Modified silicas as supports for single-site zirconocene catalysts

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Abstract

The reactivity of Cp_2ZrCl_2 towards partially dehydroxylated silica was evaluated and the effects of chemical modification of this silica were studied. Different modified silicas were prepared by reaction of the original partially dehydroxylated silica with silicon ethers, $EtOSiMe_3$ and $(Me_3Si)_2O$, or a silazane, $(Me_3Si)_2NH$. The resulting materials were activated with MAO and the catalytic systems were evaluated in ethylene polymerization. The different reactions were monitored by FT-IR spectroscopy. The catalysts were characterized by elemental analysis as well as by infrared and UV–vis spectroscopy. Grafting of organosilanes occurs by reaction with reactive siloxane bridges. The new SiR_3 groups formed on the surface react with Cp_2ZrCl_2 to form volatile $ClSiMe_3$ and oxo zirconium species. These latter species are active, after the addition of MAO, in ethylene polymerization. The effects caused by changing the nature of the modifier in the grafting reaction with the metallocene, as well as the catalytic activities of the resulting materials, are presented and discussed.
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1. Introduction

Supported single-site catalysts are being used around the world to make 2 billion lb of polyethylene a year. In comparison with conventional Ziegler–Natta systems, metallocene-based catalysts offer greater versatility and flexibility both for the synthesis and the control of the structures of polyolefins: high density polyethylene, stereoregular polypropylene and copolymers. Polymers made using metallocene-catalyzed reactions offer superior product properties ranging from toughness to clarity.

The influence of the nature of the metallocene on the catalytic performance and the properties of the final polymer is the subject of considerable research in the field of applied organometallic chemistry [1]. The main routes reported in the literature for metallocene immobilization have been classified by Ribeiro et al. [2]. The first method involves direct impregnation of the metallocene onto the support, either with or without prior modification of the support. Soga et al. [3] prepared a number of supported catalysts in which silica was initially modified by treatment with Cl_2SiMe_2, followed by MAO, and finally grafting of Cp_2ZrCl_2. Such systems were shown to be active in the presence of common trialkylaluminium cocatalysts. Moroz et al. [4] prepared a supported metallocene catalyst by treating a silylated silica, obtained by the reaction of dehydroxylated silica with $ClSiMe_3$, with Cp_2ZrCl_2. The resulting material had a zirconium content of 0.1% and, in combination with MAO, was found to be an active catalyst for ethylene polymerization ($55\,KgPE\,molZr^{-1}\,h^{-1}\,bar^{-1}$, $Al/Zr = 100$). However, polyethylene obtained under these conditions consists of shapeless aggregates similar to those obtained with homogeneous catalysts. Recently, dos Santos et al. [5] presented results concerning the influence of organosilicon modifiers on the grafting of $Cp^{nBu}_2ZrCl_2$ $[Cp^{nBu} = \eta^5\text{-}C_5H_4(^nBu)]$ onto a modified silica surface. In this case, the chemical modification of SiO_2 with organosilicons prior to zirconocene grafting seems a promising approach to prevent bimolecular deactivation. Thus, the main function of the organosilane was found to be as

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a spacer to keep apart metallocene species on the silica surface.

The work described here concerns new results on the grafting of the metallocene Cp_2ZrCl_2 ($Cp = \eta^5\text{-}C_5H_5$) onto a commercial, partially dehydroxylated silica modified with a silazane or silicon ethers. The influence of the nature of the modifier on the polymerization of ethylene, after MAO activation with a low Al/Zr ratio, was also studied. The surface reactions were monitored by transmission infrared spectroscopy (FT-IR).

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 773 K [$SiO_2(773)$], cooled and stored under dry nitrogen. Cp_2ZrCl_2 (Strem), ethylene (Alphagaz), Al^iBu_3 (TIBA, Aldrich) and MAO (EURECENE 10, Crompton) were used without further purification. $EtOSiMe_3$, $(Me_3Si)_2O$ and $(Me_3Si)_2NH$ (Aldrich) were degassed and stored under dry nitrogen over molecular sieves. Toluene was distilled over sodium under a dry nitrogen atmosphere.

2.2. Catalyst preparation

The supported catalysts were prepared under an inert atmosphere using Schlenk techniques and a glove-box. A solution of Cp_2ZrCl_2 (32 mg) (to obtain a theoretical level of 1% Zr/SiO_2) in toluene (30 mL) was added to partially dehydroxylated silica $SiO_2(773)$ (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. A similar procedure was followed for modified silicas. In this case, $SiO_2(773)$ (1 g) was treated with an excess (5 mL) of the corresponding organosilane and the mixture stirred at 333 K for 16 h. The solids were carefully washed with toluene, dried and the resulting materials were impregnated with metallocene solution as described above.

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 773 K for 16 h. Samples were exposed to an excess of organosilicon vapours, warmed at 333 K for 16 h and dried in vacuo for 6 h until reproducible spectra were observed. Zirconocene grafting was performed using a $10^{-2}\,M$ solution of the metallocene in toluene to give approximately 1% Zr/SiO_2. 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 light excess complex was observed). MAO was added as a 10% solution in toluene and the amount was calculated to give an Al/Zr ratio of ca. 1:150. After evaporation of solvent, the sample was 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 toluene-d^8 using a Varian Unity 300 spectrometer. UV–vis analyses were performed using a Shimadzu UV-2501PC spectrophotometer. The samples were suspended in Nujol to form a slurry and placed in special cells under dry nitrogen (1.0 cm path length). The absorption spectra were recorded between 190 and 900 nm and Nujol was used as a reference. Zr and C contents were determined at the Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany).

2.4. Polymerization tests

Polymerizations were carried out in a 1 L glass reactor using toluene as a solvent (ca. 250 mL). Catalysts (300 mg) were treated with the appropriate quantity of a solution of MAO in toluene (10% Al) for 15 min. The solvent and the volatiles were removed in vacuo. Toluene (230 mL), TIBA scavenger (2 mL) and activated catalyst in freshly distilled toluene (20 mL) were introduced, in this order, into the reactor and thermostated at 343 K. 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.

3. Results and discussion

Fig. 1 shows IR spectra corresponding to the reaction between a toluene solution of Cp_2ZrCl_2 (1) and the surface of an unmodified partially dehydroxylated silica, after removal of the solvent (see Section 2). The spectrum of silica preheated at 773 K [$SiO_2(773\,K)$] has a sharp band at $3747\,cm^{-1}$ (assigned to isolated OH groups [6]) with a small, broad shoulder at $3670\,cm^{-1}$, which can be attributed to silanols that are perturbed due to interparticle contacts [6] or to OH groups retained deep within the pores [7] (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 [8]. Bands at 1866 and $1640\,cm^{-1}$ are combinations and overtone bands of Si–O network bonds. After contact with the metallocene solution and removal of
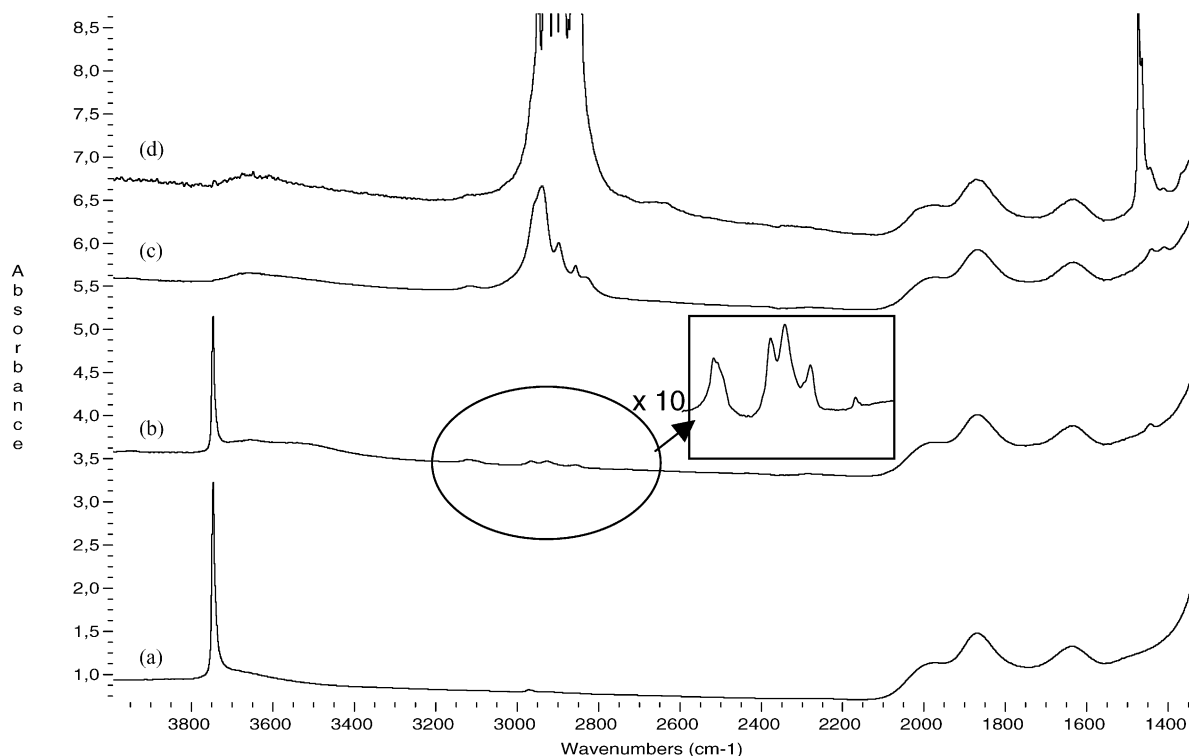
Fig. 1. (a) SiO$_2$(773); (b) after grafting of Cp$_2$ZrCl$_2$ (**1**); (c) after addition of MAO and; (d) after contact with C$_2$H$_4$.

the solvent (Fig. 1b), new bands can be seen in the 2900 and 1400 cm^{-1} regions and these correspond to stretching and bending modes of Cp 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 [9]. The total intensity of the band due to the hydroxyl groups was slightly different after the addition of an excess of metallocene solution, a situation also observed by dos Santos [10] in the reaction between partially dehydroxylated silica and Cp^{nBu}$_2$ZrCl$_2$.

The amount of metallocene grafted onto silica from toluene solutions was determined by increasing the zirconium contents in the initial solutions. The resulting adsorption isotherm, at 333 K, is shown in Fig. 2. The curve shows that the zirconium loading approaches a saturation limit, near to 1%, that is typical of chemisorption. In addition, the limit is very low, even when a large excess of metallocene 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 5.5% Zr on the assumption that one metallocene molecule reacts with one silanol group. The weak basicity of chloro ligands and the weak acidity of Si–OH groups could explain the difficulty in obtaining higher loadings.

In addition, chlorine and zirconium elemental analyses of metallocenes grafted onto silica at 333 K show a Cl/Zr ratio of around 0.90:1. In a grafting reaction involving only silanol groups, a 1:1 Cl/Zr ratio would be expected and is in

fact essentially obtained. In contrast, when the metallocene was grafted at 298 K, a 1.21:1 Cl/Zr ratio was obtained.

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 [11] such as the Si–O bond in silicon ethers or the N–H in ammonia (Scheme 1).

Basset and coworkers [12] have proposed the reaction between a supported zirconium hydride with vicinal SiOSi bridges on silica dehydroxylated at 723 K. Recently, Yoshida and coworkers [13] 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.
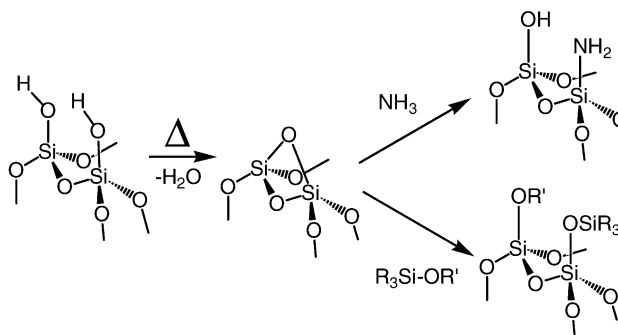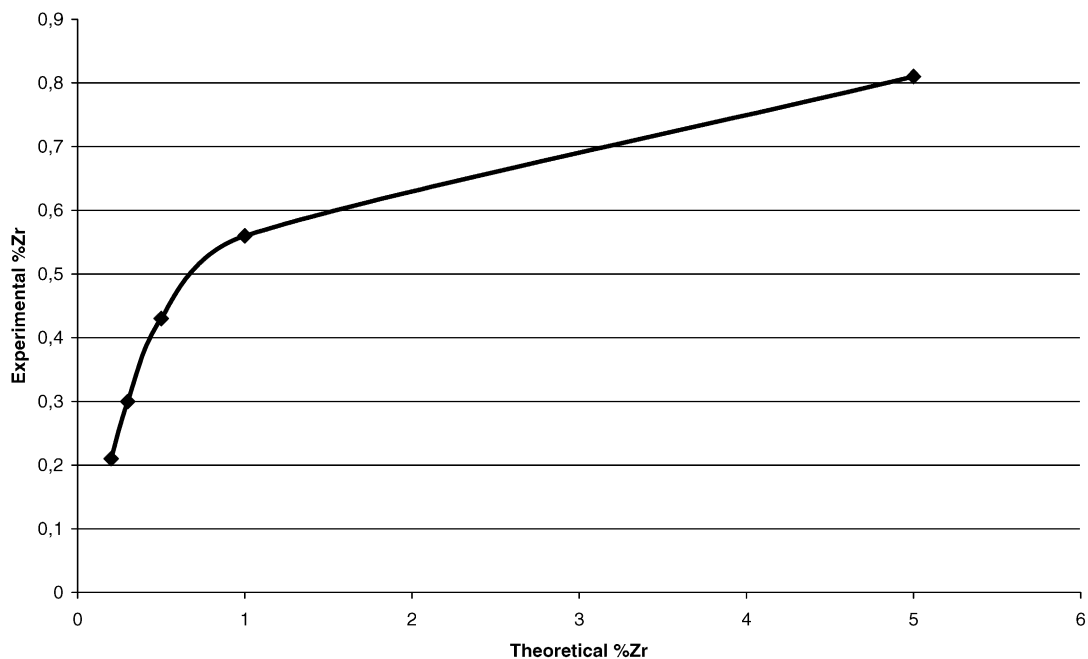

Scheme 1.

Fig. 2. Absorption isotherm of Zr incorporated onto $SiO_2(773)$ as a function of the theoretical expected loading, from solutions of **1** in toluene.

The IR region for SiOSi groups both before and after addition of **1** is shown in Fig. 3. After contact with metallocene, the previously observed weak bands at 908 and $897\,cm^{-1}$, which were assigned to siloxane groups, are no longer present, indicating a reaction between **1** and these groups. A new band is observed at $900\,cm^{-1}$ and this can be tentatively assigned to Zr–O–Si bonds.

In an effort to obtain more information concerning the real behaviour of Cp_2ZrCl_2 towards the silica surface, we studied the reactions of this complex with two systems: Ph_3SiOH,
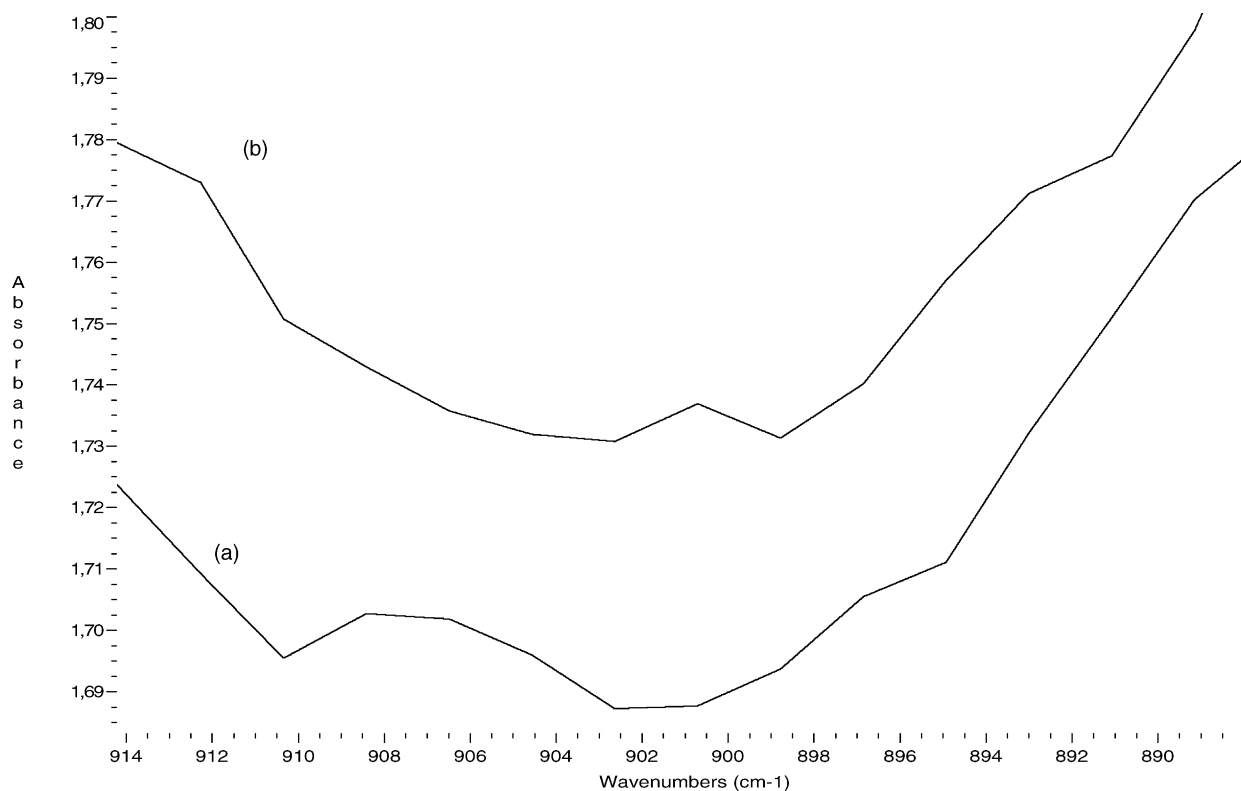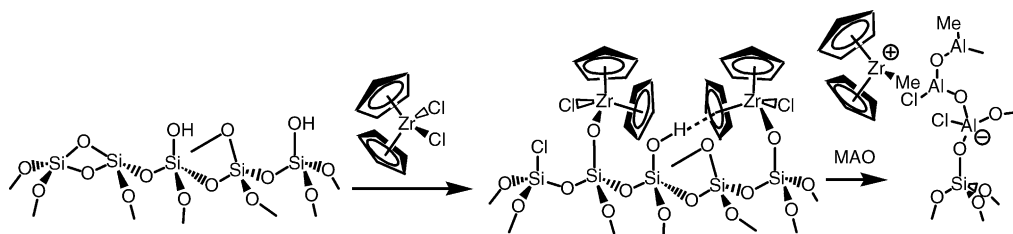

Fig. 3. (a) FT-IR spectrum of $SiO_2(773)$ in the region of siloxane bridges and (b) after reaction with **1**.

Scheme 2.

proposed by Duchateau et al. [14] as a homogeneous support to mimic the grafting of metallocenes onto partially dehydroxylated silica, and $ISiMe_3$, proposed by Lee et al. [15] as a model compound with a similar reactivity to a siloxane reactive bridge. When Cp_2ZrCl_2 (^1H NMR, $\delta = 5.88$ ppm) was treated with a toluene-d^8 solution of Ph_3SiOH in a 5-mm NMR tube, no reaction was observed at room temperature. After 1 h at 333 K the Cp_2ZrCl_2 remained unaltered. In contrast, the reaction between Cp_2ZrCl_2 and a toluene-d^8 solution of $ISiMe_3$ occurs instantaneously at room temperature and a new, sharp peak is observed, probably due to $Cp_2Zr(Cl)(I)$ ($\delta = 5.92$ ppm) and $ClSiMe_3$ ($\delta = 0.19$ ppm). After 1 h at 333 K it was found that 60% of Cp_2ZrCl_2 had been transformed. These results, in conjunction with the literature precedents, seem to indicate that the reaction be-

tween **1** and the silica surface, at mild temperatures, occurs with the acidic silanol groups but also, in a minor extension, with the reactive siloxane bridges, giving rise to similar oxo surface species [**1**.$SiO_2(773)$] (Scheme 2).

The behaviour of the catalyst system after the addition of the MAO cocatalyst was also studied by FT-IR spectroscopy. The IR spectrum of a sample of **1**.$SiO_2(773)$ treated with MAO (approximately Al/Zr = 150) is shown in Fig. 1c. After this treatment, the infrared band attributed to isolated silanol groups (at 3747 cm^{-1}) disappeared completely at room temperature, indicating a reaction between some basic methyl groups of MAO and acidic silanols. 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 stretch-
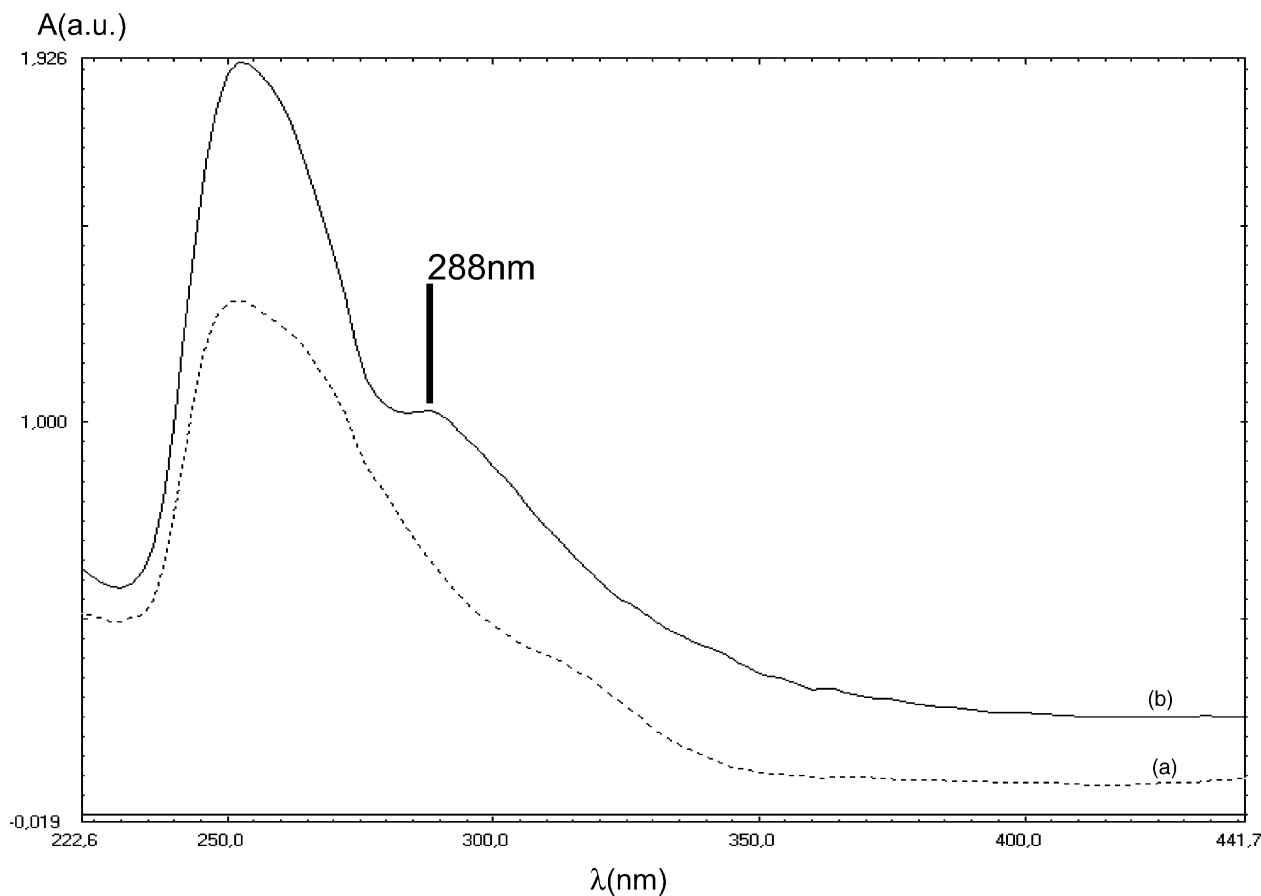
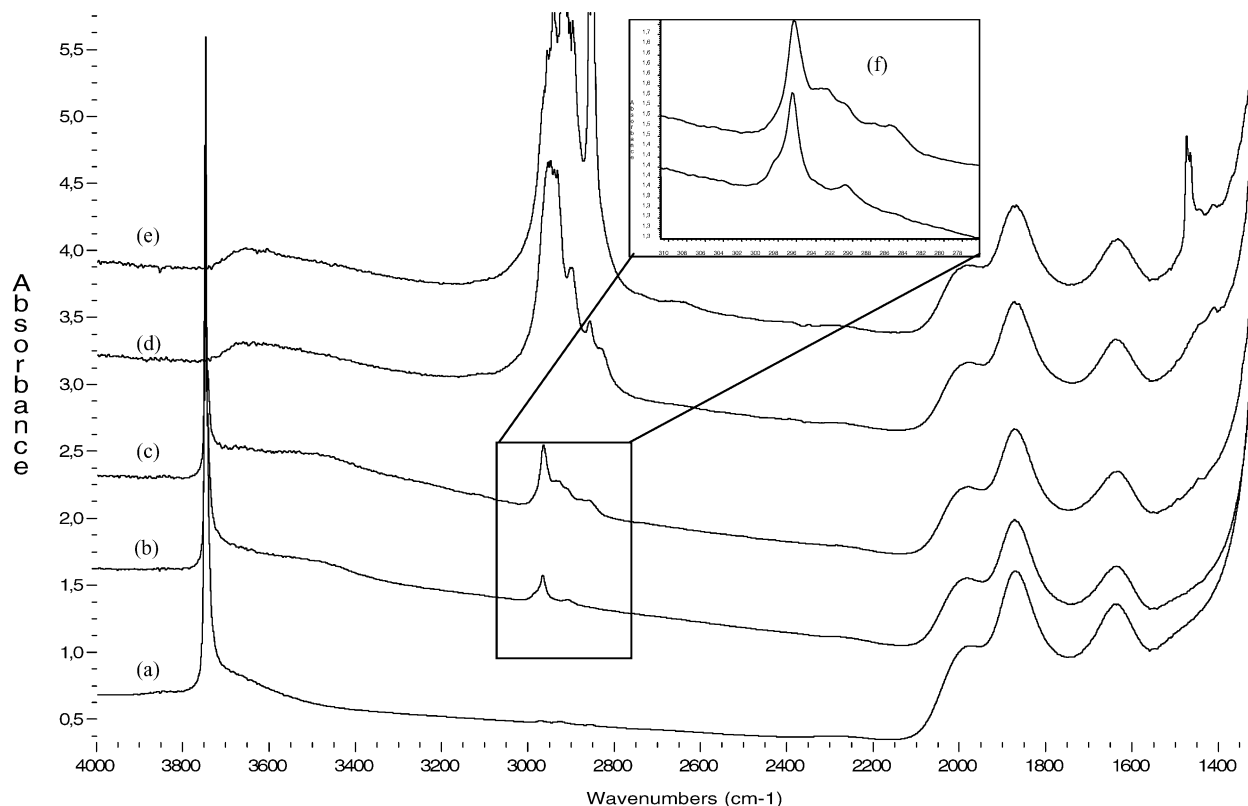Fig. 4. UV–vis spectra of (a) **1**.$SiO_2(773)$ and (b) after the addition of MAO.

Fig. 5. (a) $SiO_2(773)$; (b) after modification with $(Me_3Si)OEt$; (c) after reaction with **1**; (d) after addition of MAO; (e) after contact with C_2H_4; (f) detail of (b) and (c).

ing vibrations of C–H bonds of the methyl groups in MAO. In this way, the grafted MAO could activate the surface oxo-bonded zirconocenes of the neighbouring regions [16] by metal-siloxy bond cleavage, as observed in the molecular model $[(C_5H_9)_7Si_7O_{12}]ZrCp^*$ [17]. This situation could lead to the formation of the potentially active alkylcationic surface species (Scheme 2). The activity of $\mathbf{1}.SiO_2(773)$, after activation with MAO, towards ethylene polymerization was confirmed by following the appearance of vibrations due to polyethylene in the regions $3000–2800\,cm^{-1}$ and $1500–1300\,cm^{-1}$ (Fig. 1d). Intense bands were observed at 2970, 2850 and $1380\,cm^{-1}$, which correspond, respectively, to the $\nu(CH)$ and $\delta(CH)$ vibrations of polyethylene.

A UV–vis analysis of the supported catalyst is represented in Fig. 4. A broad band can be seen at 250 nm, corresponding to the SiO_2 support, with a shoulder at 260 nm, assigned to the supported complex. After the addition of MAO (Al/Zr = 100, Fig. 4b), an increase in the 250 nm band was observed due to the presence of supported MAO. In addition, a new shoulder appeared at 288 nm. This bathochromic shift suggests the formation of the monomethyl cation [18].

In order to gain a deeper understanding of the grafting reaction between **1** and siloxane bridges, we performed the reactions of $SiO_2(773)$ with various silanes.

Alkoxysilane coupling agents, e.g. $(R'O)_3SiR$, are used to bond to surfaces by reaction with silanol groups with the elimination of R′OH. A new mechanism was proposed by Dubois and Zegarski [19] and is consistent with the nucleophilic attack of the alkoxysilane on a highly strained siloxane ring. The extent of the reaction increases with dehydroxylation, but does not modify the surface hydroxyl concentration at mild temperatures. Monoethoxysilane $(EtOSiMe_3)$ reacts in a similar way [20] with a partially dehydroxylated silica. This reagent has the additional advantage of avoiding cross-linking and therefore gives rise to well-defined surface bonded species. In this case, each trimethylsilyl group that is bound to the surface has an adjacent ethoxy group.

The IR spectra of the silica treated with excess $EtOSiMe_3$ are shown in Fig. 5. The mixture was warmed at 333 K and, after subsequent removal of the unreacted compound, new weak bands were observed at 2986, 2967, 2908 and $2856\,cm^{-1}$. The bands were assigned to ethoxy and methyl groups [20] and, as in the case of complex **1**, the $\nu(OH)$ vibration of isolated silanol groups was only partially perturbed to lower frequencies. This modified silica was reacted with a solution of **1** in toluene. The reaction mixture was warmed at 333 K, excess metallocene was washed away with toluene and the solid was dried in vacuo. The spectrum of the resulting solid still contained bands assigned to Cp ligands (Fig. 5c). MAO grafting and activation of the surface metallocene species was performed and, after this treatment,
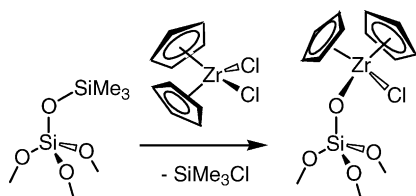
Scheme 3.

ethylene polymerization was carried out in the same way as for unmodified **1**.SiO$_2$(773) (Fig. 5d and e).

Surprising results were obtained when the silica was modified with (Me$_3$Si)$_2$O. This compound was selected to obtain only SiMe$_3$ groups on the surface without the elimination of OH. The spectra of SiO$_2$(773) modified with (Me$_3$Si)$_2$O both before and after the addition of the metallocene are shown in Fig. 6. As expected, weak bands due to grafted compound can be observed after the addition of (Me$_3$Si)$_2$O and removal of the physisorbed excess of unreacted material. This compound reacts only with reactive siloxane bridges, which are present in a low concentration. After reaction with **1**, the difference spectrum (Fig. 6f) clearly shows a decrease in intensity of the bands assigned to trimethylsilyl groups in addition to the appearance of new bands attributed to grafted metallocene. Thus, a reaction on the surface seems to take place between the molecular zirconium complex and the surface SiMe$_3$ groups. An analogous reaction has been de-

scribed [21] between a silylated silica, prepared by reaction with the silazane (Me$_3$Si)$_2$NH, and TiCl$_4$ at 723 K. In this case, the (CH$_3$)$_3$Si groups bonded to the surface were removed as the volatile compound ClSiMe$_3$. We propose that similar behaviour occurs in the reaction of Cp$_2$ZrCl$_2$ with these modified silicas (Scheme 3).

Finally, SiO$_2$(773) was treated with an excess of (Me$_3$Si)$_2$NH. The reaction was warmed at 393 K for 30 h and after this time the ν(OH) vibration due to silanol groups could no longer be observed. In addition, new intense bands in the 2900 and 1450 cm^{-1} regions were seen (Fig. 7). A weak band at 3374 cm^{-1} was tentatively assigned to [NH(SiMe$_3$)] surface groups, which would result from the reaction between (Me$_3$Si)$_2$NH and siloxane bridges in a similar way to the reaction with ammonia (see Scheme 1). The broad band at 3670 cm^{-1}, assigned to unreactive silanols, remained unchanged. The resulting material was treated with **1**, warmed at 333 K, washed with toluene and dried in vacuo. However, bands indicating the presence of grafted metallocene were not found in this case. The subsequent addition of MAO and contact with ethylene gave rise to weak polyethylene bands in the spectrum (Fig. 7d and e).

The different grafting reactions were repeated on a larger scale in order to perform surface elemental analyses (C, Zr) of the resulting surface species. The promediate results of several samples are summarized in Table 1.
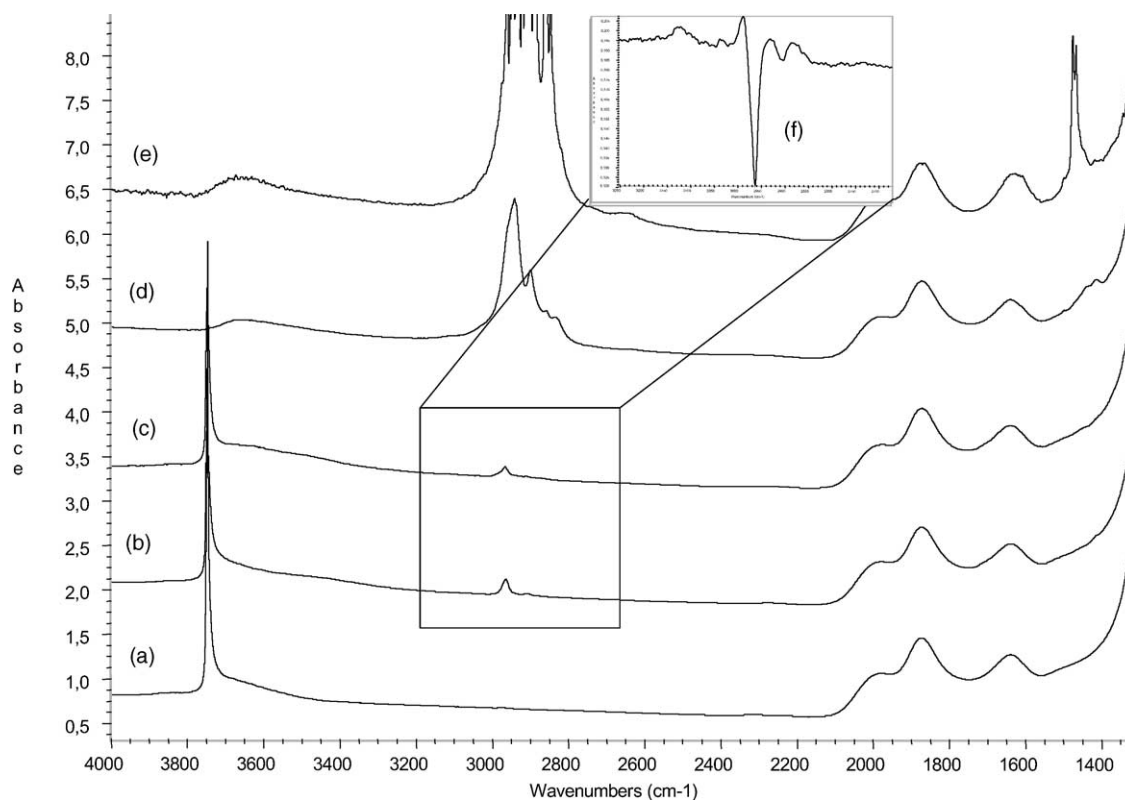

Fig. 6. (a) SiO$_2$(773); (b) after modification with (Me$_3$Si)$_2$O; (c) after reaction with **1**; (d) after addition of MAO; (e) after contact with C$_2$H$_4$; (f) difference spectrum (c)−(b).
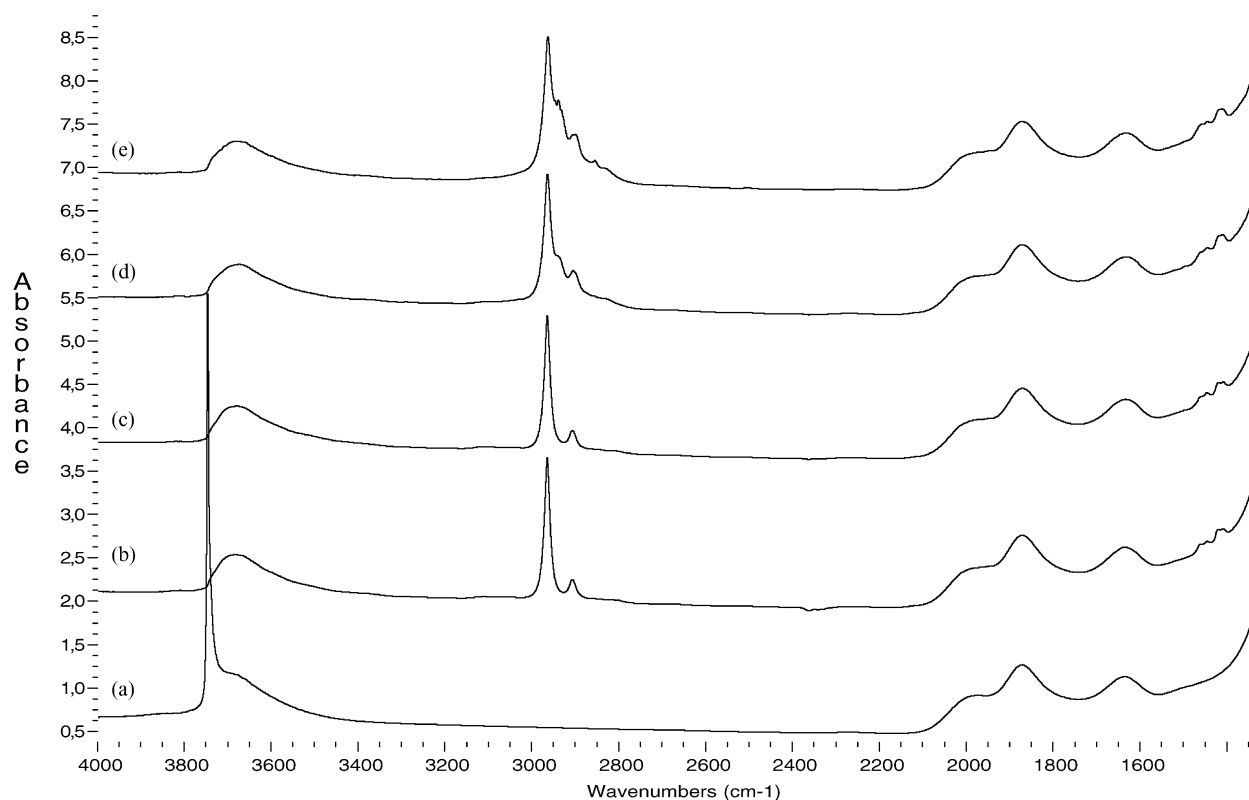
Fig. 7. (a) SiO$_2$(773); (b) after modification with (SiMe$_3$)$_2$NH; (c) after contact with an excess of **1** and warming at 333 K; (d) after addition of MAO; (e) after contact with C$_2$H$_4$.

In contrast to the literature results [5] concerning zirconium contents of organosilane-modified silicas, our samples showed the highest contents for some of the modified supports. In addition, the zirconium loading for EtOSiMe$_3$- and (SiMe$_3$)$_2$O-modified silicas is higher than that obtained for the unmodified one (Table 1). This situation could indicate a favourable reaction between the metallocene and the surface organic groups, as described above, and hence a better grafting of the metallocene in these modified silicas. In the cases reported in the literature, a high level of silylation of the surface was achieved, making it unlikely that the metallocene could react with the surface. In our examples,

Table 1
Zirconium and carbon contents in samples

Sample	% Zirconium loading	% Carbon loading
Cp$_2$ZrCl$_2$/SiO$_2$	0.34	0.56
Cp$_2$ZrCl$_2$/[SiO$_2$-EtOSiMe$_3$]	0.57	1.51
Cp$_2$ZrCl$_2$/[SiO$_2$-(SiMe$_3$)$_2$O]	0.46	0.72
Cp$_2$ZrCl$_2$/[SiO$_2$-(SiMe$_3$)$_2$NH][a]	0.18	2.10
Cp$_2$ZrCl$_2$/[SiO$_2$-(SiMe$_3$)$_2$NH][b]	0.30	2.88
[SiO$_2$-(SiMe$_3$)$_2$O]	–	0.53
[SiO$_2$-(SiMe$_3$)OEt]	–	1.44
[SiO$_2$-(SiMe$_3$)$_2$NH]	–	2.62

[a] Metallocene grafting at 333 K.
[b] Metallocene grafting at 383 K.

however, a slight modification occurred when silicon ethers were used, making it possible for the interactions between metallocene molecules and the surface organic groups to take place. A value of 0.53% C was found after modifying SiO$_2$(773) with (Me$_3$Si)$_2$O. Addition of Cp$_2$ZrCl$_2$ produced a material with values of 0.72% C and 0.46% Zr from the corresponding elemental analyses. It is worth noting that, for a value of 0.46% Zr in Cp$_2$ZrCl$_2$, a theoretical level of 0.60% C is calculated. The close experimental value found allows us to propose that almost all the carbons in the sample can be assigned to grafted metallocene, meaning that previously attached surface SiMe$_3$ groups have been removed in the previous reaction—a situation consistent with the IR spectra (Fig. 5, Scheme 3). A similar result was obtained for a EtOSiMe$_3$-modified sample (Table 1). In contrast, when (Me$_3$Si)$_2$NH was used, which gives extensive silylation of the surface, a value of only 0.18% Zr was found for the corresponding material, a result similar to those found previously with chlorosilanes [4]. The grafting of the metallocene was also performed at 383 K on a silica modified with (Me$_3$Si)$_2$NH and, in this case, a value of 0.30% Zr was found for the sample. This indicates that the reaction with a given SiMe$_3$ surface group has a kinetic barrier such as, for example, the steric effect of the neighbouring SiMe$_3$ groups. In addition, the carbon elemental analysis value shows only a 10% increase (a value of 2.88% C was obtained) after reaction between (Me$_3$Si)$_2$NH-modified silica and the met-
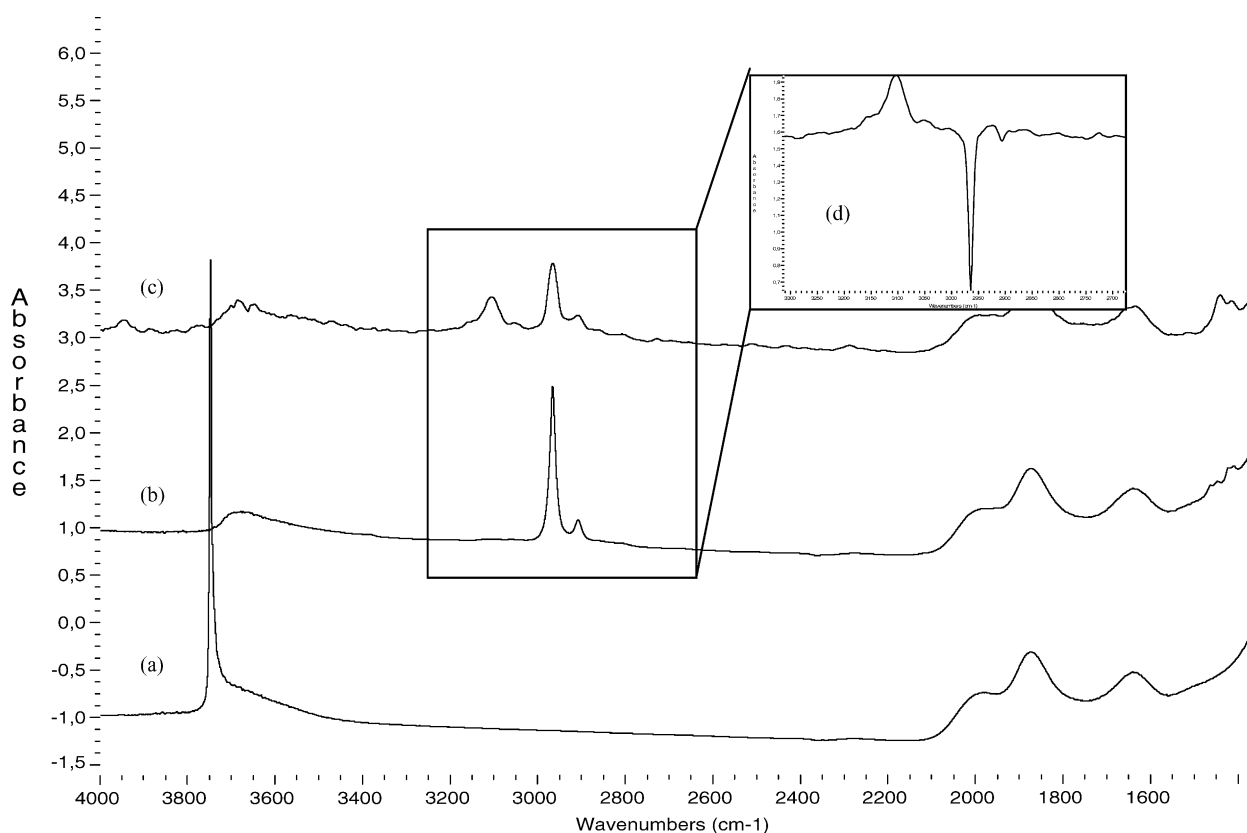
Fig. 8. (a) SiO$_2$(773); (b) after modification with (SiMe$_3$)$_2$NH; (c) after contact with an excess of **1** and warming at 383 K; (d) difference spectrum (c)−(b).

allocene at 383 K (a value of 3.01% C was expected for a 0.30% Zr value). This result indicates that some proportion of the surface SiMe$_3$ groups had been eliminated in the reaction. In order to rule out the possibility of a condensation between adjacent surface SiOSiMe$_3$ groups, we heated a (Me$_3$Si)$_2$NH-modified sample at 383 K in the absence of metallocene but under the same conditions as for the grafting reaction. The final sample showed no change in the % C value, indicating that reaction does not occur without the presence of **1**. The reaction between highly silylated silica and the metallocene was followed by FT-IR and a decrease in the intensity of the SiMe$_3$ band at 2900 cm^{-1} was observed after contact with excess metallocene and warming at 383 K for 2 h (Fig. 8).

Blitz and coworkers [22] reported a similar reaction between **1** and a fully-silylated silica. In this case, the reaction between the metallocene and the modified silica surface was performed at room temperature for only 2 h. A small amount (0.03% Zr) of metallocene was then grafted in a similar way to our experiment. These authors concluded that little if any of the metallocene dichloride reacts with hydrogen bonded silanols on silica gel, although spectroscopic evidence was not described. In our case (Fig. 8), after contact with an excess of **1** and heating at 383 K, the IR spectrum does not show significant modification of the band due to these hydrogen bonded silanols (near 3670 cm^{-1}),

even when the bands assigned to grafted metallocene are significant. In an attempt to gain more information about the possible elimination of ClSiMe$_3$, we performed the reaction between a fully-silylated silica and a toluene-d^8 solution of Cp$_2$ZrCl$_2$ in an NMR-tube. After some minutes at room temperature, only the Cp$_2$ZrCl$_2$ peak was observed in the ^{1}H NMR spectrum ($\delta = 5.86$ ppm). The mixture was heated at 383 K for 16 h and the ^{1}H NMR spectrum was recorded (Fig. 9). The spectrum shows two close and broad peaks (due to the inhomogeneity of the suspension), which are assigned to ClSiMe$_3$ ($\delta = 0.19$ ppm) and its hydrolysis product (Me$_3$Si)$_2$O ($\delta = 0.11$ ppm). This result confirms the reaction between Cp$_2$ZrCl$_2$ and the SiMe$_3$ groups of the functionalized silica. We propose a similar type of behaviour for the other supports (although the low concentration of the organic groups in the other silylated silicas does not allow clear results to be obtained from similar NMR studies).

Catalytic activities in ethylene polymerization were tested for the metallocene supported on unmodified and modified silicas. The results found when MAO was used as a cocatalyst are summarized in Table 2. In accordance with the surface species described, similarly high activities were found for unmodified and partially silylated EtOSiMe$_3$ and (Me$_3$Si)$_2$O-modified systems. The latter system shows the highest activity, indicating that more active species were

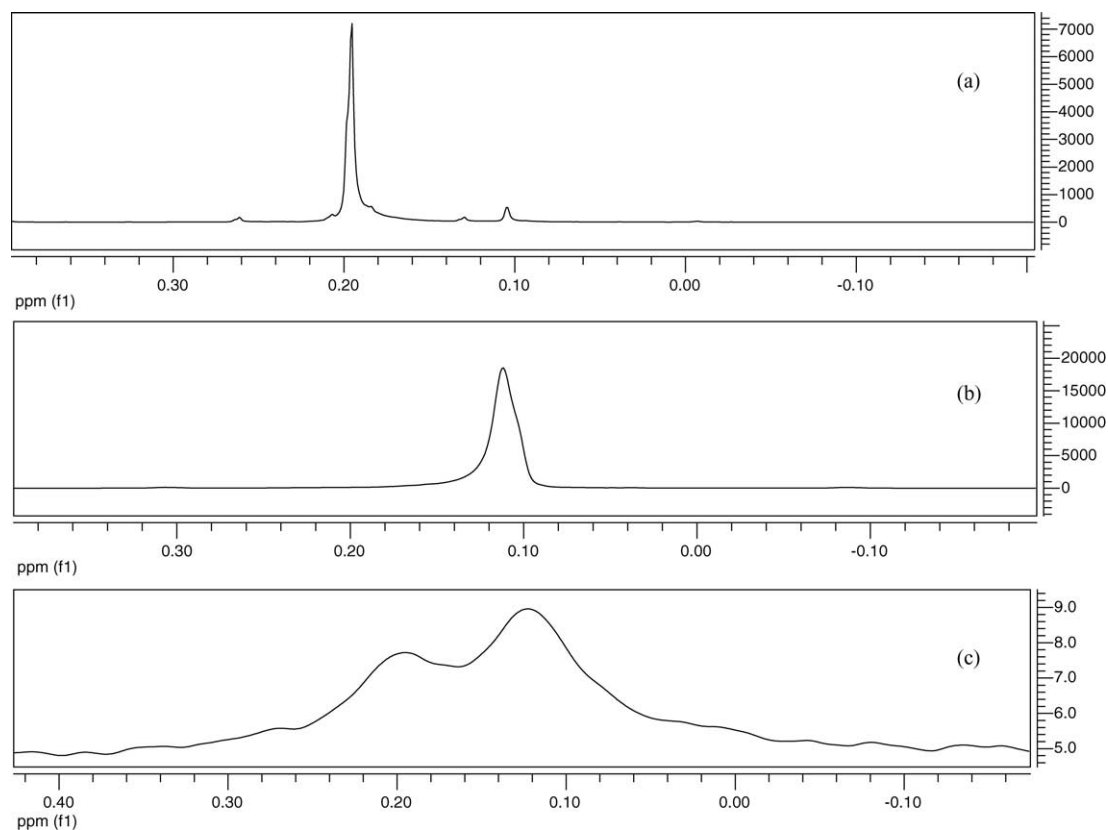Fig. 9. (a) ^{1}H NMR spectrum of ClSiMe₃ in toluene-d[8]; (b) ^{1}H NMR spectrum of (Me₃Si)₂O in toluene-d[8]; (c) ^{1}H NMR spectrum of the soluble products of the reaction between **1** and (SiMe₃)₂NH-modified silica, in toluene-d[8] (see text).

Table 2
Catalytic activities in ethylene polymerization for different supported Cp₂ZrCl₂ systems on unmodified and modified silicas

Catalyst	Activity [10^3 gPE molZr^{-1} h^{-1}]
Cp₂ZrCl₂/SiO₂	465
Cp₂ZrCl₂/[SiO₂-EtOSiMe₃]	441
Cp₂ZrCl₂/[SiO₂-(SiMe₃)₂O]	620
Cp₂ZrCl₂/[SiO₂-(SiMe₃)₂NH]	Traces

Polymerization conditions are as follows: $P = 1.5$ bar; 300 mg of catalyst; [Al]/[Zr] = 100; $T = 343$ K; solvent: toluene (200 mL); scavenger: TIBA (2 mL); time: 30 min.

obtained by this method—probably owing to a better dispersion of the active centres. These results are very similar to those found in previous studies [4,10,23], even when the new grafted species were activated with a low Al/Zr ratio of 100. In contrast, when the catalyst was modified with (Me₃Si)₂NH (with 0.13% Zr content) only traces of polyethylene were obtained, as evidenced by the IR experiments.

4. Conclusions

The reaction of Cp₂ZrCl₂ and SiO₂(773), at a mild temperature, produces grafting of the metallocene by reaction between the weakly acidic silanol groups and the reactive siloxane bridges on the surface and the Zr–Cl bonds. This process gives rise to oxo-bonded zirconocene surface species. When silica was modified with EtOSiMe₃ or (Me₃Si)₂O to create surface SiMe₃ groups in a low concentration, the reaction with metallocene occurred probably by elimination of ClSiMe₃ and formation of the same oxo species. This route led to a higher content in supported zirconium, a situation in contrast with previously described organosilane-modified silicas. These species have a high activity in ethylene polymerization after activation with a low concentration of MAO. High degrees of silylation with (Me₃Si)₂NH produce deactivation of the surface towards metallocene grafting at mild temperature. In this case, only low catalytic activity was found.

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