# The effect of silica dehydroxylation temperature on the activity of SiO$_2$-supported zirconocene catalysts

João Henrique Zimnoch dos Santos [a,*], Cristiano Krug [a], Marcelo Barbosa da Rosa [a], Fernanda Chiarello Stedile [a], Jaïrton Dupont [a], Madalena de Camargo Forte [b]

[a] *Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500, Porto Alegre, RS, Brazil 91509-900*
[b] *Escola de Engenharia, Dept. de Materiais, UFRGS, R. Osvaldo Aranha, 99, Porto Alegre, RS, Brazil 90035-190*

## Abstract

A series of heterogeneous catalyst systems was prepared by the immobilization of bis($n$-butylcyclopentadienyl) zirconium dichloride, ($n$BuCp)$_2$ZrCl$_2$, on silica supports activated at different temperatures. Silica dehydroxylation was evaluated in terms of retained metal loading and activity in ethylene homopolymerization. Characterization of the catalyst systems was accomplished by Rutherford back-scattering spectrometry and infrared spectroscopy. The highest metal loading (0.48 wt.% Zr/SiO$_2$) was achieved with silica treated under vacuum at room temperature (298 K), but the catalyst showed only a minor polymerization activity which may be attributed to a large number of inactive Zr-support bidentate species formed at a high surface density of OH in silica. IR spectroscopic data show that, regardless of support activation temperature, a significant number of isolated OH groups remains after zirconocene fixation. The presence of bulky ligands in the catalyst molecule seems to prevent the remaining OH groups from reacting with additional metallocene complexes, keeping the metal loading around 0.35 wt.% Zr/SiO$_2$ for silica activated between 373 and 723 K. High polymerization activity observed for the system based on 373 K-activated silica suggests a role for these OH groups in the generation of active alkylated species when methylaluminoxane and trimethylaluminum (contained in MAO itself) are added at the beginning of the polymerization reaction. IR analysis shows that TMA, which is a less sterically demanding compound than MAO, can effectively access the remaining OH groups consuming them thoroughly. Practically all the prepared systems presented activity in ethylene polymerization with MAO as cocatalyst, the highest activity ($5.1 \times 10^5$ PE g mol$^{-1}$ Zr h$^{-1}$) having been obtained with silica dehydroxylated at 723 K. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Silica; Zirconocenes; Methylaluminoxane; FT-IR; RBS

## 1. Introduction

Metallocene complexes activated with MAO combine high activity with excellent stereoregularity in the polymerization of α-olefins. However, homogeneous metallocene/MAO systems present some disadvantages in practical applica-

tions. In fact, heterogeneous catalyst systems are required for modern gas-phase and slurry polymerization processes and for large-scale polymer production. Only heterogeneous catalysts can lead to the formation of uniform polymer particles with a narrow particle size distribution and a high bulk density. Thus, in the last few years a significant number of papers describing the preparation of supported metal-

---

* Corresponding author

locene catalyst systems appeared in the literature [1–5].

Among metallocene complexes, a large number of patents report the potential of immobilized $(nBuCp)_2ZrCl_2$ in ethylene homopolymerization. In many cases, modified silicas are employed as supports. For instance, the catalyst system prepared by pressurized impregnation of a mixture of $(nBuCp)_2ZrCl_2$ and MAO into silica is claimed to reduce fouling and sheeting in the reactor during ethylene homopolymerization [6]. Similar results were observed when the zirconocene was supported on alkylaluminum-modified silica by the wet impregnation method [7]. The same catalyst combined with $Al(i-Bu)_3$ and $(EtO)_3PO$-modified MAO produced ethylene polymers with a high melt tension [8].

Supported $(nBuCp)_2ZrCl_2$ has also been used in copolymerization reactions. The system resultant from the treatment of silica with the catalyst, MAO, and alkylaluminum compounds exhibits activity for the production of linear ethylene 1-hexene copolymers. These products are used to manufacture containers for medical and food packing purposes; their melting points $(T_m)$ are higher than sterilization temperatures [9]. More complex systems, obtained from the combination of dibutylmagnesium, titanium tetrachloride, MAO, and $(nBuCp)_2ZrCl_2$, have also been used to prepare ethylene 1-hexene copolymers with bimodal molecular weight distributions [10].

In a previous work [11] we determined the surface saturation isotherms of Zr and Al compounds on different commercial silicas (Grace 948, 952, and 956) employing $Cp_2ZrCl_2$, MAO, and TMA as precursors. Those results suggest a stronger interaction between the metallocene and Grace 948 silica. This paper presents a comparative analysis of the behavior of $(nBuCp)_2ZrCl_2$ supported on Grace 948 silica pretreated at different temperatures and activated by MAO in the homopolymerization of ethylene. Surface metal loadings were determined by the Rutherford back-scattering spectrometry (RBS); surface reactions were monitored by transmission

infrared spectroscopy (FT-IR). The catalytic behavior of the supported systems was evaluated in terms of activity in ethylene slurry homopolymerization; molecular weights and melting $(T_m)$ and crystallization $(T_g)$ points of the polymers were also obtained.

## 2. Experimental

### 2.1. Materials

Grace 948 silica ($255$ m$^2$/g) was used for RBS analysis and polymerization tests, and pyrogenic silica Degussa Aerosil 200 ($200$ m$^2$/g) was used for transmission FT-IR analysis. The silicas were activated under vacuum for 16 h at various temperatures between 298 and 723 K. The supports were cooled to room temperature under vacuum and stored under dried argon. MAO (Witco, 10.0 wt.% toluene solution, 1.7 Al as TMA, average molar mass 900 g/mol), TMA (Witco, 10.0 wt.% toluene solution), and $(nBuCp)_2ZrCl_2$ (Witco) were used without further purification. Ethylene, provided by COPESUL, and argon were deoxygenated and dried over columns of activated molecular sieve (13 Å) prior to use. Toluene (purum grade) was deoxygenated and dried by standard techniques.

### 2.2. Preparation of supported catalyst systems

All experiments were performed under argon using the Schlenk technique. 1.5 wt.% Zr/SiO$_2$ toluene solutions of $(nBuCp)_2ZrCl_2$ were added to 1.0 g of pretreated Grace 948 silica and the mixtures were stirred for 30 min at room temperature. The slurries were then filtered through fritted disks. The resulting solids were washed with 12 times 2 cm$^3$ of toluene and dried under vacuum for 4 h.

### 2.3. Polymerization reactions

Ethylene homopolymerization reactions were performed in 0.25 dm$^3$ of toluene in a 1.00 dm$^3$

Pyrex glass reactor connected to a constant temperature circulator and equipped with a mechanical stirrer and inlets for argon and the monomer. MAO or TMA was used as cocatalyst in an Al/Zr molar ratio in the range of 100–5000. For each experiment, $10^{-5}$ mol of Zr ($\sim$ 50–60 mg of catalyst system) was suspended in 0.01 $dm^3$ of toluene and transferred into the reactor under argon, followed by the introduction of the corresponding amount of a cocatalyst. The reactions were performed at an atmospheric pressure of ethylene at 343 K for 30 min. Acidified ethanol was used to quench the processes, and reaction products were separated by filtration, washed with distilled water and dried under reduced pressure. Each polymerization reaction was repeated at least 3 times under identical conditions, leading to similar products.

## 2.4. Analytical procedures

### 2.4.1. Rutherford back-scattering spectrometry (RBS)

Zirconium loadings in catalysts were determined by RBS using $\alpha$-particle beams of 2.0 MeV incident on homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems. The method is based on the determination of the number and the energy of the detected particles of a monoenergetic ion beam which are elastically scattered in the Coulombic field of the atomic nuclei in the target [12]. The most commonly used incident beam is $^4He^+$, and backscattered-particle detection is usually accomplished with surface barrier detectors placed at 165° with respect to the incidence direction of the ion beam (Fig. 1, inset). Among other factors [12], the energy of the scattered particles depends on their energy of incidence, on the atomic masses of the atoms involved (probe and target), and on the depth in the sample where the scattering event occurs. The height of the signal (number of counts) corresponding to a certain element is proportional to the surface density of that element in the thick-
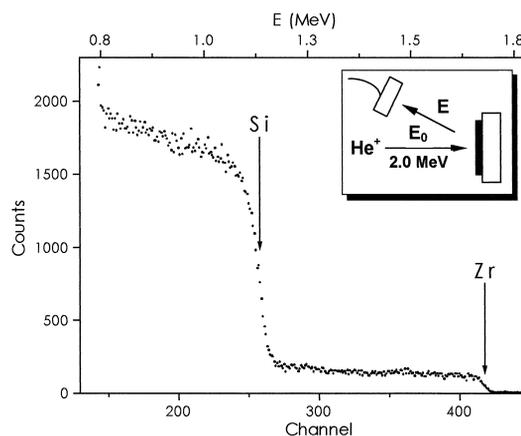


Fig. 1. RBS spectrum of $(nBuCp)_2ZrCl_2$ on Grace 948 silica, at the calculated wt.% $Zr/SiO_2$ ratio of 0.48. The spectrum was obtained using an $\alpha$-particle beam of 2.0 MeV with normal incidence on the sample and detection at 165° with respect to the incidence direction (see scheme in the inset). The channel number is proportional to the energy of the scattered particles (see energy scale at the top). The arrows indicate the outermost position of the corresponding elements in the sample.

ness in which scattering occurs. In this study, the Zr/Si atomic ratio was determined from the ratio of the signals corresponding to each of the elements (Fig. 1) and converted to wt.% $Zr/SiO_2$. Homogeneity of element distribution in the samples in the probing depth can be assured from the plateaus obtained for the Zr and Si signals. The plateaus in the Zr and Si signals mean that the same amount of element (Zr or Si) is found in the whole probing depth, characterizing their depth concentration homogeneity.

### 2.4.2. Fourier-transform infrared spectroscopy (FT-IR)

Transmission FT-IR spectra were recorded on a Bomem MB-102 Spectrometer, (32 scans at a 4 $cm^{-1}$ resolution). The study was restricted to the mid-infrared region (4000–1300 $cm^{-1}$) due to strong bulk absorption of silica at lower wavenumbers. The samples analyzed by this technique consisted of 50–60 mg of Aerosil silica pressed under 12 MPa into a self-supporting tablet ($\varnothing = 17$ mm) which was introduced into a Pyrex cell with $CaF_2$ windows. The unit was attached to a greaseless glass gas/vacuum

handling system and the silica tablet was activated in situ under vacuum ($< 10^{-4}$ mbar) at temperatures between 373 and 723 K for 16 h. Zirconocene impregnation was then conducted from a toluene solution containing an amount of catalyst calculated to produce the same Zr/Si ratio as determined by RBS in the sample obtained when Grace 948 silica was pretreated at the same temperature.

### 2.4.3. Polymer characterization

Polymer melting points ($T_m$) and glass transition temperatures ($T_g$) were determined with a DuPont DSC 2910 differential scanning calorimeter calibrated with indium, using a heating rate of 10 K min$^{-1}$ in the temperature range of 313–513 K. The heating cycle was performed twice, the results of the second scan are reported. Intrinsic viscosities of the polymers were measured at 408 K using an Ubbelohde viscometer and decalin (decahydronaphthalene) as a solvent, and were used to calculate the viscosity-average molecular weights ($M_v$).

## 3. Results and discussion

The surface metal loadings determined for the systems under investigation are presented in Fig. 2 (left Y-axis). For comparative reasons, the result observed for a totally hydroxylated
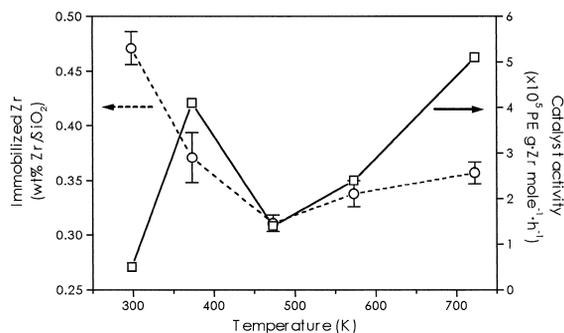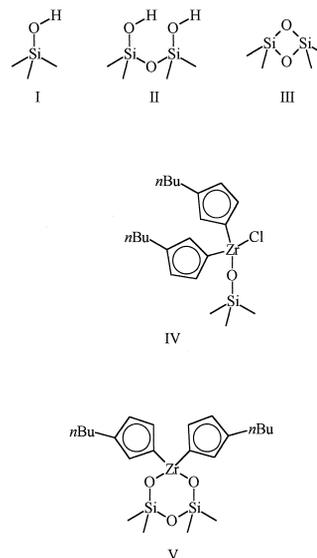


Scheme 1.



Fig. 2. (○) Zr loading (left) in silicas activated between 298 and 723 K. The neat ($n$BuCp)$_2$ZrCl$_2$ toluene solutions contained 1.5 wt.% Zr/SiO$_2$ (typical error bars are shown); (□) the corresponding activities of these catalyst systems (right) in ethylene homopolymerization using MAO (3000 Al/Zr) as cocatalyst.

silica (pretreated under vacuum at 298 K) is also included. This silica has the highest zirconium loading (0.48 wt.% Zr/SiO$_2$) in accordance with what is expected from mechanisms of metallocene immobilization and thermal activation of silica. Immobilization takes place by elimination of one or more of the original organometallic ligands (such as halides or alkoxides) in a 1:1 ratio with hydrogen atoms from silanol groups (Si–OH) in the support. It is well established that the surface OH density in silica decreases with thermal activation temperature, so that after treatment at high temperatures ($> 723$ K) the silica surface presents mainly isolated (**I**) and, to a lesser extent, geminal (**II**) hydroxyl groups, as well as surface siloxane bridges (**III**) [13] (Scheme 1). Since the number of substitution reaction sites is maximum at room temperature, the amount of Zr loading should also be the highest.

In our temperature interval, the surface density of OH in silica decreases from 4.5 nm$^{-2}$ at 298 K to around 1.7 nm$^{-2}$ at 723 K [14], which corresponds to a 60% reduction of the initial value. According to Fig. 2, the reduction in the amount of supported catalyst over the same range is only one fourth. This fact suggests that

the steric effect of ligands that remain attached to zirconium after immobilization hampers loadings in the potential immobilization sites of the vicinities when in the presence of high OH coverages, as in the case of a partially hydroxylated silica pretreated at 373 K. Another evidence of the steric effect of ligands on the immobilization of organometallic compounds is the difference in metal loadings observed between the systems reported here and those with $Cp_2ZrCl_2$ [11]. Under identical experimental conditions, the latter leads to metal loadings between 0.57 and 0.45 wt.% $Zr/SiO_2$ (on silicas pretreated at 373 and 723 K, respectively). Iiskola et al. [15] recently found that $CpZrCl_3$, an even less sterically demanding metallocene, produces a higher zirconium loading (0.90 wt.% $Zr/SiO_2$) when grafted on a 320 $m^2/g$ silica pretreated at 873 K in air.

The attainment of the same Zr loading on silicas pretreated at different temperatures (Fig. 2) does not mean that the surface species are the same. In fact, the lower OH surface density in the support activated at the highest temperature preferentially leads to monodentate Si–O–Zr surface species (**IV**), while a totally or partially hydroxylated silica, in which species (**II**) are present, leads to elimination of both Cl ligands of the original metallocene and produces bidentate (**V**) species (Scheme 1). This last species should be inactive in polymerization reactions since the absence of a labile ligand (Cl) prevents the formation of the active centers which are generated through alkylation of the complex in a reaction with MAO. Indeed, totally hydroxylated silica produces systems with a lower activity ($0.5 \times 10^5$ PE g Zr $mol^{-1}$ $h^{-1}$) when compared to those supported on thermally pretreated silicas. As the pretreatment temperature is raised, an increment in the fraction of monodentate species formed in immobilization is expected, and an increasing catalytic activity is accordingly observed (Right $Y$-axis of Fig. 2). An apparent paradox is raised by the catalyst system prepared with silica activated at 373 K, which exhibits a surprisingly high activity. One would expect this system to have a significant amount of inactive bridged-metallocene species due to a high OH surface density prior to catalyst immobilization. The fact that this system is even more active than those supported on silica pretreated at 473 and 573 K suggests that the presence of surface monodentate species is not the only factor that is responsible for a high polymerization activity. The residual surface OH groups probably react with MAO (and with the TMA that it invariably contains) prior to polymerization originating active catalytic species. The reaction between TMA and silanol groups is known for a long time and it is the basis of a well-established method for surface OH determination [16–19], and AlMe groups in MAO have also shown reactivity towards OH species [11]. Another reason for a high activity was presented in a recent article [20]: high polymerization activities supposedly observed for supported systems may be due to desorption of metallocene complexes and formation of homogeneous catalytic species. However, according to our polymer characterization data, this should not be the case in the present study. Further experiments are currently in progress to provide a better understanding of the catalytic properties shown by the system based on silica pretreated at 373 K.

Fig. 3 presents IR spectra of the reaction products between $(nBuCp)_2ZrCl_2$ and silica. The number and types of $\nu_{(OH)}$ bands in the IR region is well documented [21,22]. Spectrum **a** (collected before modification with the metallocene complexes, silica pretreated at 723 K) has a sharp band at 3746 $cm^{-1}$ attributed to isolated surface OH groups with a broad shoulder centered at 3694 $cm^{-1}$ and assigned to OH groups perturbed by hydrogen bonding. Broad bands centered at 1971, 1867, and 1632 $cm^{-1}$ are overtones and combinations of intense Si–O fundamental modes. When the metallocene solution is added to the pretreated silica, new bands, characteristic of aromatic and alkyl groups, appear in the following regions (spectrum **b**): 3100–2800 $cm^{-1}$ (C–H stretching)
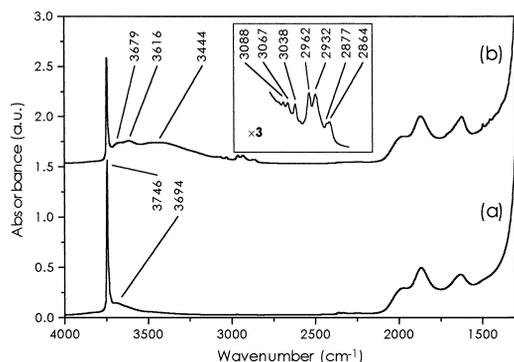
Fig. 3. IR spectra in the 4000–1300 cm$^{-1}$ range: (**a**) SiO$_2$ dehydroxylated at 723 K for 16 h; (**b**) after impregnation at 298 K with a 0.34 wt.% Zr/SiO$_2$ toluene solution of ($n$BuCp)$_2$ZrCl$_2$. In the inset, the absorbance in the region correspondent to C–H stretching from Bu and ring is multiplied by 3.

Table 1
IR bands assigned to neat and silica-supported ($n$BuCp)$_2$ZrCl$_2$

| Band wavenumber (cm$^{-1}$) | | Vibrational mode [23] |
|---|---|---|
| ($n$BuCp)$_2$ZrCl$_2$ | ($n$BuCp)$_2$ZrCl$_2$/SiO$_2$ | |
| 3108 | 3088, 3067, 3038 | $\nu$(CH ring) |
| 2955 | 2962 | $\nu_{as}$(CH$_3$) |
| 2927 | 2932 | $\nu_{as}$(CH$_2$) |
| 2870 | 2877 | $\nu_s$(CH$_3$)$^a$ |
| 2857 | 2864 | $\nu_s$(CH$_2$)$^b$ |
| 1491 | 1495 | $\delta_{as}$(CH$_3$) |
| 1457 | 1452 | $\delta_s$(CH$_3$) |

$^a$Fermi resonance between $\nu_s$(CH$_3$) and 2$\delta$ (CH$_3$).
$^b$Fermi resonance between $\nu_s$(CH$_2$) and 2$\delta$ (CH$_2$).

and 1500–1300 cm$^{-1}$ (methyl and methylene deformation modes). Table 1 gives the wavenumbers for these bands, as well as their vibrational modes, whose attributions are based on the literature [23]. The butyl groups in a ($n$BuCp)$_2$ZrCl$_2$ are slightly affected by immobilization, as it can be observed from the shift of the bands assigned to them to higher wavenumbers ($\approx 7$ cm$^{-1}$). Similar results are reported to other silica-supported organometallic compounds with butyl ligands [24].

The grafting of the metallocene complex is also accompanied by the appearance of three bands in the region of aromatic $\nu_{(CH)}$, all of them at much lower wavenumbers compared to the aromatic $\nu_{(CH)}$ of the metallocene complex itself. Simultaneously, three other bands appear in the $\nu_{(OH)}$ region: 3679, 3616, and 3444 cm$^{-1}$. The existence of three different $\nu_{(CH)}$ for the Cp groups and three bands in the $\nu_{(OH)}$ region suggests that a part of the surface silanol groups is strongly affected by the presence of the grafted metallocene. Those bands may result from an interaction between surface silanol and aromatic Cp groups, in analogy with literature data attributing surface silanol $\nu_{(OH)}$ bands at 3645 and 3510 cm$^{-1}$ to vicinal OH groups interacting through hydrogen bonding [25]. Similar results have been reported concerning the adsorption of anisole onto surface silanol groups [26],

the IR bands in the 3600–3400 cm$^{-1}$ region having been attributed to surface species resulting from the interaction between hydroxyl groups and the $\pi$-electron system of the aromatic ring.

According to band absorbance measurements at 3746 cm$^{-1}$, only 30% of the initially isolated OH groups are consumed or perturbed (generating the wide $\nu_{(OH)}$ bands at lower wavenumbers) by metallocene grafting. IR spectra (Fig. 4) of a 723 K pretreated silica after successive impregnations of ($n$BuCp)$_2$ZrCl$_2$ from solution (employing multiple aliquots of the surface saturation concentration as determined by RBS on Grace 948), shows that the OH surface density remains practically constant for up to 1.36 wt.% Zr/SiO$_2$. When the total amount of metallocene
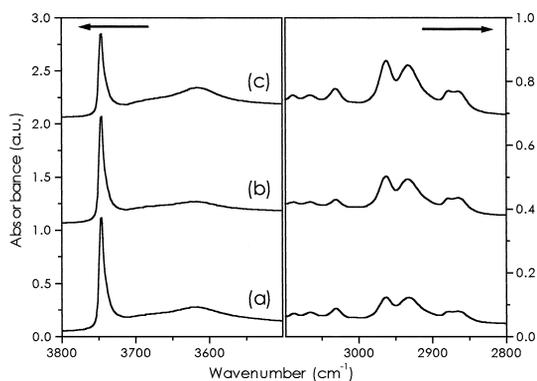


Fig. 4. IR spectra in the 3800–2800 cm$^{-1}$ range of SiO$_2$ dehydroxylated at 723 K and impregnated at 298 K with toluene solutions corresponding to the saturation loading (0.34 wt.% Zr/SiO$_2$) of ($n$BuCp)$_2$ZrCl$_2$: (**a**) twice; (**b**) 4 times; (**c**) 8 times the aliquot. The right-hand side of the spectra is multiplied by 3.

employed is eight times higher than the saturation loading (left side of spectrum **c**), a small reduction in the band peak at 3746 cm$^{-1}$ is observed, but it is accompanied by the increase of the intensity of the broad band at a lower wavenumber suggesting that it may not correspond to OH consumption but probably to its perturbation. Indeed, it seems that the bulky $n$BuCp ligands from the grafted metallocene reduce the access of the complex to the remaining OH sites solely by steric reasons. This hypothesis may explain why the intensity of the IR band corresponding to isolated OH groups remains almost constant after the addition of four aliquots of metallocene solution to the silica. Morrow and McFarlan [27,28], in an attempt to develop a method for silanol number determination, have already observed that the OH reaction rate is inversely proportional to a reagent size: bulky chemically adsorbed species in silica are capable of preventing the neighboring silanol groups from reacting. It is worth mentioning that concerning $n$Bu ligands (right side of Fig. 4), the relative absorbance of the bands at different wavenumbers is not affected by the successive impregnation, only the intensity at a given wavenumber increases as the amount of added metallocene does.

Besides isolated and bridged silanol groups, siloxane (**III**) sites are also expected on the silica surface. Tait and Ediati [29] have recently suggested a reaction of metallocene complexes with siloxane bridges formed in silica dehydroxylated at 733 K. On the other hand, Hair [30] has shown that at temperatures below 773 K hydrogen-bonded silanol groups are removed to generate large, unstrained rings similar to those found in the bulk of silica. Only above this temperature the dehydroxylation of isolated silanols can create edge-shared tetrahedral defects presenting strained bond angles which render silica highly reactive towards dissociative chemisorption. Thus, it is very unlikely that under our thermal pretreatment conditions the metallocene is grafted by a reaction with surface siloxane bridges.

Finally, the behavior of the catalyst system after the cocatalyst addition was studied by the IR method. Spectrum **a** in Fig. 5 corresponds to a sample activated at 373 K and then impregnated with $(n\mathrm{BuCp})_2\mathrm{ZrCl}_2$. The broad band centered at 3563 cm$^{-1}$ indicates a high surface density of vicinal OH groups at this lower pretreatment temperature, while the bands corresponding to $n$Bu groups do not differ significantly from those observed on 723 K activated Aerosil (compare to spectrum **b** in Fig. 3). From the three bands assigned to ring $\nu_{(\mathrm{CH})}$ in that system, only one band at 3038 cm$^{-1}$ is now barely observed, the other two being probably part of the wide band centered at 3563 cm$^{-1}$. Treatment of the supported system with MAO (200 Al/Zr) (spectrum **b** of Fig. 5) generates two sets of bands in the $\nu_{(\mathrm{CH})}$ region, one at 2936 cm$^{-1}$ ($\nu_{\mathrm{as(CH)}}$) and another one at 2857 cm$^{-1}$ ($\nu_{\mathrm{s(CH)}}$), attributed to methyl groups. The shoulder observed at 2857 cm$^{-1}$ could also be attributed to methoxy groups from MAO, in analogy with the structure of the $(\mathrm{Al}_7\mathrm{O}_6\mathrm{Me}_{16})^-$ anion proposed by Atwood et al. [31]. After treatment with MAO, the band at 3038 cm$^{-1}$ assigned to $\nu_{\mathrm{as(CH)}}$ of the Cp ring is shifted to 3016 cm$^{-1}$ and its intensity increases, probably
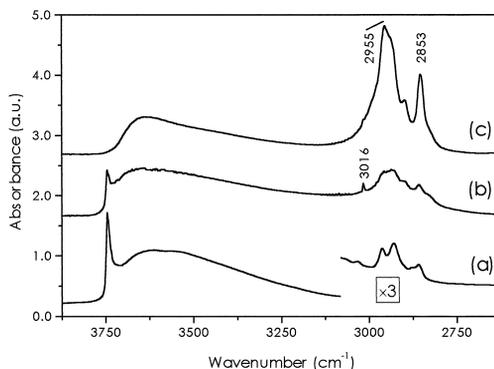


Fig. 5. IR spectra in the 4000–2600 cm$^{-1}$ range: (**a**) SiO$_2$ dehydroxylated at 373 K and impregnated at 298 K with a 0.37 wt.% Zr/SiO$_2$ toluene solution of $(n\mathrm{BuCp})_2\mathrm{ZrCl}_2$; (**b**) same as (**a**) followed by additional impregnation with 10 wt.% MAO toluene solution (200 Al/Zr); (**c**) same as (**a**) followed by additional impregnation with 10 wt.% TMA toluene solution (200 Al/Zr). The low energy part of the spectrum (**a**) was multiplied by 3.

indicating a modification of surface species. A wide band centered at 3645 cm$^{-1}$ also indicates the interaction of MAO with the surface. Nevertheless, isolated silanol groups ($\nu_{OH}$ at 3746 cm$^{-1}$) are only partially consumed. This is reasonable since one considers that $n$BuCp groups prevent the access of bulky MAO molecules to these Si–OH groups. Experiments at Al/Zr ratios higher than 200 led to a significant loss of transmittance, rendering the analysis difficult.

In contrast to MAO, addition of TMA at the 200 Al/Zr ratio to a metallocene-grafted Aerosil activated at 373 K leads to a complete consumption of isolated OH groups as indicated by the disappearance of the band at 3746 cm$^{-1}$ in spectrum **c** in Fig. 5. This is an evidence that TMA is small enough to access the OH groups protected by $n$BuCp ligands and to react with them. After TMA impregnation, three bands centered at 2955, 2898, and 2853 cm$^{-1}$ appear in the $\nu_{(CH)}$ region, resembling the spectrum produced with MAO (spectrum **b**) and suggesting in situ hydrolysis of TMA yielding MAO. As it was pointed out previously for the system impregnated with MAO, the Cp ring $\nu_{(CH)}$ is detected as a shoulder at 3016 cm$^{-1}$.

It has been claimed that methylaluminum surface species in the presence of zirconocenes may lead to ion pair formation, producing zirconocenium ions ($Zr^{+}$) weakly attached to silica in such a manner that they would be free to move within the surface layer. Using different MAO-modified silicas, Tait and Ediati [29] observed that the $SiO_2/MAO/Et(Ind)_2ZrCl_2$ system exhibits the higher polymerization activity when the support is pretreated at relatively low temperatures, i.e., when a fairly high number of OH groups is present (recall the high activity obtained at 373 K). This result reinforces the idea that the reaction between silanol groups and an organoaluminum compound, either TMA or MAO, might be a very important step in the formation of the catalytic species. Indeed, a patent has already been issued claiming the preparation of a supported metallocene catalyst system in whose preparation undehydrated silica

gels (containing 7.2 wt.% $H_2O$) are treated with TMA in solution, bearing very active systems for high-pressure polymerization of olefins [32].

Only traces of polyethylene were obtained when the zirconocene complex grafted on 373 K-pretreated silica was tested as a catalyst in presence of TMA (3000 Al/Zr) instead of MAO at the same Al/Zr ratio. Experiments conducted with lower or higher TMA Al/Zr ratios (100, 1000, 2000 and 5000) did not indicate any activity. It was recently postulated that the role of MAO is that of a carrier and delivery agent of TMA (contained in MAO itself) in suitably low concentrations, such that controlled alkylation of the zirconium species is achieved [33]. Furthermore, there is a general consensus on the idea that MAO may assist the formation of the $Zr^{+}Cl^{-}$ pair acting as a receptor of the negatively charged moiety. Under our experimental conditions, the large OH density at 373 K would permit the production of separated $SiO_2/(nBuCp)_2Zr^{+}Me$ and $SiO_2/MAO(TMA)Cl^{-}$ ion pairs in the reactor when the cocatalyst is added, leading to a higher activity.

The supported systems produced polymers with practically constant melting (408–409 K) and crystallization (391–393 K) temperatures typical of polyethylene. All samples (including the one prepared with the system based on 373 K-activated silica) had higher molecular weights ($\sim 3.6 \times 10^5$ g/mol) when compared to those produced by $(nBuCp)_2ZrCl_2$ in a homogeneous reaction ($\sim 1.1 \times 10^5$ g/mol). In the case of supported catalysts, the necessary bimolecular reaction between two metallocene centers, that makes the β-hydrogen transfer possible, is hindered, resulting in a longer growth of the polymer chain (higher molecular weight).

## 4. Conclusion

RBS analysis of catalyst systems produced by grafting $(nBuCp)_2ZrCl_2$ on Grace 948 silica dehydroxylated at different temperatures showed a saturation loading around 0.35 wt.% $Zr/SiO_2$

when 1.5 wt.% $Zr/SiO_2$ catalyst solutions in toluene were employed. The highest metal loading was achieved with untreated silica. This low temperature activation produces a highly hydroxylated support which, in turn, leads mainly to bridged $(nBuCp)_2Zr$ species which are inactive in polymerization reactions. Monodentate surface species, as expected, are obtained from silicas pretreated at higher temperatures yielding catalysts with higher activities in ethylene polymerization reactions.

IR analyses showed that, at the catalyst saturation levels, most of the isolated silanol groups are not consumed. They did not react with MAO either, but TMA could efficiently reach them and react. In these processes, the steric effect of $n$BuCp ligands was seen to play an important role. Moreover, it was observed that the silanol groups remaining on silica after impregnation of the metallocene complex may also have an important effect on polymerization activity, as evidenced by the high polymer yield achieved with the system based on 373 K pretreated silica, most probably for allowing the formation of active cocatalyst species after MAO (or TMA contained in MAO itself) is added to the systems.

## Acknowledgements

## References

[1] See, for example: J.D. Kim, J.B. Soares, G.L. Rempel, B. Monrabal, Proceedings of MetCon'97, June 4–5, 1997, Houston, USA.

[2] K. Soga, T. Uozumi, T. Arai, H.T. Ban, E. Kaji, Proceedings of MetCon'97, June 4–5, 1997, Houston, USA.

[3] K. Soga, E. Kaji, T. Uozumi, J. Polym. Sci. Part A: Polym. Chem. 35 (1997) 823.

[4] S.S. Sarma, S. Sivaram, Macromol. Chem. Phys. 198 (1997) 495.

[5] T. Arai, H.T. Ban, T. Uozumi, K. Soga, Macromol. Chem. Phys. 198 (1997) 229.

[6] M. Chang, (Exxon Chemical Patents, USA), PCT Int. Appl. WO (1996).

[7] M. Chang, (Exxon Chemical Patents, USA), PCT Int. Appl. WO (1995).

[8] Y. Satake, K. Yoshikawa, K. Matsuoka, S. Inasawa, (Showa Denko, Japan), Jpn. Kokai Tokkyo Koho JP (1996).

[9] T. Yamamoto, Y. Waga, (Mitsui Petrochemical, Japan), Jpn. Kokai Tokkyo Koho JP (1997).

[10] R.I. Mink, T.E. Nowlin, P.P. Shirodkar, S.D. Schregenberger, G.O. Tsien, (Mobil Oil, USA), PCT Int. Appl. WO (1996).

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

[12] W.A. Grant, Methods of surface analysis, in: J.M. Walls, (Ed.), Cambridge University Press, Chap. 9, Cambridge, 1989, p. 299.

[13] E.F. Vansant, P. van der Voort, K.C. Vrancken, Stud. Surf. Sci., 1995, 93, Chap. 3.

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

[15] E.I. Iiskola, S. Timonen, T.T. Pakkanen, P. Lehums, O. Härkki, J.V. Seppälä, Metallocene Europe's 97, 3rd International Congress on Metallocenes and Polymer, Düsseldorf, Germany, April, 1997.

[16] J. Kunawicz, P. Jones, J.A. Hockey, Trans. Faraday Soc. 67 (1970) 848.

[17] J.C.W. Chien, J. Am. Chem. Soc. 93 (1971) 4675.

[18] M.J.D. Low, A.G. Severdia, J. Low, J. Catal. 69 (1981) 384.

[19] B.A. Morrow, A.H. Hardiei, J. Phys. Chem. 83 (1979) 3135.

[20] N.V. Semikolenova, V.A. Zakharov, Macromol. Chem. Phys. 198 (1997) 2889.

[21] R.K. Iller, The Chemistry of Silica, Wiley, New York, 1979.

[22] A. Burneau, O. Barrés, J.P. Galles, J.-C. Lavalley, Langmuir 6 (1990) 1364.

[23] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, 2nd edn., Academic Press, New York, 1975, p. 277.

[24] D. Ballivet-Tkatchenko, J.H.Z. dos Santos, M. Malisova, Langmuir 9 (1993) 3513.

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

[26] M.J.D. Low, J.A. Cusumano, Can. J. Chem. 47 (1969) 3906.

[27] B.A. Morrow, A.J. McFarlan, J. Non-Cryst. Solids 120 (1990) 61.

[28] B.A. Morrow, A.J. McFarlan, Langmuir 7 (1991) 1695.

[29] P.J. Tait, R. Ediati, Proceedings of MetCon'97, June 4–5, 1997, Houston, USA.

[30] M.L. Hair, J. Non-Cryst. Solids 19 (1975) 299.

[31] J.L. Atwood, D.C. Hrnicir, R.D. Priester, R.D. Rogers, Organometallics 2 (1983) 985.

[32] M. Chang, (Exxon Chemical Patents, USA), Eur. Pat. Appl. EP 361866 Al 900404 (1990).

[33] P.J. Tait, A.A. Abozeid, A.S. Paghaleh, Metallocenes '96, 26–27 April, Brussels, Belgium (1995).