Supported modified zirconocene catalyst for ethylene polymerization

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Abstract

The reactivity of the silyl ether-substituted zirconocene $[Zr\{\eta^5\text{-}C_5H_4(CH_2)_3OSiMe_3\}(\eta^5\text{-}C_5H_5)Cl_2]$ (**1**) towards dehydroxylated silica was evaluated and comparative studies with respect to the unmodified analogue $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ (**2**) were performed. The different reactions were monitored by FT-IR spectroscopy. The resulting materials were activated with MAO and the catalytic systems were evaluated in ethylene polymerization. The catalysts were characterized by elemental analysis as well as by FT-IR and UV–vis spectroscopy. In addition to the classical reaction between Zr−Cl bonds and acidic silanol surface groups, grafting of complex **1** occurs to some extent by reaction between the silyl ether group and reactive siloxane bridges on the silica surface. In contrast, complex **2**, as one would expect, only reacts through the Zr−Cl groups. Supporting zirconocene **1** on MAO-modified silica gives rise to a more efficient catalyst. The effects caused by these different grafting reactions, as well as the catalytic activities of the resulting materials, are presented and discussed.
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Keywords: Zirconocene; Supported; Silica; Ethylene; Polymerization

1. Introduction

The production of polyolefins is continuously growing as they are indispensable materials in society. Increasing research effort is being directed towards olefin polymerization catalysts in an attempt to develop and improve new catalytic systems suitable for industrial applications and capable of producing new polyolefinic materials.

In comparison with Ziegler–Natta catalysts, zirconocene-based systems offer high activity and versatility [1–4]. However, these new polymerization catalysts are soluble systems. A solution polymerization process requires separation of the polymer and recovery and purification of the solvent. As most of the existing polymerization plants run slurry or gas-phase processes with heterogeneous Ziegler–Natta or chromium catalysts, the homogeneous catalysts must be heterogenized [5] on a sup-

port (in most cases silica) in order to apply these processes. In addition, the heterogenized catalysts avoid reactor fouling and produce polymer particles of a desired regular morphology. The main routes reported in the literature for zirconocene immobilization have been classified by Ribeiro et al. [6]. The first method involves direct impregnation of the zirconocene onto the support, either with or without prior modification of the support. This method has been extensively studied by dos Santos and co-workers [7–9] for different zirconocenes. Silica that had been dehydroxylated at higher temperatures led to lower catalyst loadings but, after reaction with MAO, afforded highly active catalyst systems. High grafting temperatures and long contact times led to higher metal contents but led to a reduction in the activity of the system. Lower activity was found when high grafting temperatures or long reaction times were used. In the first case, μ-oxo surface species of the type ≡Si−O−Zr(Cp)₂Cl were proposed. These species are believed to form an active species with MAO, presumably by metathesis of the surface Si−O−M bond. Alkyl substitution of the cyclopentadienyl ligand did not have a significant effect on the metal loadings of the catalyst or the activity when compared to the corresponding homoge-

neous systems. Furthermore, the ethyl-bridged indenyl derivatives gave higher metal contents than the bulkier dimethylsilyl-bridged analogues. More active systems were obtained when the same zirconocenes were reacted with MAO-modified silica.

One of the most promising methods for zirconocene heterogenization involves the reaction between a functional group of the zirconocene molecule and a reactive group on the carrier surface. Recently, we described the synthesis and characterization of a series of indenyl zirconocenes bearing pendant chains with silicon ether groups [10]. These supported complexes show similar or higher activities than their corresponding homogeneous catalysts and have low Al/Zr ratios.

In this paper we describe spectroscopic studies on the reaction between a similar substituted zirconocene, [Zr{η^5-C$_5$H$_4$(CH$_2$)$_3$OSiMe$_3$}(η^5-C$_5$H$_5$)Cl$_2$] (**1**) and partially dehydroxylated silica. The reactivity is compared with that of the analogous unsubstituted complex, [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$] (**2**), which we studied previously [11].

2. Experimental

2.1. Materials

Grace Davison XPO 2407 silica (200 m^2/g, according to data from supplier) was dehydroxylated under vacuum (10^{-2} mmHg) for 16 h at the desired temperature [SiO$_2$(T)], cooled and stored under dry nitrogen. [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$] (**2**) (Strem), MeMgBr (Aldrich), ethylene (Alphagaz), Al^{i}Bu$_3$ (TIBA, Aldrich) and methylalumoxane (MAO, EURECENE 10, Crompton) were used without further purification. [Zr{η^5-C$_5$H$_4$(CH$_2$)$_3$OSiMe$_3$}(η^5-C$_5$H$_5$)Me$_2$] (**1**) and [Zr(η^5-C$_5$H$_5$)$_2$Me$_2$] (**4**) were prepared as described in the literature [12,13]. Toluene was distilled over sodium under a dry nitrogen atmosphere.

2.1.1. Synthesis and characterization of [Zr{η^5-C$_5$H$_4$(CH$_2$)$_3$OSiMe$_3$}(η^5-C$_5$H$_5$)Me$_2$] (3)

MeMgBr (3 M in THF) (0.53 mL, 1.60 mmol) was added to a solution of **1** (0.30 g, 0.71 mmol) in THF (50 mL) at 195 K. The reaction mixture was allowed to warm up to room temperature and stirred for 4 h. The solvent was removed in vacuo and hexane (25 mL) was added. After filtration, the solution was concentrated to 5 mL and cooled to −20 °C overnight to afford the title complex (0.15 g, 45%). ^{1}H NMR (ppm, C$_6$D$_6$): δ = −0.17 (s, 6H, ZrMe$_2$), 0.07 (s, 9H, SiMe$_3$), 1.89 (m, 2H, CpCH$_2$C*H$_2$*CH$_2$O), 2.62 (m, 2H, CpC*H$_2$*CH$_2$CH$_2$O), 3.64 (m, 2H, CpCH$_2$CH$_2$C*H$_2$*O), 5.59 (m, 2H, H^{3}H^4, C$_5$H$_4$(CH$_2$)$_3$OSiMe$_3$), 5.81 (m, 2H, H^{2}H^5, C$_5$*H$_4$*(CH$_2$)$_3$OSiMe$_3$), 5.88 (s, 5H, C$_5$H$_5$). ^{13}C NMR (ppm, C$_6$D$_6$): δ = −0.47 (SiMe$_3$), 26.42 (CpC*H$_2$*CH$_2$CH$_2$O), 30.15 (ZrMe$_2$), 34.64 (CpCH$_2$C*H$_2$*CH$_2$O), 61.74 (CpCH$_2$CH$_2$C*H$_2$*O), 107.77 (C^{3}C^4, C$_5$H$_4$(CH$_2$)$_3$OSiMe$_3$), 110.23 (C$_5$H$_5$), 110.61 (C^1, C$_5$H$_4$(CH$_2$)$_3$OSiMe$_3$), 110.93 (C^{2}C^5, C$_5$H$_4$(CH$_2$)$_3$OSiMe$_3$). Anal. calcd. for ZrC$_{18}$H$_{30}$OSi: C, 56.93, H, 7.92; found: C, 56,80, H, 7.90.

2.2. Catalyst preparation

The supported catalysts were prepared under an inert atmosphere using Schlenk techniques and a glove-box. A solution of the zirconocene in toluene (30 mL) was added to partially dehydroxylated silica (1 g) and the mixture was stirred at 333 K for 16 h. The slurries were filtered through fritted discs and washed 10 times with toluene (20 mL). The resultant solids were dried under vacuum at 343 K for 16 h. In the case of MAO-modified silica, SiO$_2$(298, 473, or 733) (1 g) was treated with 5 mL of the toluene MAO solution. The mixture was stirred at 333 K for 1 h and dried in vacuo. The resulting materials were impregnated with zirconocene toluene solutions, and the mixtures were stirred for 6 h at 333 K. The slurries were filtered through fritted discs and washed 10 times with toluene (20 mL). The resultant solids were dried under vacuum at 343 K for 16 h.

2.3. Characterization

Infrared spectra were recorded on a Nicolet Magna 550-FT spectrophotometer using an infrared cell equipped with CaF$_2$ or KBr windows; this set-up allowed *in situ* studies. A total of 32 scans were typically accumulated for each spectrum (resolution 2 cm^{-1}). The samples consisted of ca. 20 mg of silica pressed into a self-supported disc of 1 cm diameter. The samples were dehydroxylated at the desired temperature for 16 h. MAO-modified samples were treated with a 10% solution in toluene and dried in vacuo. Zirconocene grafting was performed using a 10^{-2} M solution of the zirconocene in toluene. The samples were warmed at 333 K for 1 h, washed with toluene and dried in vacuo at 343 K until no further change was observed (sublimation of a slight excess complex was observed in some cases). For unmodified silica, MAO was also added. Finally, the samples were exposed to ca. 50 Torr of ethylene for 10 min and evacuated in vacuo. The FT-IR analyses were repeated on three different samples in order to ensure reproducibility. NMR analyses were performed in CDCl$_3$ or toluene-d^8 using a Varian Unity 300 spectrometer. UV–vis analyses were performed using a Shimadzu UV-2501PC spectrophotometer. The soluble complexes were dissolved in dry toluene and placed in special cells under dry nitrogen (1.0 cm path length). The solid samples were suspended in Nujol to form a slurry. The absorption spectra were recorded between 190 and 900 nm and toluene or Nujol was used as a reference. The catalyst and polyethylene morphologies were identified by scanning electron microscopy (SEM) using a Philips XL 30 microscope. The solids were fixed on a carbon tape and then coated with gold by conventional sputtering techniques. Elemental analyses were determined at the Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany).

2.4. Polymerization tests

Polymerizations were carried out in a 250 mL glass reactor using toluene as a solvent. Catalysts (6×10^{-6} mol for the homogeneous reactions and 300 mg for the heterogeneous ones) were treated with the appropriate quantity of a solution of MAO in toluene (10% Al) for 15 min. In the case of
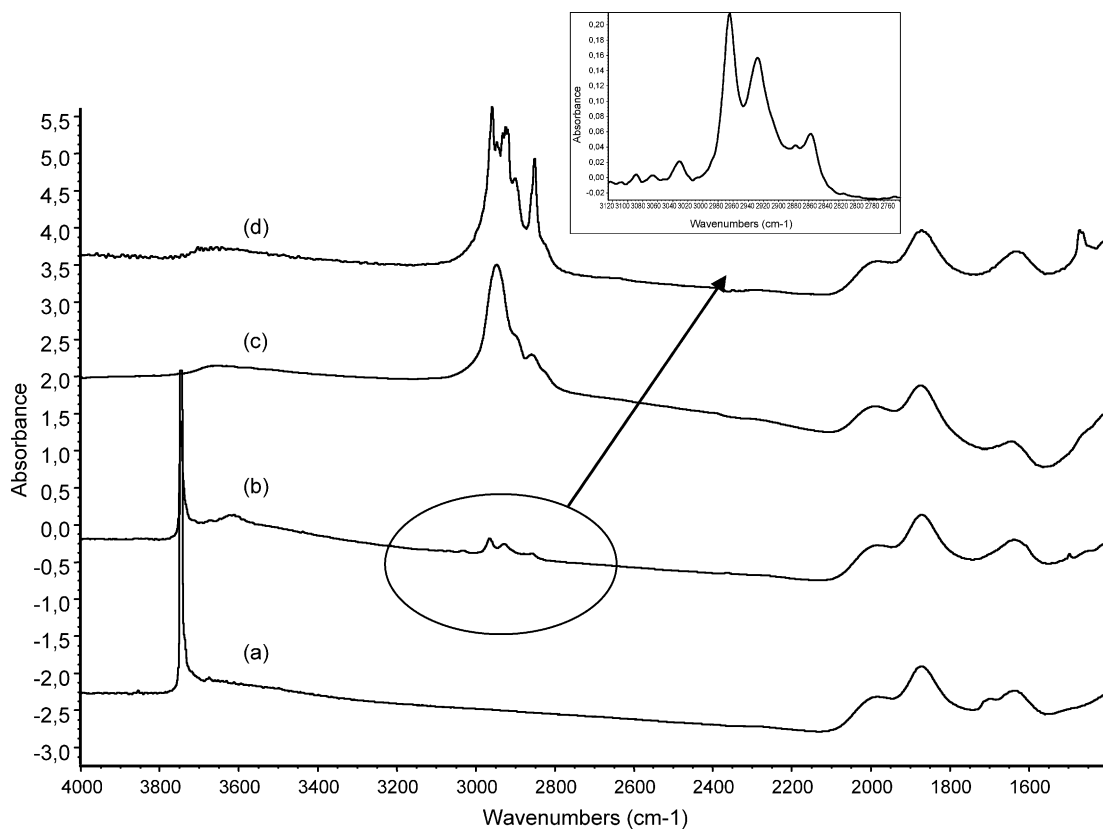
Fig. 1. (a) SiO$_2$(773). (b) After grafting of **1**. (c) After addition of MAO. (d) After contact with C$_2$H$_4$.

MAO-modified silica, additional MAO was not added. Toluene, TIBA scavenger (2 mL) and the activated catalyst (final volume ca. 100 mL) were introduced, in this order, into the reactor and thermostated at the desired temperature. Nitrogen was removed and a continuous flow of ethylene (1.5 bar) was introduced for 30 min. The reaction was then quenched by the addition of acidified methanol. The polymer was collected, washed with methanol and dried under vacuum at room temperature for 24 h.
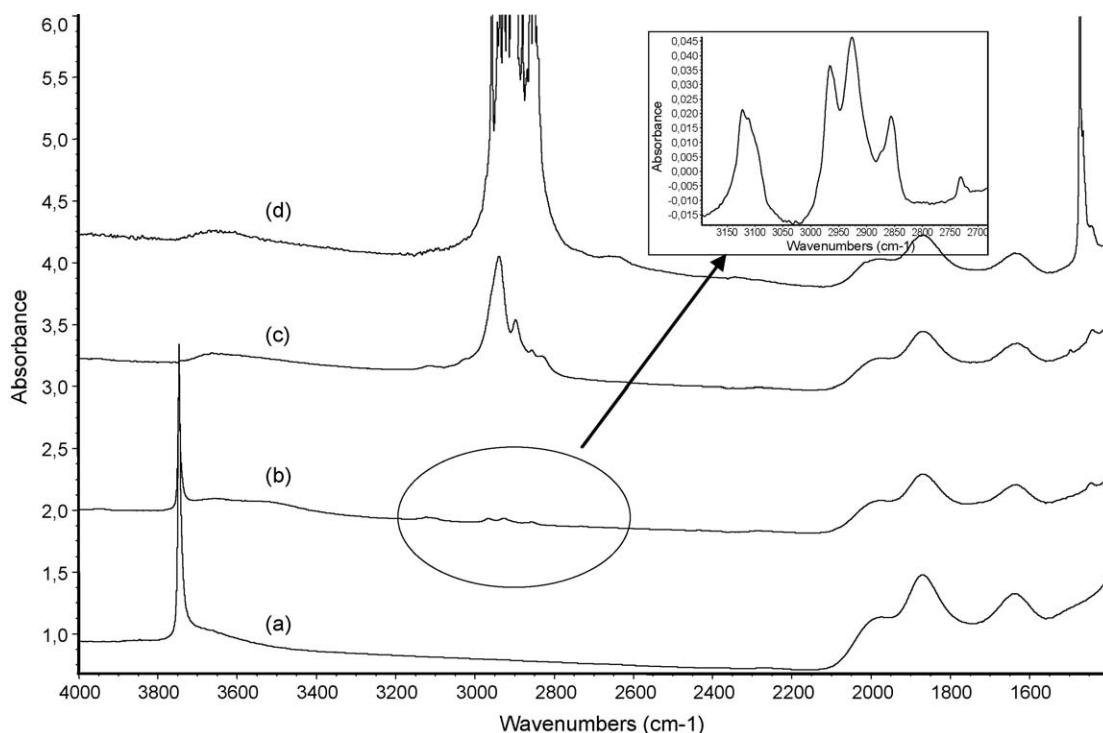

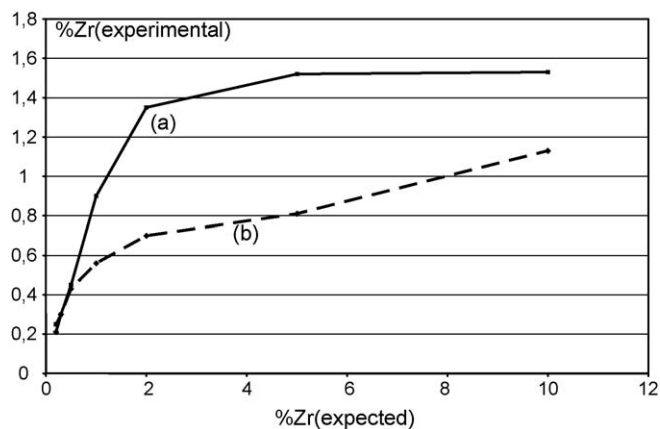Fig. 2. (a) SiO$_2$(773). (b) After grafting of **2**. (c) After addition of MAO. (d) After contact with C$_2$H$_4$.

Fig. 3. Adsorption isotherms (333 K) of Zr incorporated onto $SiO_2(773)$ as a function of the theoretical expected loading, from solutions of **1** (a) and **2** (b) in toluene.

3. Results and discussion

The IR spectra corresponding to the reaction between a toluene solution of **1** and the surface of partially dehydroxylated silica after removal of the solvent (see Section 2) are shown in Fig. 1. The spectrum of silica preheated at 773 K in vacuo [SiO_2(773 K)] has a sharp band at 3747 cm^{-1} (assigned to isolated OH groups [14]) with a small, broad shoulder at 3670 cm^{-1}, which can be attributed to silanols that are perturbed due to interparticle contacts [14] or to OH groups deeply retained within the pores [15] (Fig. 1a). The magnitude of the silanol number, which is independent of the origin and structural characteristics of amorphous silica, is considered to be ca.

1.8 OHnm^{-2} for a silica dehydroxylated at 733 K [16]. Bands at 1866 cm^{-1} and 1640 cm^{-1} are combinations and overtone bands, respectively, of Si–O network bonds. After contact with the zirconocene solution and removal of the solvent (Fig. 1b), new bands can be seen in the 2900 cm^{-1} and 1400 cm^{-1} regions and these correspond to stretching and bending modes of organic ligands. The OH groups that were initially isolated are now partially perturbed, generating broad ν(OH) bands at lower frequencies due to an interaction with the Cp π-electron system through hydrogen bonding [17]. The total intensity of the band due to the hydroxyl groups was slightly different after the addition of an excess of zirconocene solution, a situation also observed by dos Santos et al. [7] in the reaction between partially dehydroxylated silica and Cp$^{nBu}_2$ZrCl$_2$. Similar spectra were obtained with complex **2** (Fig. 2).

The amount of zirconocene grafted onto silica from toluene solutions was determined by increasing the zirconium contents in the initial solutions. The resulting adsorption isotherms, at 333 K, are shown in Fig. 3. The curves show that the zirconium loading approaches a saturation limit, near to 1%, that is typical of chemisorption. The limit was very low, even when a large excess of zirconocene and long reaction times were used. Taking in account the aforementioned [OH] of about 1.8 OHnm^{-2}, one can expect a theoretical maximum loading of 5–6% of Zr on the assumption that one zirconocene molecule reacts with one silanol group. The weak basicity of the chloro ligands and the weak acidity of the Si–OH groups could explain the difficulty in obtaining higher loadings. It is noteworthy that complex **1** allows us to obtain more grafted complex than the unsubstituted complex **2** for solutions with similar concentrations.
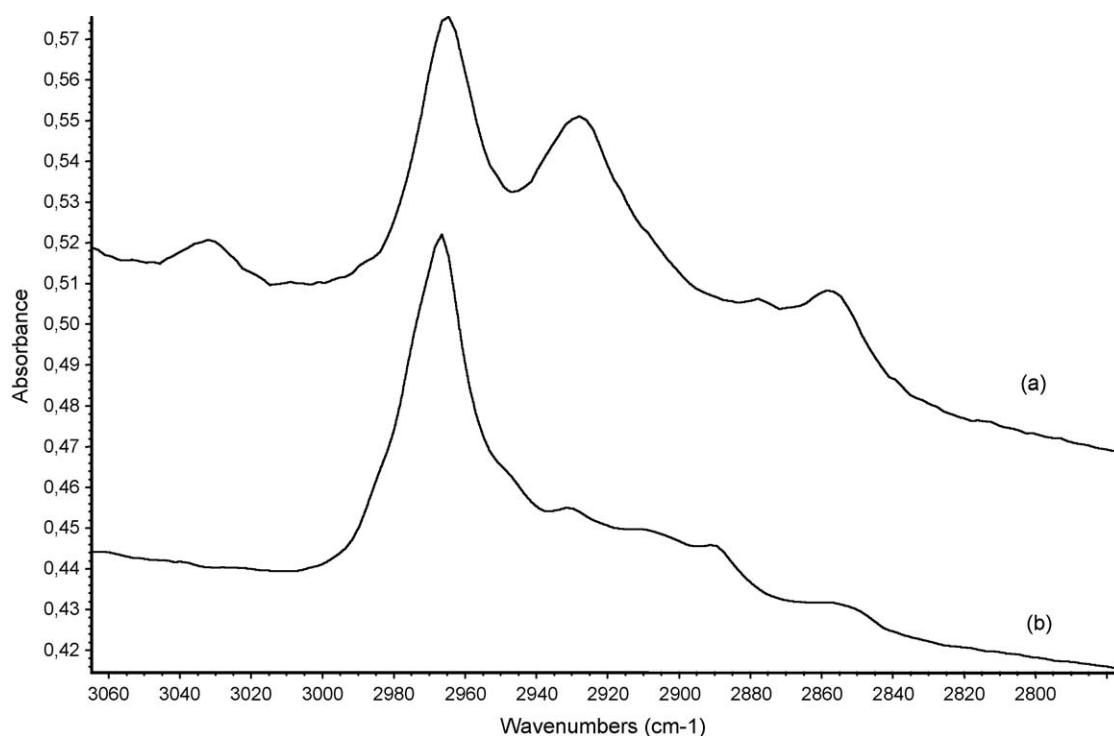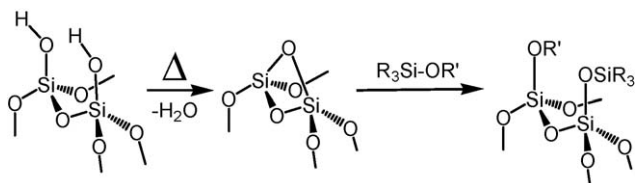

Fig. 4. (a) FT-IR spectrum of 1.SiO_2(773). (b) FT-IR spectrum of ^{n}PrOSiMe$_3$·SiO_2(773).

Scheme 1.

It is well established that the surface hydroxyl density in silica decreases with thermal activation as result of an increase in the number of siloxane reactive bridges. These strained groups can activate covalent bonds [18] such as the Si−O bond in silicon ethers (Scheme 1).

Basset et al. proposed [19] the reaction between a supported zirconium hydride and vicinal SiOSi bridges on silica dehydroxylated at 723 K. Yoshida et al. [20] proposed that the strained siloxane groups are, in fact, radical sites of the type $\equiv$Si–O$^\bullet$ and $^\bullet$Si$\equiv$ present in silicas dehydroxylated above 673 K. These sites are characterized by bands at 891 and 910 cm^{-1} in their IR spectra. Similar weak bands at 908 and 897 cm^{-1} were observed in the spectra of SiO$_2$(773). After contact with zirconocenes, these bands are no longer present, indicating a reaction between **1** or **2** and these groups. A new band is observed at 900 cm^{-1} and this can be tentatively assigned to ZrOSi bonds.

In order to gain a deeper insight into the possible type of reaction between complex **1** and the surface of the dehydroxylated silica, we carried out the reaction with ^{n}PrOSiMe$_3$ in an attempt to provide a simpler model for this zirconocene. The IR spectra corresponding to both grafted complex **1** and model ^{n}PrOSiMe$_3$ are shown in Fig. 4. We observed a similar spectrum to those described in the literature, where this silyl ether was proposed to reacts with the reactive siloxane bridge groups [21,22]; a decrease in the intensity of the signal due to the isolated silanol groups was not observed, although a broad neighbouring wide appeared when the compound was fixed, due to the perturbation of these silanol groups by the anchored silyl ether. If we compare the bands of this supported organosilane with those of the supported complex **1**, a clear similarity can be observed. The similar bands could be due to the trimethylsilyl group (2960 cm^{-1}; the free organosilane compound shows a strong band at 2970 cm^{-1}) and alkyl chains of the two materials, although an additional band corresponding to the methyl group (1985 cm^{-1}) is observed in the spectrum of the silyl ether but is not present in the supported zirconocene spectrum. This similarity in the two spectra indicates that complex **1** may be able to react with the surface of the silica in a similar way to the organosilane, namely through the interaction with siloxane bridge groups. However, this possibility does not rule out the alternative interaction between the chloro ligands and the more acidic silanol groups in the reaction of complex **1** with the silica surface.

In addition, elemental analysis of supported complex **1** reveals a Cl/Zr = 1.2/1 ratio, which is slightly higher than one would find for a typical reaction with only silanol groups.

These results, in conjunction with the literature precedents, seem to indicate that the reaction between **1** or **2** and the silica surface, at mild temperatures, can occur through the interaction with the acidic silanol groups but also, to some extent, with the reactive siloxane bridges (Scheme 2). Complex **2** only can follow such a pathway by using the Zr−Cl groups [11], while complex **1** also has the possibility of reacting through the silicon ether functional group with the bridge siloxane groups (Scheme 2). This possibility would allow us to obtain a higher level of fixed complex **1** in comparison with complex **2** under similar conditions.

The behaviour of the catalyst systems after the addition of the MAO cocatalyst was also studied by FT-IR spectroscopy. The IR spectra of samples of 1.SiO$_2$(773) and 2.SiO$_2$(773) treated with MAO (approximately Al/Zr = 100) are shown in Figs. 1c and 2c. After this treatment, the infrared band attributed to isolated silanol groups (at 3747 cm^{-1}) disappeared completely at room temperature, indicating that a reaction between some basic methyl groups of MAO (or TMA present in MAO) and acidic silanols had taken place. At the same time, new bands appeared in the ν(CH) region—one strong band at 2940 cm^{-1} and three weak bands at 2898, 2856 and 2838 cm^{-1}. These bands are assigned to stretching vibrations of C−H bonds of the methyl groups in MAO. In this way, the grafted MAO could activate the surface bonded zirconocenes of the neighbouring regions [23].
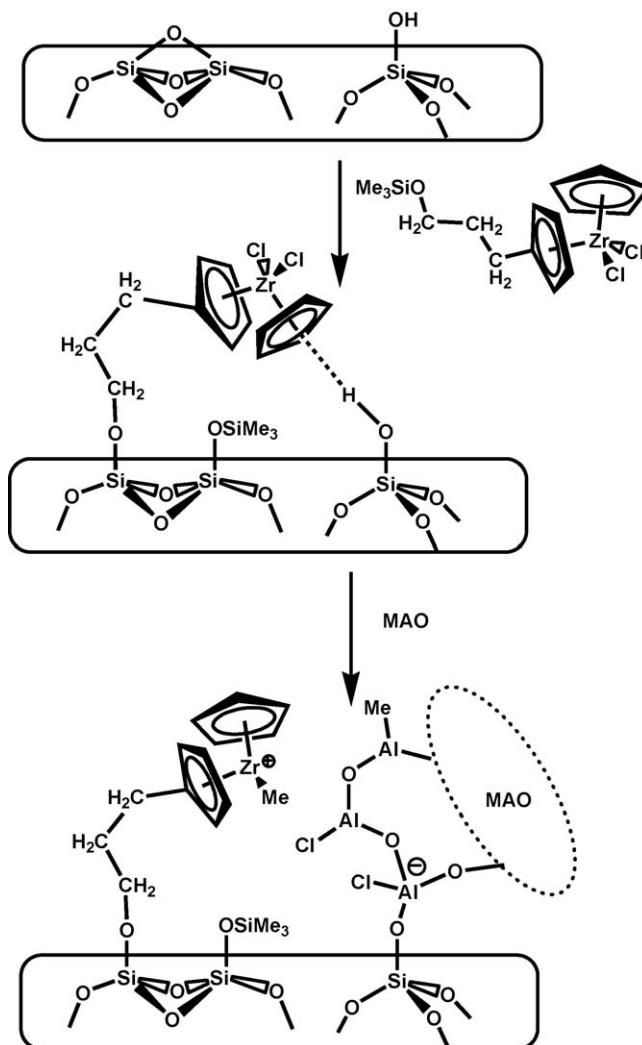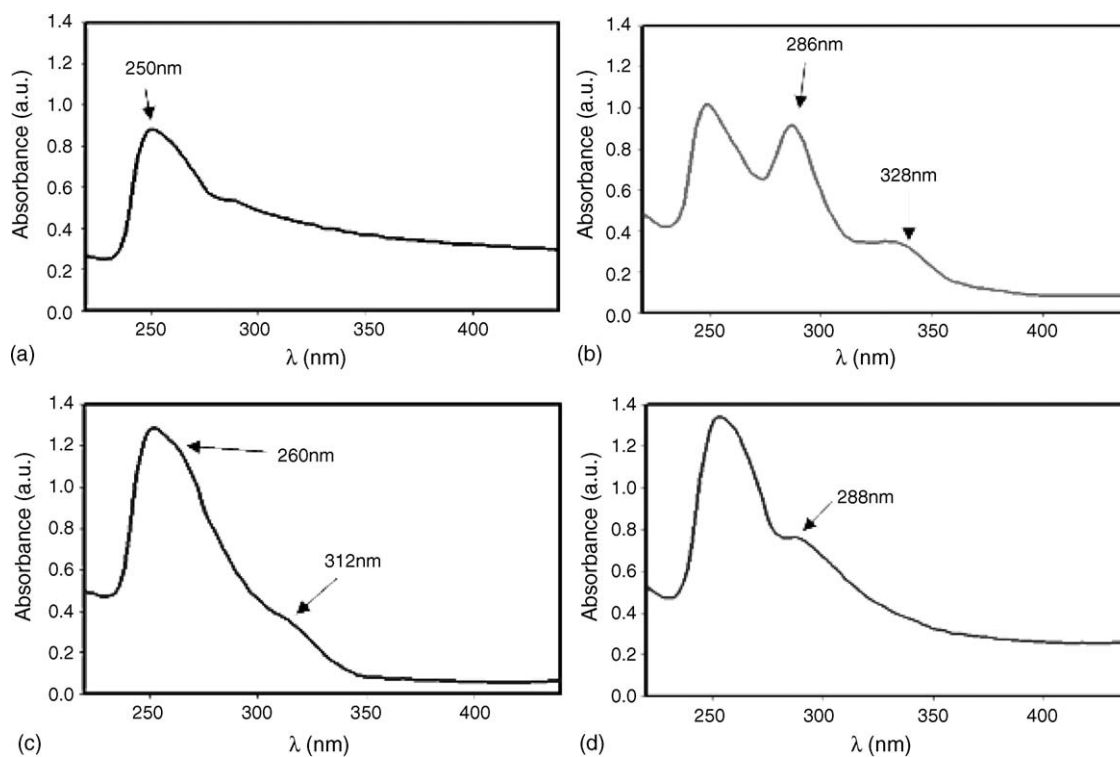

Scheme 2.

Fig. 5. UV–vis spectra of: (a) SiO$_2$(773); (b) complex **2**; (c) 2.SiO$_2$(773); (d) after the addition of MAO.

This situation could lead to the formation of the potentially active alkylcationic surface species. The activity of these supported zirconocenes, after activation with MAO, towards ethylene polymerization was confirmed by following the appearance of vibra- tions due to polyethylene in the regions 3000–2800 cm^{-1} and 1500–1300 cm^{-1} (Figs. 1d and 2d). Intense bands were observed at 2970, 2850 and 1380 cm^{-1}, which correspond, respectively, to the ν(CH) and δ(CH) vibrations of polyethylene.
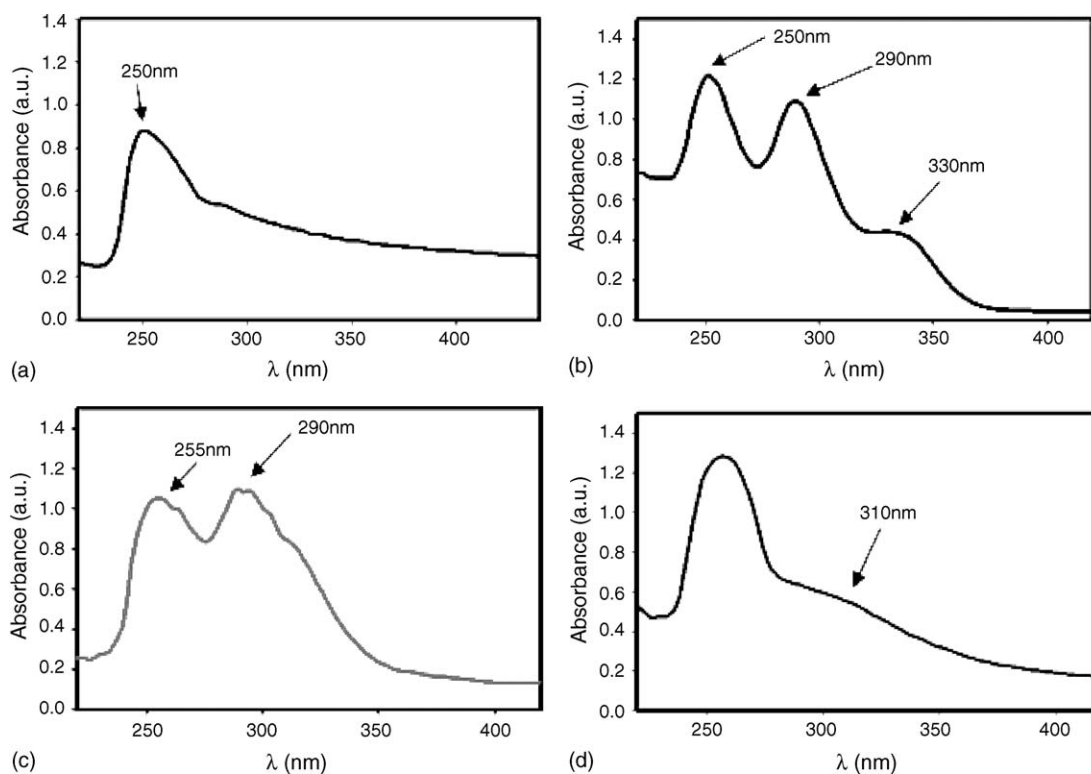

Fig. 6. UV–vis spectra of: (a) SiO$_2$(773); (b) complex **1**; (c) 1.SiO$_2$(773); (d) after the addition of MAO.

We carried out an analysis of the activation process by UV–vis spectroscopy. A UV–vis analysis of the supported catalyst **2** is represented in Fig. 5. After grafting, a broad band can be seen at 250 nm, corresponding to the SiO$_2$ support, and two shoulders appear at 260 and 312 nm, assigned to the supported complex **2** (Fig. 5c). There is a notable difference with the spectrum of free complex **2** in Nujol (Fig. 5b). After the addition of MAO (Al/Zr = 100, Fig. 5d), an increase in the 250 nm band was observed due to the presence of supported MAO and, in addition, a weak band appeared at 288 nm. This bathochromic shift suggests the formation of the active monomethyl cations [24].

In contrast with these results (Fig. 6), supported complex **1** shows a similar spectrum to that of the free complex, i.e., slightly shifted to higher wavelengths, indicating some similarity between the structure of the free molecular complex and the grafted one (Scheme 2). A new spectrum was obtained after the addition of MAO and this had a broad band at 310 nm, tentatively assigned to the active species on the basis of the spectrum of complex **1** activated by MAO in solution (Fig. 7). We also carried out UV–vis analyses of complexes **1** and **2** in solution. At low Al/Zr ratios (Fig. 7b and f) the spectra of solution samples show a maximum wavelength shifted to lower values than those of the original complexes (λ_{max} = 298 nm for complex **1** and 302 nm for complex **2**), as proposed in other zirconocene systems [25–27]. These spectra can be attributed to the monomethyl chloride species by exchange of a chloro ligand with a methyl group of TMA or MAO. If we compare the bands obtained at low Al/Zr ratios with those of the spectra of dimethyl derivatives **3** and **4** (Fig. 7c and g, λ_{max} = 284 nm for **3** and 293 nm for **4**), it can be observed that the spectra of the dimethyl species show bands shifted to lower wavelengths. The higher electronic densi-

ties associated with these dialkyl zirconocenes lead to a greater hypsochromic shift from the starting complex in comparison to the respective monomethyl derivatives.

A shift to higher wavelengths was observed for higher aluminium contents, indicating a decrease in the electronic density around the metal centre due to the formation of active cation-like species (Fig. 7d and h, λ_{max} = 326 nm for **1** and 308 nm for **2**). These bands are very similar to those found in the spectra of the supported species. It is noteworthy that complex **1** can be activated at lower Al/Zr ratios than complex **2** (Al/Zr = 300 and 500, respectively).

In order to determine the influence of the sequence of steps in the preparation of the catalyst, complex **1** was supported in previously modified MAO silicas. Silica was first dehydroxylated at different temperatures (298, 473, 773 K) and then treated with a toluene MAO solution. For example, the IR spectrum of a sample of SiO$_2$(473) treated with MAO is shown in Fig. 8b. After this treatment, the infrared band attributed to isolated silanol groups disappeared, indicating a reaction between the basic methyl groups of MAO and acidic silanols. At the same time, new bands appeared in the ν(CH) region which were assigned to stretching vibrations of the methyl groups in MAO. The impregnation with a toluene solution of complex **1** and further solvent elimination gives rise to the appearance in the spectrum (Fig. 8c) of new bands at 2953 and 2856 cm^{-1}, assigned to the supported complex. We postulate a possible bonding between the Lewis basic oxygen atom of the silyl ether and some aluminium centres in MAO.

The activation process was followed by UV–vis spectroscopy. The spectra of the proposed active species are shown in Fig. 9 for the sample in which zirconocene **1** was first supported and then activated by MAO (Fig. 9b) along with that in which the
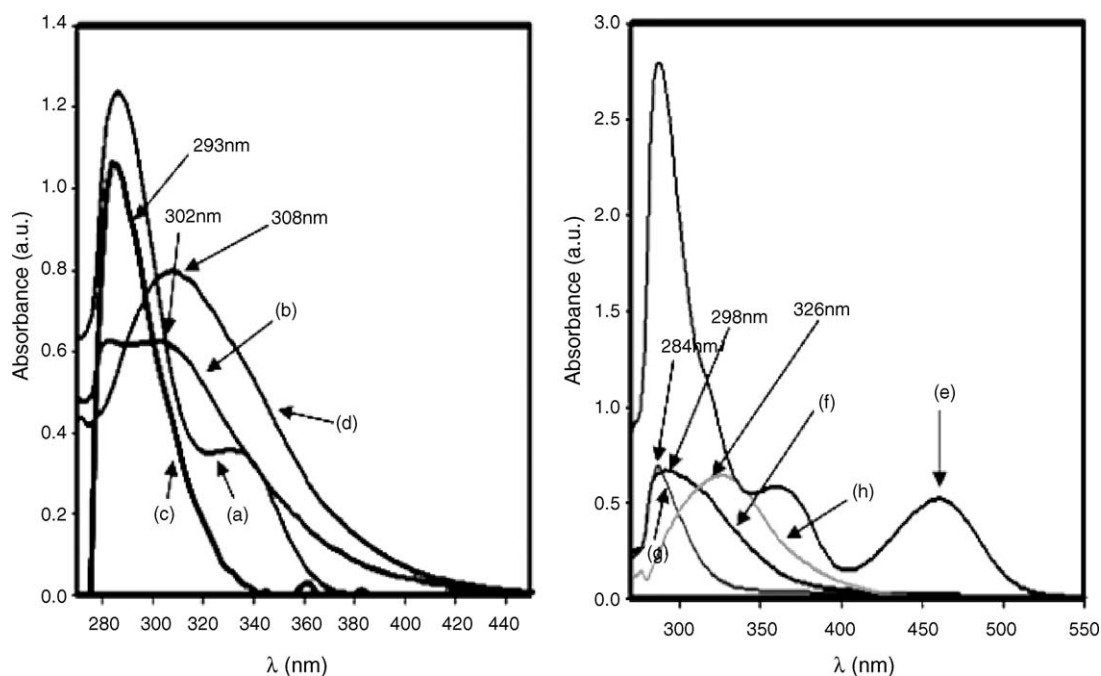

Fig. 7. UV–vis solution spectra of: (a) complex **1**; (b) complex **1** after MAO addition Al/Zr = 10; (c) complex **3**; (d) complex **1** after MAO addition Al/Zr = 300; (e) complex **2**; (f) complex **2** after MAO addition Al/Zr = 70; (g) complex **4**; (h) complex **2** after MAO addition Al/Zr = 500.
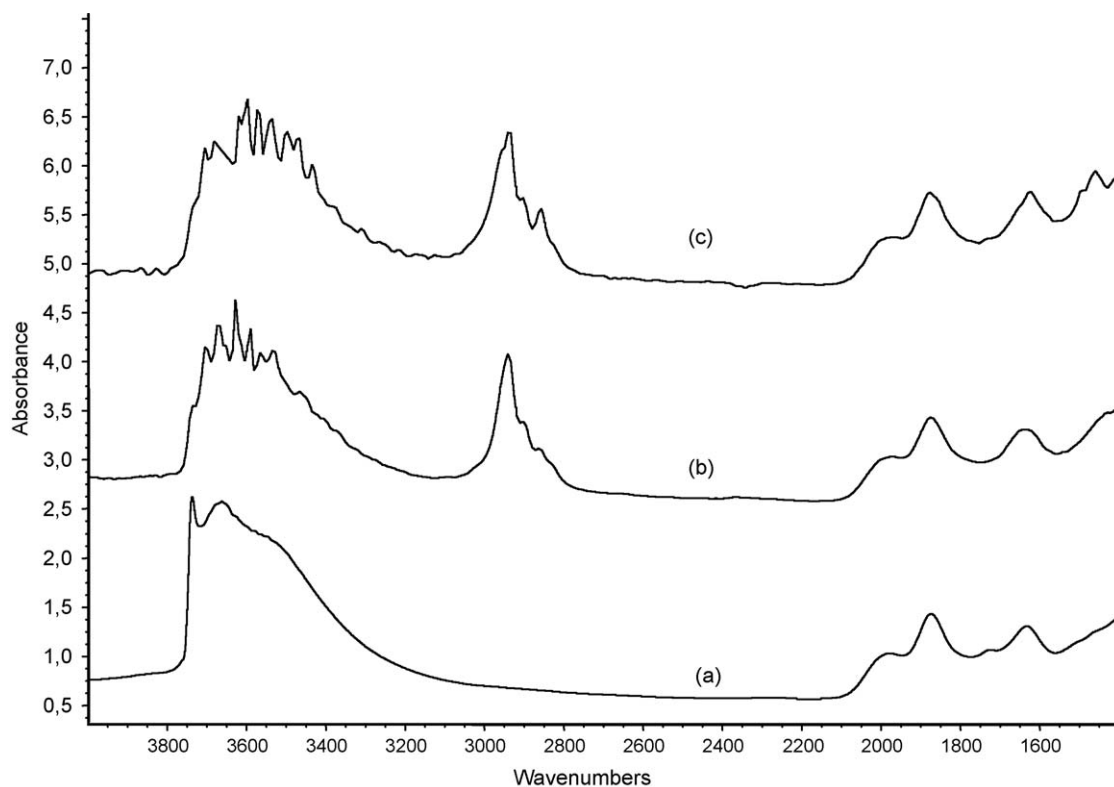
Fig. 8. FT-IR spectra of: (a) SiO$_2$(473); (b) after modification with (MAO); (c) after addition of complex **1**.

complex was supported on MAO-modified silica (Fig. 9b and d). In both cases, a similar λ_{max} band was observed (near 310 nm) but the intensity of this band was higher in the MAO-modified supported samples, thus indicating a possible higher content in active species.

Catalytic activities in ethylene polymerization were tested for the zirconocene supported on unmodified and modified silicas. The results are summarized in Table 1. In accordance with the surface species described, the catalysts based on complex **1**, which probably contains surface zirconocene molecules

anchored by the functional ether group, in comparison to the free zirconocene generally have higher activities than those based on complex **2**. In the latter case, the activation by MAO involves the breaking of strong Zr−O(surface) bonds [11]. In addition, these activity results are very similar to those found in previous studies [7,8,28], even when the new grafted species were activated with a low Al/Zr ratio of 200. Better results were obtained when silica was previously modified by MAO, as expected from the UV–vis spectra (see above). It can be seen that the dehydroxylation temperature has a significant influence on the final activity of the catalyst. Silica dehydroxylated at room temperature probably contains enough physisorbed water to deactivate the majority of the MAO. On the other hand, high temperature dehydroxylation eliminates reactive surface groups, i.e., acidic silanols, which probably reduces the possibilities for adequate
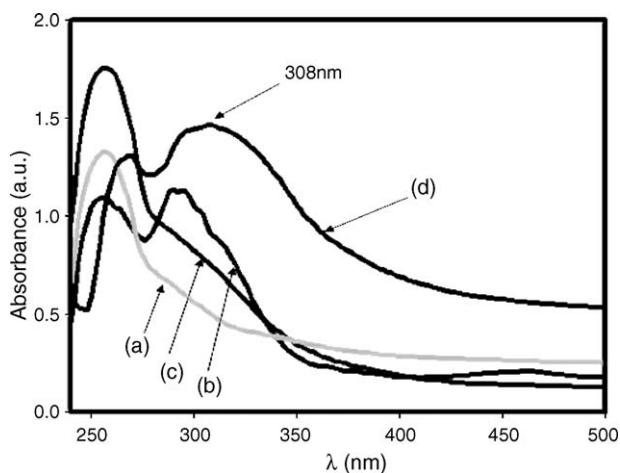

Fig. 9. UV–vis spectra of: (a) MAO-modified SiO$_2$(473); (b) complex **1** supported on SiO$_2$(773); (c) complex **1** supported on SiO$_2$(773) after reaction with MAO; (d) complex **1** supported on MAO-modified SiO$_2$(473).

Table 1
Catalytic activities in ethylene polymerization for the different supported systems on unmodified and modified silicas

Catalyst	% Zr	% Al	Activity (kg PE/mol Zr h^{-1})
1.SiO$_2$(773)	0.30	–	247
2.SiO$_2$(773)	0.35	–	111
1.[SiO$_2$(298)-MAO]	0.25	17.5	316
1.[SiO$_2$(473)-MAO]	0.24	15.6	555
1.[SiO$_2$(773)-MAO]	0.29	15.5	343
2.[SiO$_2$(473)-MAO]	0.31	14.9	79

Polymerization conditions are as follows: $P = 1.5$ bar; 300 mg of catalyst; [Al]/[Zr] approximately 200; $T = 343$ K; solvent = toluene (200 mL); scavenger = TIBA (2 mL); time = 30 min.
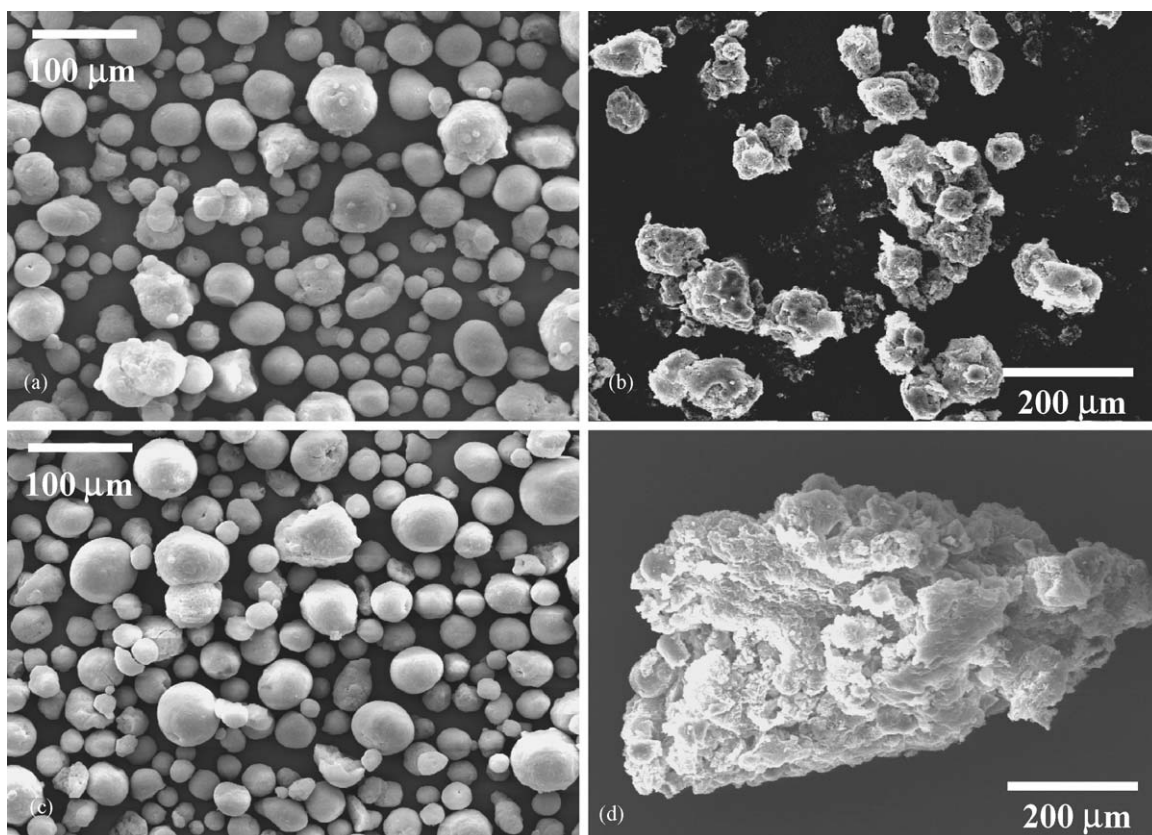
Fig. 10. SEM images of: (a) 1.[SiO$_2$(473)-MAO] (200×); (b) the polyethylene produced with 1.[SiO$_2$(473)-MAO] (100×); (c) 1.SiO$_2$(773) (200×); (d) the polyethylene produced with 1.SiO$_2$(773) (100×).

MAO fixation. Once again, complex **1** proved to be more active than complex **2**. Furthermore, these supported catalysts produce polymers with good morphology. Scanning electron microscope (SEM) images of supported catalyst on unmodified and MAO-modified silica as well as the resulting polyethylene are shown in Fig. 10. The catalyst images predominantly show round particles of around 50 μm. Likewise, the polyethylene obtained using the MAO-modified silica catalysts grew as particles with a regular round shape (Fig. 10b), but shapeless aggregates were found for the samples prepared from directly supported zirconocene supported (Fig. 10d). This could be due to a better dispersion of the catalyst in the former samples. From a practical point of view, and considering both the results of catalytic activity and the polymer morphology, it seems that the procedure involving previous modification the silica with MAO and subsequent supporting of the complex is the more effective.

4. Conclusions

The reaction of [Zr{η^5-C$_5$H$_4$(CH$_2$)$_3$OSiMe$_3$}(η^5-C$_5$H$_5$)Cl$_2$] (**1**) or [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$] (**2**) and SiO$_2$(773) at a mild temperature produces grafting of the zirconocene by reaction between the weakly acidic silanol groups and the reactive siloxane bridges on the surface and the Zr–Cl bonds. In addition, complex **1** was able to react with the surface of the silica by means of its silicon ether substituent, as proposed for similar organosilane compounds. This latter process gives rise to more active zirconocene surface species. A better catalyst was obtained when dehydroxylated silica was modified with MAO. In addition, this supported catalyst allows to produce polyethylene particles with a regular shape.

References

[1] W. Kaminsky, J. Chem. Soc., Dalton Trans. 1413 (1998).
[2] H.G. Alt, A. Koppl, Chem. Rev. 100 (2000) 1205.
[3] H.-H. Brintzinger, D. Fisher, R. Muelhaupt, B. Rieger, R. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143.
[4] S. Miyake, Y. Okumura, S. Inazawa, Macromolecules 28 (1995) 3074.
[5] J.R. Severn, J.C. Chadwick, R. Duchateau, N. Friederichs, Chem. Rev. 105 (2005) 4073.
[6] M.R. Ribeiro, A.D. Deffieux, M.F. Portela, Ind. Eng. Chem. Res. 36 (1997) 1224.
[7] J.H.Z. dos Santos, C. Krug, M.B. da Rosa, F.C. Stedile, J. Dupont, M.deC. Forte, J. Mol. Catal. A: Chem. 139 (1999) 199.
[8] J.H.Z. dos Santos, A. Larentis, M.B. da Rosa, C. Krug, I.J.R. Baumvol, J. Dupont, F.C. Stedile, M.deC. Forte, Macromol. Chem. Phys. 200 (1999) 751.

[9] R. Guimaraes, F.C. Stedile, J.H.Z. dos Santos, J. Mol. Catal. A: Chem. 206 (2003) 353.

[10] C. Alonso-Moreno, A. Antiñolo, F. Carrillo-Hermosilla, P. Carrión, I. López-Solera, A. Otero, S. Prashar, J. Sancho, Eur. J. Inorg. Chem. (2005) 2924.

[11] C. Alonso, A. Antiñolo, F. Carrillo-Hermosilla, P. Carrión, A. Otero, J. Sancho, E. Villaseñor, J. Mol. Catal. A: Chem. 220 (2004) 285.

[12] J. Sancho, G. Hidalgo, A. Muñoz-Escalona, M.F. Martínez-Núñez, C. Martín, P. Lafuente, B. Peña, Eur. Pat. Appl. 839836 (1998).

[13] E. Samuel, M.D. Rausch, J. Am. Chem. Soc. 95 (1973) 6263.

[14] B.A. Morrow, Stud. Surf. Sci. Catal. 57 (1990) 161.

[15] M.C. Haag, C. Krug, J. Dupont, G. Barrera, J.H.Z. dos Santos, T. Uozumi, T. Sano, K. Soga, J. Mol. Catal. A: Chem. 169 (2001) 275.

[16] P. Hoffman, E. Knoezinger, Surf. Sci. 188 (1987) 181.

[17] L.T. Zhuraviev, Colloids Surf. A: Physicochem. Eng. Aspects 74 (1993) 71.

[18] B.A. Morrow, I.A. Cody, J. Phys. Chem. 80 (1976) 1998.

[19] J. Corker, F. Lefebvre, C. Lécuyer, V. Dufaud, F. Quignard, A. Choplin, J. Evans, J.-M. Basset, Science 271 (1996) 966.

[20] Y. Inaki, H. Yoshida, T. Yoshida, T. Hattori, J. Phys. Chem. B 106 (2002) 9098.

[21] J. Blümel, J. Am. Chem. Soc. 117 (1995) 2112.

[22] L.H. Dubois, B.R. Zegarski, J. Am. Chem. Soc. 115 (1993) 1191.

[23] J.C.W. Chien, Top. Catal. 7 (1999) 23.

[24] J.H.Z. dos Santos, H.F. Ban, T. Teranishi, T. Uozumi, T. Sano, K. Soga, J. Mol. Catal. A: Chem. 158 (2000) 541.

[25] A. Deffieux, H. Cramail, J.N. Pédeutour, Polym. Prepr. 41 (2000) 1887.

[26] J.N. Pédeutour, D. Coevoet, H. Cramail, A. Deffieux, Macromol. Chem. Phys. 200 (1999) 1215.

[27] D. Coevoet, H. Cramail, A. Deffieux, Macromol. Chem. Phys. 199 (1998) 1451.

[28] B.L. Moroz, N.V. Semikolenova, A.V. Nosov, V.A. Zakharov, S. Nagy, N.J. O'Reilly, J. Mol. Catal. A: Chem. 130 (1998) 121.