoluble under standard analysis procedures. In a previous work, insoluble polymers with such systems were also produced [2]. GPC analyses were only possible under special analytical conditions employed for ultra-high molecular weight polyethylene. M_w lay between 2.7×10^6 and 5.5×10^6 Da (Fig. 2).

3.2. Influence of polymerization parameters on the performance of *1* in situ supported on SMAO-4

Taking into account the highest activity displayed by **1** in situ supported on SMAO-4, some additional studies were carried out
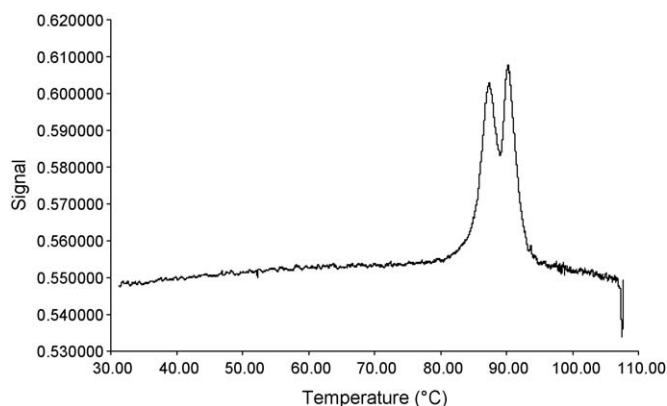

Fig. 2. Microcalorimetric analysis of polyethylene produced with **1**/STMA-3 system.

Table 3
Effect of cocatalyst type on activity of in situ **1**/SMAO-4 supported system[a]

Entry	Cocatalyst	Activity (kg of PE/mol [V] h atm)	Productivity (g PE/g cat.)	T_m (°C)
9	MAO	560	376	123/133 (sh)
10	TMA	620	405	122
11	IPRA	525	344	126

[a] Polymerization conditions: Fischer–Porter reactor, 100 mL; hexane, 70 mL; $P_{C_2H_4}$, 3.0 atm; T, 30 °C; pre-contact of **1** and SMAO-4, 30 min; polymerisation, 10 min; [Al]/[V], 150; 0.02% in weight of V/g support; [V], 1×10^{-6} mol V; sh, shoulder.

in order to verify the influence of the cocatalys type, [Al]/[V] molar ratio and temperature on the activity and polymer characteristics. Since under Al/V = 400 and polymerization time of 5 min the systems were shown to be very active, leading to diffusion problems within the reactor, in the following reactions the Al/V was reduced and the polymerization time extended to 10 min. The results are shown in Table 3.

According to Table 3, the polymerization results showed that the activity is just slightly affected by use of different types of cocatalyst (TMA, trimethylaluminum; IPRA, isoprenylaluminum), with the activity lying between 525 and 620 kg PE/mol [V] h atm. This variation is not significant, considering the accuracy of the activity data is on the order of 10%. It seems that the nature of these evaluated cocatalysts did not affect catalyst activity. Nevertheless, they are totally necessary, since in their absence, no polymerization is observed.

DSC curves corresponding to the PE produced by TMA and IPRA show a T_m of 122 and 126 °C, respectively. These values are characteristics of branched polyethylenes, and they are in agreement with the cocatalyst nature, since TMA and IPRA are good chain transfer agents [11]. The decrease of melting temperature can be explained, assuming that the predominant process of termination is the chain transfer to TMA (present in MAO solution), as demonstrated in previous studies involving a similar complex [11]. In the case of PE produced by MAO, a thermogram showed a T_m of 123 °C and one shoulder in 133 °C. Similar results were observed for catalyst **1** supported on MAO-modified silica [2]. Attempts to perform GPC analysis were also unsuccessful, since such polymers were insoluble under standard analysis conditions.

To investigate the effects of the [Al]/[V] molar ratio on activity, polymerization of ethylene was performed with in situ **1**/SMAO-4 supported catalyst using TMA as the external cocatalyst at 30 °C and varying the [Al]/[V] ratio from 150 to 1000. Data are summarized in Table 4.

In the Al/V studied range, the maximum activity was achieved at 1000:1 (entry 15, 735 kg of PE/mol [V] h atm). DSC curves of the resulting polymers show that PE produced with 100 equiv. of TMA exhibits a T_m of 122 °C, while for the other [Al]/[V] molar ratios, the T_m does not change (127 °C). These T_m values suggest in all cases the probable formation of branched polyethylenes.

The influence of polymerization temperature on the activity of in situ **1**/SMAO-4 catalyst has been evaluated in the range of 0–60 °C, at [Al]/[V] = 600, and using TMA as external cocatalyst. The polymerization results are shown in Table 5. Higher

Table 4
Effect of the [Al]/[V] molar ratio on activity of in situ **1**/SMAO-4 supported system[a]

Entry	Al/V	Activity (kg of PE/mol [V] h atm)	Productivity (g PE/g cat.)	T_m (°C)
12	150	620	405	122
13	300	635	416	127
14	600	660	432	127
15	1000	735	481	127

[a] Polymerization conditions: Fischer–Porter reactor, 100 mL; hexane, 70 mL; $P_{C_2H_4}$, 3.0 atm; T, 30 °C; pre-contact of **1** and SMAO-4, 30 min; polymerization time, 10 min; TMA as external cocatalyst; 0.02% in weight of V/g support; [V], 1×10^{-6} mol V.

Table 5
Effect of temperature on activity of in situ **1**/SMAO-4 supported system[a]

Entry	Temperature (°C)	Activity (kg of PE/mol [V] h atm)	Productivity (g PE/g cat.)	T_m (°C)
16	0	595	390	122
17	30	660	432	127
18	60	470	306	130

[a] Polymerization conditions: Fischer–Porter reactor, 100 mL; hexane, 70 mL; $P_{C_2H_4}$, 3.0 atm; pre-contact of **1** and SMAO-4, 30 min; polymerization time, 10 min; TMA as external cocatalyst; [Al]/[V], 600; 0.02% in weight of V/g support; [V], 1×10^{-6} mol V.

activities were obtained at 30 °C, with a slight decrease at 60 °C suggesting that higher temperatures can result in higher rates of catalyst deactivation.

In contrast to the results in homogeneous medium [12], in which a decrease in catalyst activity was observed for varying the polymerization temperature from 30 to 0 °C, the use of in situ supported catalyst at low temperature (0 °C) afforded a catalyst system as active as that operating at 30 °C (compare entries 16 and 17). From the DSC analysis, it was observed that the temperature does not seem to have a relevant effect on the melting temperatures of the resulting polyethylenes ($T_m = 122–130$ °C).

4. Final remarks

The in situ immobilization of **1** and **2** on SiO$_2$ and on MAO- or TMA-modified SiO$_2$ affords active ethylene polymerization systems which are more active than the homogeneous counterparts, suggesting that the support might somehow engender a chemical stability of the catalyst species.

In the case of the in situ supported **1**/SMAO-4 system, the presence of MAO on the support surface seems to be responsible for the generation of the active species, since the resulting catalyst is active in the presence of common alkylaluminum, with its activity being independent of the nature of the alkylaluminum or of the [Al]/[V] molar ratio. It is worth noting that the activity of such systems in the presence of alkylaluminum, in which the necessary amount of MAO is already present on the support, is very attractive. They are active in the presence of common alkylaluminum, without the necessity of external MAO. Thermograms suggest the possibility of the formation of more than a catalyst species, according to the support. The impossi-

bility of dissolving them in a common solvent for GPC analysis denotes that such polymers might present very high molecular weights.

In sum, in situ immobilization procedures, as already reported for metallocene catalysts, were also shown to be effective in the preparation of non-metallocene supported catalysts.

Acknowledgments

References

[1] (a) J.R. Severn, J.C. Chadwick, R. Duchateau, N. Friederichs, Chem. Rev. 105 (2005) 4073;
(b) G.G. Hlatky, Chem. Rev. 100 (2000) 1347.

[2] A.C.A. Casagrande, T.T.R. Tavares, M.C.A. Kuhn, O.L. Casagrande, J.H.Z. Dos Santos, T. Teranishi, J. Mol. Catal. A: Chem. 212 (2004) 267.

[3] M.P. Gil, J.H.Z. Dos Santos, O.L. Casagrande Jr., J. Mol. Catal. A: Chem. 209 (2004) 163.

[4] (a) K.J. Chu, J.B.P. Soares, A. Penlidis, Macromol. Chem. Phys. 201 (2000) 552;
(b) C.L.P. Shan, K.J. Chu, J.B.P. Soares, A. Penlidis, Macromol. Chem. Phys. 201 (2000) 2195;
(c) K.J. Chu, J.B.P. Soares, A. Penlidis, J. Polym. Sci. A: Polym. Chem. 38 (2000) 462.

[5] (a) A.C.A. Casagrande, MSc thesis, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil, 2000;
(b) A.C.A. Casagrande, PhD thesis, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil, 2005.

[6] D. Bianchini, J.H.Z. dos Santos, T. Uozumi, T. Sano, J. Mol. Catal. A: Chem. 185 (2002) 223.

[7] S. Ogasawara, Shokubai 18 (1976) 124.

[8] J.H.Z. Dos Santos, S. Dorneles, F.C. Stedile, J. Dupont, M.M.C. Forte, I.J.R. Baumvol, Macromol. Chem. Phys. 198 (1997) 3529.

[9] J.S. Beck, J.C. Vartuli, W.J. Toth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[10] P.P. Greco, R. Brambilla, S. Einloft, F.C. Stedile, G.B. Galland, J.H.Z. dos Santos, N.R.S. Basso, J. Mol. Catal. A: Chem. 240 (2005) 61.

[11] S. Murtuza, O.L. Casagrande Jr., R.F. Jordan, Organometallics 21 (2002) 1747.

[12] A.C.A. Casagrande, M.P. Gil, O.L. Casagrande, J. Braz. Chem. Soc. 116 (2005) 1283.