

# XPS and EXAFS characterization of Ziegler–Natta catalyst systems

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**ABSTRACT:** A series of Ziegler–Natta catalysts, with and without diisobutylphthalate as an internal donor, were modified with alkylaluminum (triethylaluminum or diethylaluminum chloride) and an external donor (diisopropyl-dimethoxysilane or methyltrimethoxysilane), in increasing complexity. The resulting catalysts were characterized by X-ray photoelectron spectroscopy and extended X-ray absorption fine structure analysis (EXAFS) and evaluated in propylene polymerization. According to EXAFS oscillation, systems bearing diisobutylphthalate as an internal donor displayed a well-defined pattern, suggesting a more ordered structure around the Ti atom. EXAFS data treat-

ment provided two Ti–Cl distances:  $\sim 1.96$  and  $2.5 \text{ \AA}$ . The former was shown to have a linear dependence on the Ti ( $2p^{3/2}$ ) binding energy as the catalyst is modified with TEA or with external donors. Conversely, the longest distance is reduced as Ti ( $2p^{3/2}$ ) binding energy increases with catalyst modification. Correlations involving the catalyst activity, Ti ( $2p^{3/2}$ ) binding energy, and Ti–Cl distances could be denoted. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1675–1683, 2008

**Key words:** EXAFS; donors, poly(propylene); XPS; Ziegler–Natta polymerization

## INTRODUCTION

Ziegler–Natta catalysts have been used in the olefin polymerization industry for roughly 50 years. Different routes have been developed for the preparation of the supported catalysts depending on the purpose. For polypropylene, the mechanical route is based on comilling  $\text{MgCl}_2$ ,  $\text{TiCl}_4$ , and a Lewis base (the so-called internal donor) for several hours. Alternatively, chemical routes can be used both to generate active  $\text{MgCl}_2$  and to incorporate Ti compound and the Lewis base. Among internal donors, aromatic esters (benzoates and phthalates) and diethers have been shown to be particularly suitable. Finally, the catalyst is activated by the addition of an alkylating reducing agent [triethylaluminum (TEA), for instance], possibly mixed with a second electron donor (the so-called external donor, usually an alkoxysilane). The resulting active system is of extreme chemical complexity, and the resulting polypropylenes present very different properties depending on the synthesis condition. The nature of the added Lewis base can strongly modify the tacticity of the resulting polymers, which can range from

atactic polymers to extremely isotactic polypropylenes, the molecular mass distribution, which can be rather narrow or rather large, and the response to molecular hydrogen, which clearly affects the molecular mass of the resulting polymers.<sup>1</sup>

Ziegler–Natta catalysts have been studied in the literature as real catalysts and as model catalysts. In spite of much research devoted to improve such catalysts, questions concerning the role of the catalyst components in the polymerization process and in the polymer properties have not until been completely answered. This is due mainly to the high sensitivity to oxygen and to atmospheric humidity, which makes investigation at the atomic level very complicated. Many spectroscopic techniques and probe molecules have been employed in these investigations. It has been suggested that, during the preparation of the catalyst,  $\text{TiCl}_4$  is chemisorbed on uncoordinated Mg atoms exposed at the lateral cuts of the  $\text{MgCl}_2$  crystallites. Tetra- and pentacoordinated Mg atoms present at (110) and (100) faces of  $\text{MgCl}_2$  are thought to be binding sites for  $\text{TiCl}_4$ .<sup>2,3</sup>

Surface sensitive techniques, in combination with other spectroscopic instrumental analyses, have provided information on the structure, composition, and oxidation state of the catalyst components. Among these techniques, two of them are very powerful: The extended X-ray absorption fine structure analysis (EXAFS) and X-ray photoelectron spectroscopy (XPS). The first allows the determination of the num-

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ber of the nearest neighbors of the target atom and the calculation of the interatomic distance of the neighbor atoms from the target one, while the latter determines the oxidation state by the binding energy (BE) determination.

A few studies dealt with the characterization of Ziegler–Natta catalysts by EXAFS. Potapov et al.<sup>4</sup> investigated the bonding of Ti atoms in a  $\text{TiCl}_4/\text{MgCl}_2$  catalyst suggesting an asymmetric structure which justifies the ease of the Ti atoms' alkylation by alkylaluminum. Comparing  $\alpha\text{-TiCl}_3$ ,  $\gamma\text{-TiCl}_3$ , and  $\text{TiCl}_3/\text{MgCl}_2$ , Usami et al.<sup>5</sup> observed that the Ti–Cl distance, in the case of the supported catalyst, was shorter in comparison to the Ti neat compounds. Also, the same authors concluded that the number of neighbors was reduced from 6.0 (in the case of  $\alpha\text{-TiCl}_3$ ) to 2.42 (in the case of  $\text{TiCl}_3/\text{MgCl}_2$ ). Similar results were reported by Vlaic et al.<sup>6</sup> Reed et al.,<sup>7</sup> based on Ti–Cl (2.22 Å) distance, suggested that there is a strong covalent character in it.  $\text{TiCl}_4$  supported on  $\text{SiO}_2$  and on  $\text{MgH}_2$  were also characterized by EXAFS.<sup>8</sup> Jones and Oldman conducted a systematic study by analyzing the EXAFS signal of various  $\text{TiCl}_4$ /ester complexes and concluded that the Ti center are bound to  $\text{MgCl}_2$  via a double Cl bridge as a  $\text{Ti}^{\text{IV}}$  complex.<sup>9</sup>

Ziegler–Natta catalysts have been also characterized by XPS. Furuta<sup>10</sup> employed it to estimate the surface elemental content in terms of Ti after catalyst treatment with alkylaluminum. Terano's group has investigated Ziegler–Natta catalysts.<sup>11–13</sup>  $\text{TiCl}_4/\text{MgCl}_2$  systems prepared by ball milling showed a broad electronic environment distribution of Ti species on the supported catalyst, which was suggested plays an important role on the nature of the active sites. The effect of electron donors on the oxidation state of Ti was also investigated by this group. XPS was also employed to distinguish surface titanocene species from Ti species of a fourth generation Ziegler–Natta catalyst in a hybrid catalyst.<sup>14</sup> Modifications of the Ti chemical environment in a supported Ziegler–Natta catalyst along thermal treatment was monitored by XPS.<sup>15</sup> Model catalysts prepared by  $\text{MgCl}_2$  sublimation onto a Au foil<sup>16</sup> or by spin coating of  $\text{Si}(110)/\text{SiO}_2$  substrate<sup>17</sup> were also studied by XPS. Very recent publications have been also devoted to investigating the nature of the surface of Ziegler–Natta catalysts by XPS.<sup>18–20</sup>

The studies using EXAFS or XPS focused mainly on the catalyst characterization. The purpose of this article was to investigate the nature of active species in Ziegler–Natta in two  $\text{TiCl}_4/\text{MgCl}_2$  catalysts, one of them bearing an internal donor, of increasing complexity, varying the alkylaluminum catalyst [TEA or diethylaluminum chloride (DEAC)] and the external electron donor (diisopropyldimethoxysilane and methyltrimethoxysilane). The catalysts were

characterized by XPS and EXAFS in succession and evaluated by propylene polymerization.

## EXPERIMENTAL

### Materials

All the manipulations were performed under Argon using the Schlenk technique. TEA (99.6%) and DEAC (100%) were purchased from Akzo (Jundiaí, Brazil). Diisopropyldimethoxysilane (DIPMS, 100%) was provided by Degussa (Paulínia, Brazil), while methyltrimethoxysilane (MTMS, 100%) by Witco (Bergkamen, Germany).

### Catalyst preparation

The spherical  $\text{MgCl}_2 \cdot n\text{C}_2\text{H}_5\text{OH}$  adduct was added to paraffin at 10°C under nitrogen flux. Then 100 mL of  $\text{TiCl}_4$  was added under mechanical stirring for 30 min. The temperature was raised to 100°C and maintained for 2.5 h. The mixture was then filtered and 100 mL of  $\text{TiCl}_4$  were once again added at 110°C, under stirring for an additional 2.5 h. The solid was washed with hexane and dried by nitrogen flux for 3 h. The resulting Ti content in the catalyst was 2.9 wt %. Textural properties of this system were: specific area (BET method), 239  $\text{m}^2 \text{g}^{-1}$ ; pore diameter, 36 Å; pore volume, 0.25  $\text{cm}^3 \text{g}^{-1}$ .

In the case of the supported catalysts bearing an internal donor, the same procedure was employed in which the internal donor was added before the  $\text{TiCl}_4$  impregnation step. The final internal donor content varied between 7 and 10%. The final metal content was 2.3 wt % of Ti. Textural properties of this system were: specific area (BET method), 200  $\text{m}^2 \text{g}^{-1}$ ; pore diameter, 39 Å; pore volume, 0.21  $\text{cm}^3 \text{g}^{-1}$ .

The external donor was added to the catalyst in an alkylaluminum/alkoxysilane molar ratio of 20.

### Catalyst characterization

#### X-Ray Photoelectron Spectroscopy

The X-ray photoelectron spectra were obtained on a PHI 5600 Esca System ( $\Phi$  Physical Electronics) [Eden Prairie, MN], using monochromated Al  $K\alpha$  radiation (1486.6 eV). Spectra were taken at room temperature in low resolution (pass energy 235 eV) in the range of 1000–0 eV and in high-resolution (pass energy 23.5 eV) modes for the Ti (2p) region.

The samples were mounted on an adhesive copper tape as thin films. Samples were prepared in a glove box, transferred under nitrogen atmosphere, and then evacuated at  $10^{-6}$  Torr by a turbomolecular pump in an introduction chamber for 90 min. During data collection, the ion pumped mass chamber was maintained at  $5 < 10^{-9}$  Torr. Each sample was analyzed at a 75° angle relative to the electron detec-

tor. Normally, 50 scans were signal averaged for selected BE windows and processed by the software supplied by the manufacturer. The neutralizer environment was 21.5 mA.

Ti 2p BEs were examined in the range 455–469 eV. Previous measurements using Au as external standard were reference charged to the Au 4f<sup>7/2</sup> peak at 84.0 eV. No significant variation along the samples was observed. Therefore, all BE values were then charge referenced to the Mg 2p (53.0 eV) of MgCl<sub>2</sub>. Three measurements per sample were made, and the reproducibility of the XPS analysis was confirmed. For each of the XPS spectra reported, an attempt has been made to deconvolute the experimental curve in a series of peaks that represent the contribution of the photoelectron emission from atoms in different chemical environments. These peaks are described as a mixture of Gaussian and Lorentzian contributions to take into account the effects of the instrumental error on the peak shape characteristic of the photoemission process.

### Extended X-ray absorption fine structure

The samples were prepared as pellets in a globe box and covered by Kapton<sup>®</sup> tape. The EXAFS measurements were performed at the XAS beam line of the LNLS facility.<sup>21</sup> The data were collected at the Ti K edge using a Si(111) monochromator and 1.5-mm vertical slits. The data were collected at room temperature using an ion chamber filled with Helium and a Ge 15 detector. The samples were placed in the beam line at 45° with respect to the incident beam. The spectra were collected in the range 4880–5420 eV with a 2 eV step and 6 s/pt. At least four spectra were averaged to obtain a better signal-to-noise ratio.

The EXAFS spectra were analyzed using the Winxas package.<sup>22</sup> The analysis was performed using the following general procedure: removal of the isolated atom background function from the experimental X-ray absorption coefficient data, and then a Fourier transform (FT) in the range 2.9–10.7 Å<sup>-1</sup> was applied using a Bessel window. Structural parameters were obtained from a least-squares fit to the data in *r*-space using phase shift and amplitudes obtained from the FEFF code.<sup>23</sup>

### Polymerization reactions

Polymerizations were conducted in liquid propylene. The reactions were performed in a 4-L steel reactor provided with mechanical stirring. In a typical procedure, the external electron donor was introduced into an alkyl hexane solution (12%) corresponding to Al/Ti = 2, and stirred for 5 min. Then, this solution was put into contact with the catalyst for an addi-

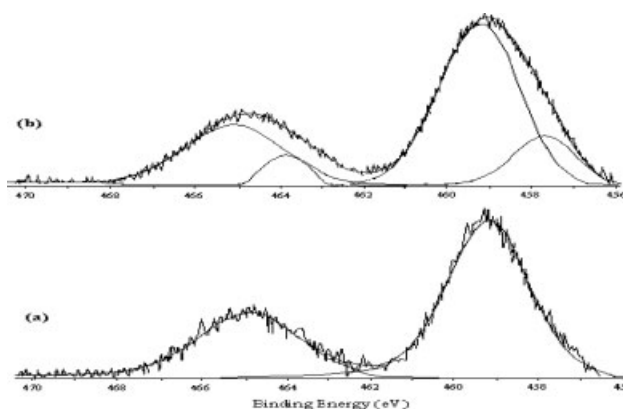
tional 5 min. After the precontact, the catalyst system was introduced into the reactor, which was already fed with liquid propylene and hydrogen at the polymerization temperature (75°C). Pressure (35 bar) was maintained using liquid propylene. Molecular weight control was performed by hydrogen feeding (1.6 bar). The polymerization was performed for 2 h and it was ended by the introduction of an acidic methanol solution into the reactor.

## RESULTS AND DISCUSSION

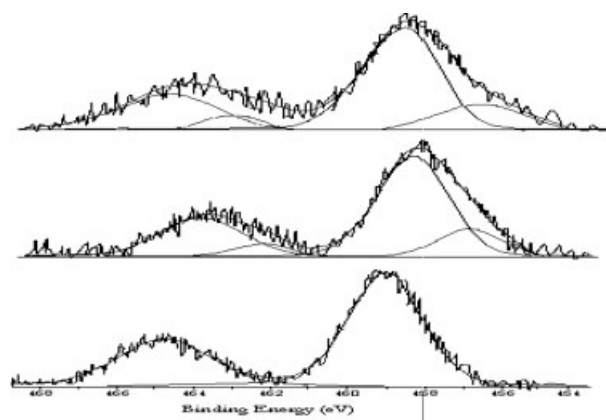
### Catalyst characterization

Spectrum (a) of Figure 1 shows the Ti 2p XPS core-level of the ZN catalyst of TiCl<sub>4</sub> supported on MgCl<sub>2</sub>. The Ti 2p core level spectrum of the catalysts presents a doublet centered at 458.9 and 465.0 eV due to spin-orbit coupling of the 2p electrons of Ti and corresponds to 2p<sup>3/2</sup> and 2p<sup>1/2</sup> photoelectrons, respectively. For the sake of simplicity, in the following discussion, we will mention the alteration only concerning the 2p<sup>3/2</sup> signal, although the BE shifts take place in both peaks.

Spectrum (b) of Figure 1 shows the spectrum of a supported Ziegler–Natta catalyst bearing an internal donor, diisobutylphthalate (DIBP), Ti/DIBP/MgCl<sub>2</sub>. The Ti 2p<sup>3/2</sup> core level spectrum presents a peak centered at 458.9 eV. This peak is close to that reported in the literature in the case of TiCl<sub>4</sub>/EB/MgCl<sub>2</sub> (EB = ethylbenzoate), TiCl<sub>4</sub>/DPB/MgCl<sub>2</sub> (DBP = dibutylphthalate),<sup>12</sup> or to that reported for TiCl<sub>4</sub>/PIP/MgCl<sub>2</sub> (PIP = piperidine), in this case a nitrogen electron donor (458.6 eV).<sup>24</sup> Comparing both spectra in Figure 1, that of Ti/DIBP/MgCl<sub>2</sub> is broader, suggesting the potential presence of other species. Deconvolution of the XPS signal resulted in two peaks: One centered at 458.9 eV and another at 457.5 eV, corresponding, respectively, to 80% and 20% of the total signal. The latter can be assigned to



**Figure 1** High-resolution XPS spectra in the Ti 2p core level: (a) Ti/MgCl<sub>2</sub>; (b) Ti/DIBP/MgCl<sub>2</sub>.



**Figure 2** High-resolution XPS spectra in the Ti 2p core level: (a) Ti/MgCl<sub>2</sub>; (b) Ti/MgCl<sub>2</sub> + TEA; (c) Ti/MgCl<sub>2</sub> + TEA + DIPMS.

species which are in electron-rich environments, probably due to the presence of the internal donor. Mori et al. measured the Ti XPS signal for this catalyst system and obtained a FWHM (full width at half maximum intensity) of 3.1 eV, similar to that observed in this study, but proposed no deconvolution.<sup>12</sup>

One of the roles of the internal donor is to prevent the formation of nonstereospecific sites by adsorbing on MgCl<sub>2</sub> surface, on the sites on which TiCl<sub>4</sub> would be prone to generate nonstereospecific sites.<sup>25</sup> Although a direct interaction between the internal donor and the surface Ti is not completely proved, it seems that Ti atoms are affected by the interaction with the internal electron donor immobilized on the MgCl<sub>2</sub> surface.

BE shifts are due to contributions from both the oxidation state and electron density on the nearest neighbor atoms of the target atom. Spectrum (b) of Figure 2 reports the XPS spectrum of the product of the reaction of the supported catalyst system with TEA.

Ti 2p<sup>3/2</sup> core level spectrum (Fig. 2) can be deconvoluted into two components: One centered at 458.20 eV and another at 456.8 eV. Similar BE shifts after Ti reduction by alkylaluminum have also been reported in the literature.<sup>13,15</sup> The peak at lower BE can be attributed to species bearing lower oxidation states, probably generated due to the large excess of TEA. For instance, Ti<sup>3+</sup> species have been reported at 457.4 eV,<sup>15</sup> while Ti<sup>2+</sup> at 456.2 eV.<sup>15,17</sup> As reported by Mori et al., this BE shift depends on the nature of the alkylaluminum, being higher in the case of TEA (458.3 eV) in comparison to that of DEAC (458.7 eV).<sup>12</sup> According to Table I, a similar trend was observed in this study.

The reaction of Ti/TEA/MgCl<sub>2</sub> with an external donor (DIPMS) solution generated a catalyst system whose XPS spectrum is represented in (c) of Figure 2.

**TABLE I**  
Binding Energy of the Modified Ti/MgCl<sub>2</sub> Ziegler–Natta Supported Systems

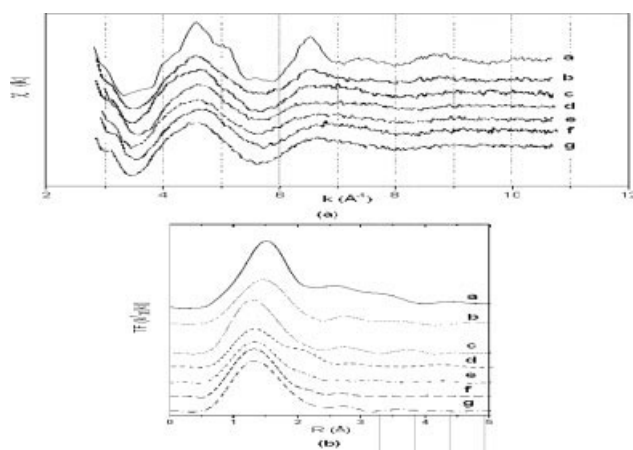
Catalyst system	Ti (2p <sup>3/2</sup> ) (eV)	
Ti/MgCl <sub>2</sub>	458.9 (2.28)	
Ti/MgCl <sub>2</sub> + TEA	458.2 (2.14)	456.8 (2.70)
Ti/MgCl <sub>2</sub> + DEAC	458.3 (2.33)	457.1 (2.26)
Ti/MgCl <sub>2</sub> + TEA + DIPMS	458.1 (2.20)	457.1 (2.50)
Ti/MgCl <sub>2</sub> + TEA + MTMS	458.5 (2.96)	457.0 (2.30)
Ti/MgCl <sub>2</sub> + DEAC + DIPMS	458.5 (2.26)	457.4 (2.22)
Ti/MgCl <sub>2</sub> + DEAC + MTMS	458.7 (2.33)	457.3 (2.35)

No significant shift is observed in comparison to spectrum (b). Nevertheless, the signal is much broader, suggesting a higher heterogeneity in this system. Similar behavior is observed in the case of MTMS (see Table I). Such external donors, functioning as Lewis base, if directly interacting with Ti centers, would cause a shift toward lower BE, because the metal centers would be in a more electron-rich environment. XPS BE shifts are in the opposite direction, suggesting that somehow the effect of the external donor affects the support environment, which in turn increases the cationic character on Ti centers or it is partially removing the alkylaluminum. Similar trend is observed in the case of Ti/DEAC/MgCl<sub>2</sub>, modified by the external donors (DIPMS or MTMS).

Table II shows the BE values determined for the system containing the internal donor: Ti/DIPB/MgCl<sub>2</sub>. As discussed earlier, the broad peak allows one to propose a deconvolution into two signals: 458.9 and 457.5 eV. Conversely to Ti/MgCl<sub>2</sub>, in which the external donor seemed not to directly interact with Ti centers, in the case of Ti/DIPB/MgCl<sub>2</sub>, the prior reaction with the internal donor seems to yield surface species in which the electron density on Ti is affected by electron donation from the internal donor. The model from Xu et al.<sup>26</sup> takes into account the direct interaction between the carbonyl from esters. In the case of Ti/DIPB/MgCl<sub>2</sub>, after reaction with TEA or DEAC and external donors,

**TABLE II**  
Binding Energy (BE) of the Modified Ti/DIPB/MgCl<sub>2</sub> Ziegler–Natta Supported Systems

Catalyst system	Ti 2p <sup>3/2</sup> (FWHM) (eV)	
Ti/DIPB/MgCl <sub>2</sub>	458.9 (2.28)	457.5 (2.00)
Ti/DIPB/MgCl <sub>2</sub> + TEA	458.2 (2.51)	456.7 (2.70)
Ti/DIPB/MgCl <sub>2</sub> + DEAC	458.3 (2.16)	457.0 (2.00)
Ti/DIPB/MgCl <sub>2</sub> + TEA + DIPMS	458.4 (2.17)	457.4 (2.85)
Ti/DIPB/MgCl <sub>2</sub> + TEA + MTMS	458.3 (2.18)	457.6 (2.70)
Ti/DIPB/MgCl <sub>2</sub> + DEAC + DIPMS	458.6 (2.00)	457.6 (2.31)
Ti/DIPB/MgCl <sub>2</sub> + DEAC + MTMS	458.4 (2.12)	457.8 (2.20)



**Figure 3** (a) EXAFS signals and (b) corresponding Fourier transform modulus. Systems: (a) Ti/DIBP/MgCl<sub>2</sub>; (b) Ti/DIBP/MgCl<sub>2</sub> + DEAC + DIPMS; (c) Ti//MgCl<sub>2</sub>; (d) Ti/MgCl<sub>2</sub> + TEA; (e) Ti//MgCl<sub>2</sub> + TEA + DIPM; (f) Ti//MgCl<sub>2</sub> + TEA + MTMS; (g) Ti//MgCl<sub>2</sub> + DEAC + DIPMS.

the same trend as in the case of Ti/MgCl<sub>2</sub> is observed.

According to XPS analysis, it is hard to extract data which makes evident any direct interaction between the external donor and the Ti centers. The systems were then further analyzed by EXAFS, as shown in Figure 3.

According to Figure 3, the comparison of the EXAFS oscillations demonstrates that sample Ti/DIBP/MgCl<sub>2</sub> displays a well defined pattern, suggesting a much more ordered structure around Ti for this sample. Sample Ti/MgCl<sub>2</sub> has exactly the same pattern as sample Ti/DIBP/MgCl<sub>2</sub>. Nevertheless, the oscillations are much more smooth, indicating an increase in disorder around Ti. The remaining samples display generally similar EXAFS oscillations. It is worth noting that in the case of sample Ti/MgCl<sub>2</sub>, which was reacted with TEA, there is an additional bump at 7.5 Å<sup>-1</sup>, suggesting that differences in the local structure might be due to interaction with the alkylaluminum.

The FTs of samples Ti/DIBP/MgCl<sub>2</sub> and Ti/MgCl<sub>2</sub> display well-defined FT peaks up to 4 Å, pointing at 1.5, 2.6, 3.3 Å (uncorrected from phase shift). The other samples display a main peak at around 1.3 Å (uncorrected from phase shift). For sample Ti/MgCl<sub>2</sub>, which was reacted with TEA, the main peak has lower amplitude and a shoulder, suggesting the presence of two distinguished shells in the coordination shell.

In the fitting procedure for samples Ti/DIBP/MgCl<sub>2</sub> and Ti/MgCl<sub>2</sub>, three distances were included, corresponding to two contributions of Ti—Cl and one of Ti—Ti. For all other samples only Ti—Cl distances were taken into account. Attempts to fit the coordination shell with Ti—O, Ti—C, or Ti—Al con-

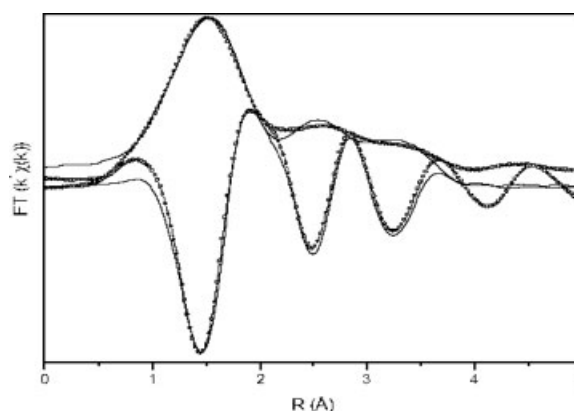
tributions yielded unsatisfactory results. A typical fitting result is shown in Figure 4 for sample Ti/DIBP/MgCl<sub>2</sub> that corresponds to two Ti—Cl and one Ti—Ti contributions.

Table III displays the quantitative analysis obtained for all samples measured by EXAFS, which provided satisfactory results. For the other ones, reliable data fittings were not possible.

According to Table III, two Ti—Cl distances could be assigned: a shorter one, in the range of 1.92–2.10 Å, and a longer, in the range of 2.12–3.08 Å. Distances between 2.06 and 3.09 Å for Ti—Cl in Ziegler–Natta catalysts have been reported in the literature.<sup>4–8</sup>

The quantitative analysis confirms that sample Ti/DIBP/MgCl<sub>2</sub> has atomic local structures where Ti is in a much more ordered environment since it is possible to point out a Ti—Ti distance at around 3.61 ± 0.04 Å. According to Soga et al., the internal donor (DIBP) coordinates on the MgCl<sub>2</sub> surface to form the highly isospecific site, which has only one vacant site. Therefore, the formation of bi- or multinuclear Ti species, which easily transforms it to nonstereospecific sites by the migration of a bridged Cl ligand, is hampered.<sup>27</sup> The trialkylaluminum (Lewis acid), which is added to the polymerization media, can extract the internal donor, yielding the nonstereospecific site. Therefore, a large excess of external donor is necessary to prevent the internal donor extraction or its replacement.<sup>28,29</sup> According to Table III, the reaction of this system with DEAC and DIPMS did not significantly alter the atomic distances at the nearest neighbors.

The absence of an internal donor (DIBP) in the Ti/MgCl<sub>2</sub> catalyst system renders it less ordered, since the Ti/MgCl<sub>2</sub> systems display only Ti—Cl contributions as the nearest neighbors. The addition of TEA to Ti/MgCl<sub>2</sub> engenders a system with a longer Ti—Cl distance. Natta et al. synthesized a bimetallic complex containing Ti and Al and characterized it



**Figure 4** Fitting of the FT modulus and imaginary part. The experimental data are the empty circles and fit the full lines for the sample Ti/DIBP/MgCl<sub>2</sub>.

**TABLE III**  
Structural Parameters Obtained from Least Square Fitting

Sample	Pair	$N \pm 1$	$R \pm 0.04$ (Å)	$\sigma^2 \pm 0.002$ (Å) <sup>2</sup>	$E_0$ (eV) $\pm 1$
Ti/DIBP/MgCl <sub>2</sub>	Ti—Cl	5	2.10	0.00976	-2.8
	Ti—Cl	1	3.08	0.00382	-5.8
	Ti—Ti	2.4	3.61	0.00217	6.08
Ti/DIBP/MgCl <sub>2</sub> + DEAC + DIPMS	Ti—Cl	4.2	2.09	0.01136	-2.8
	Ti—Cl	1.8	3.08	0.00858	-5.8
	Ti—Ti	0.9	3.59	0.00444	6.08
Ti/MgCl <sub>2</sub>	Ti—Cl	1.3	1.97	0.0051	-2.9
	Ti—Cl	2.7	2.13	0.0044	-5.2
Ti/MgCl <sub>2</sub> + TEA	Ti—Cl	1.5	1.92	0.0045	-2.8
	Ti—Cl	2.5	2.64	0.01112	-5.0
Ti/MgCl <sub>2</sub> + DEAC	Ti—Cl	1.5	1.91	0.0067	-2.8
	Ti—Cl	2.5	2.62	0.01133	-5.2
Ti/MgCl <sub>2</sub> + TEA + DIPMS	Ti—Cl	1.5	1.98	0.00794	-2.9
	Ti—Cl	2.5	2.15	0.001315	-5.2
Ti/MgCl <sub>2</sub> + TEA + MTMS	Ti—Cl	0.8	1.96	0.00876	-2.9
	Ti—Cl	3.2	2.12	0.00179	-5.2
Ti/MgCl <sub>2</sub> + DEAC + DIPMS	Ti—Cl	1.4	1.97	0.00998	-2.9
	Ti—Cl	2.6	2.14	0.00298	-5.2
Ti/MgCl <sub>2</sub> + DEAC + MTMS	Ti—Cl	0.9	1.95	0.00879	-2.8
	Ti—Cl	2.7	2.10	0.00279	-5.2

Number of neighbors ( $N$ ), distance ( $R$ ), Debye Waller factor ( $\sigma^2$ ), and energy shift ( $E_0$ ).

by X-ray diffraction. In this system, the authors proposed the presence of bridged Cl atoms between Al ones, bearing a Ti—Cl distance in the range of 2.5 Å.<sup>30</sup> It is very likely that in Ti/MgCl<sub>2</sub> system, the reaction with TEA yielded a similar structure on MgCl<sub>2</sub> surface, taking into account the distance determined by EXAFS (2.64 Å). It is worth noting that the fact that no bridged-Cl was observed for the catalyst system resulting from the addition of the external donor, and can be partially explained by the “island” model proposed by Terano.<sup>31</sup> The presence of a multinuclear Ti surface (islands of Ti) in systems bearing an internal donor affords a more effective interaction among the components (catalyst, cocatalyst, donor) of the catalyst system, hampering or even hindering, for steric reasons, the possibility of formation of bridged-Cl species. In this study, such long 2.64 Å Ti—Cl distances, attributed to bridged Ti—Cl bond, was not observed for the systems bearing internal or external donor.

According to Table III, the interaction between Ti/TEA/MgCl<sub>2</sub> and the external donors engenders the reduction in the Ti—Cl longer distance to values close to 2.15 Å. Besides, the external donor bearing the less sterically demanding ligand (MTMS) perturbs the system more, leading to a more significant distance reduction.

Table IV shows the data of BE and Ti—Cl distance for Ti/MgCl<sub>2</sub> system. There is a direct correlation between the BE of the Ti (2p<sup>3/2</sup>) signal and the shortest Ti—Cl distance determined by EXAFS for this catalyst system modified with TEA or DEAC and with the electron donors.

The correlation shown in Table IV suggests that the increase in the cationic character of the Ti species (of lower BE) is associated with the increase of the shortest Ti—Cl distance. The inclusion of electron donors might be reducing the Ti—Cl bond strength. Nevertheless, other effects might be occurring to engender an increase in Ti (2p<sup>3/2</sup>) BE. On the other hand, for the other Ti—Cl distance, the behavior is inverse: An increase in the cationic character of this Ti species is accompanied by a reduction in the longest Ti—Cl distance as electron donors are added to the Ti/TEA/MgCl<sub>2</sub> or Ti/DEAC/MgCl<sub>2</sub> system. It is likely that the increase in cationic character engenders an increase in the bonding strength between the Ti and the formerly bridged Cl atoms. And in both cases, the more sterically demanding donor (DIPMS) engenders a more significant effect.

The relationships extracted from Table IV has to be considered with caution, since data provided by

**TABLE IV**  
Relation Between Binding Energy of Ti (2p<sup>3/2</sup>) Signal and the Shortest and the Longest Ti—Cl Distance in the Ti/MgCl<sub>2</sub> Catalyst for the Systems Resulting from the Addition of TEA, DEAC, MTMS, and DIPMS

Catalyst system	Ti (2p <sup>3/2</sup> ) (eV)	Ti—Cl (Å)	Ti—Cl (Å)
Ti/MgCl <sub>2</sub> + TEA	456.8	1.92	2.64
Ti/MgCl <sub>2</sub> + TEA + MTMS	457.0	1.96	2.12
Ti/MgCl <sub>2</sub> + TEA + DIPMS	457.1	1.97	2.14
Ti/MgCl <sub>2</sub> + DEAC	457.1	1.92	2.52
Ti/MgCl <sub>2</sub> + DEAC + MTMS	457.3	1.95	2.10
Ti/MgCl <sub>2</sub> + DEAC + DIPMS	457.4	1.97	2.12

XPS measurements takes into account the electron density at Ti, determined by all the ligands (coordination sphere) at the same time. On the other hand, EXAFS measurements take into account a mean of the atoms in the neighborhood of Ti metal centers, independently of the oxidation state. Nevertheless, these results indicate that a compensating effect between these two Ti—Cl bonds is taking place: As the longest Ti—Cl is reduced, the shortest one is lengthened. The external donor seems not to directly interact with Ti centers but affects the environment. The fact that the influence of DIPMS (the bulkiest donor) is greater than MTMS suggests that the influence of the external donor is probably more of steric order. Nonetheless, its presence on the catalyst system indirectly influences the electron density on the Ti centers.

### Catalyst activity

Both catalyst systems were evaluated in propylene polymerization. Results of catalyst activity expressed in terms of kg PP/g Ti are shown in Figure 5.

Comparing both systems, catalyst activity of Ti/DIPB/MgCl<sub>2</sub> was much higher than that of Ti/MgCl<sub>2</sub>. For each catalyst system, reactions using TEA as the cocatalyst yielded much more polypropylene than those using DEAC. This behavior can be justified in terms of reducing power of the alkylaluminum, and therefore, the Ti oxidation state. TEA is a Lewis acid, with a higher reducing power than DEAC. Then, the higher reduction degree in the case of TEA affords higher catalyst activity, which in turn can be associated to the Ti species oxidation state generated after reaction with the cocatalyst.<sup>13</sup> The use of DEAC seems not to guarantee an effective number of active Ti species.

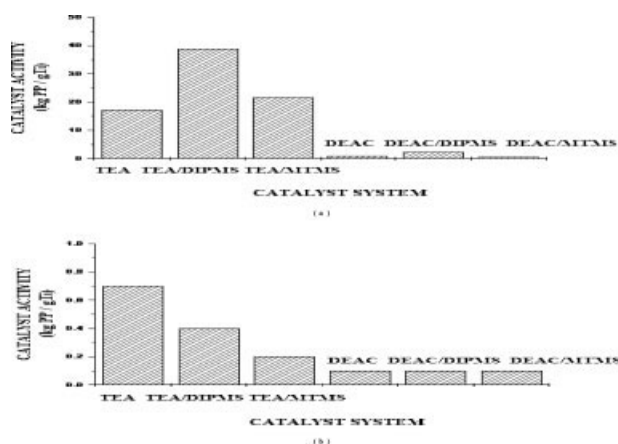
Another factor to be considered is the nature of the Lewis acid–Lewis base generated complex.

According to the literature, TEA and alkoxy silane instantly react forming 1 : 1 complex, independently of the number of alkoxy ligands in the organosilane.<sup>32</sup> This complex can dissociate interacting either with the Ti catalyst site, as with the support sites (Mg). Taking into account the lower coordinating capacity of DEAC, even in excess of alkylaluminum, free organosilane molecules would act as poison, interacting with the active centers. This could explain the lower catalyst activity of the Ti/DIPB/MgCl<sub>2</sub> having DEAC as cocatalyst instead of TEA (see Fig. 5). Besides, in the case of Ti/MgCl<sub>2</sub>, the external donors act like poison, reducing catalyst activity. This behavior is opposite to that observed in the case of Ti/DIPB/MgCl<sub>2</sub> system, in which an increase of up to 100% in catalyst activity took place after the addition of DIPMS.

The increase in activity with the addition of the external donors in the case of Ti/DIPB/MgCl<sub>2</sub> could be due to the coordination of these molecules to the support indirectly tuning the electron density on Ti catalyst centers. Comparing the effect of adding MTMS and DIPMS, the former engenders a reduction in catalyst activity. MTMS presents smaller alkoxy groups, and therefore, a higher electronic density, a large number of alkoxy groups and less steric effect than DIPMS. The ensemble of factors turns this electron donor in a strong coordinating molecule, which might more easily deactivate the active species. Some studies in the literature have shown the deactivation of active species by the external donors. Results have shown that bulky and non-linear alkyl groups reduce the deactivating effect of the alkoxy groups.<sup>33</sup> This could explain the higher catalyst activity observed in the case of DIPMS in comparison to MTMS for Ti/DIPB/MgCl<sub>2</sub> or Ti/MgCl<sub>2</sub> (in the case of TEA as the cocatalyst).

Table V correlates catalyst activity with the BE of Ti (2p<sup>3/2</sup>) species generated under several conditions.

According to Table V, for the Ti/DIPB/MgCl<sub>2</sub> system, independently of the cocatalyst, an increase in the BE engenders an enhancement in catalyst activity up to a certain point. The increase in catalyst activity might be related to the formation of more cationic species, which favor the coordination of the olefin. Nevertheless, for higher BE values (and therefore, higher cationic character), a decrease in catalyst activity is then observed, probably due to strong interaction between the coordinated olefin and the catalyst site, which in turn is translated in a reduction of propagation rate. One cannot neglect that the steric effect played by the ligand might be also imposing some effect. In the case of this system, higher activity was observed with the high steric demanding electron donor. The effect of a bulky external donor such as DIPMS on the formation of highly isospecific centers, and the increase in propagation rate con-



**Figure 5** Catalyst activity in propylene polymerization: (a) Ti/DIPB/MgCl<sub>2</sub>; (b) Ti/MgCl<sub>2</sub>.

TABLE V  
Relation Between Binding Energy of Ti ( $2p^{3/2}$ ) Signal and Catalyst Activity in Propylene Polymerization for Ti/DIPB/MgCl<sub>2</sub> and Ti/MgCl<sub>2</sub> Systems Resulting from the Addition of TEA, DEAC, MTMS, and DIPMS

Cocatalyst/ Donor	Ti/DIPB/MgCl <sub>2</sub>		Ti/MgCl <sub>2</sub>	
	Ti ( $2p^{3/2}$ ) (eV)	Catalyst activity (kg PP/g catalyst)	Ti ( $2p^{3/2}$ ) (eV)	Catalyst activity (kg PP/g catalyst)
TEA	456.7	17.2	456.8	0.7
TEA/DIPMS	457.4	38.9	457.1	0.4
TEA/MTMS	457.6	21.7	457.0	0.2
DEAC	457.0	1.0	457.1	0.1
DEAC/DIPMS	457.6	2.9	457.4	0.1
DEAC/MTMS	457.8	0.7	457.3	0.1

stant with increasing stereo- and regiospecificity cannot be neglected, and might be a dominant factor. For the Ti/MgCl<sub>2</sub> system (see Table V), considering the cocatalyst (TEA or DEAC), the same trend is observed here: as BE increases, catalyst activity is reduced. Then, it seems that the higher reducing power of TEA guarantees the generation of Ti active species, increasing, consequently, the catalyst activity. The same effect played by the external donor is also observed, where DIPMS afforded relative higher catalyst activity than MTMS. Nevertheless, the role of the alkyl seems also to be fundamental, since in the case of DEAC.

The compensating effect in the case of the two Ti—Cl distances observed in the case of Ti ( $2p^{3/2}$ ) BE for Ti/MgCl<sub>2</sub>, having TEA as the cocatalyst, was also evaluated in terms of catalyst activity (Fig. 6).

As shown in Figure 6, there is a correlation between catalyst activity and Ti—Cl distances. An enhancement in catalyst activity seems to be associated with a decrease in the longest Ti—Cl bond and to an increase in the shortest Ti—Cl one, the effect being more significant in the former. A plausible explanation could be that a longer Ti—Cl (in the case of the shortest one) signifies a more labile bond, which might be more prone and easier to be alkylated, and therefore to generate the active species.

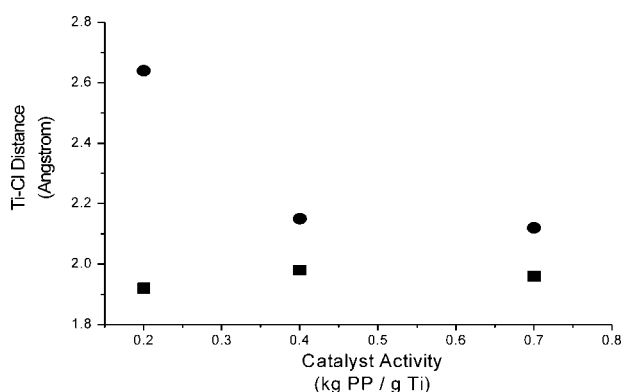


Figure 6 Correlation between catalyst activity in propylene polymerization and Ti—Cl distance.

In the case of DEAC, whose catalyst activity remains practically constant [see Fig. 5(b)], the trend is less clear. Nevertheless, the longest Ti—Cl bond decreases from 2.52, 2.14, and 2.12 Å, while the shortest one increases, 1.92, 1.95, and 1.97 Å (see Table III), respectively, along the difference systems in the absence or after the introduction of the external donor.

## CONCLUSIONS

The combination of XPS and EXAFS techniques has proved to be a helpful tool for the investigation of surface species in supported Ziegler–Natta catalysts. The interaction of electron donors with Ti centers is dependent on the preparation conditions and on its nature. Internal donors, which are introduced during the preparative step, seem to directly interact with catalyst centers. External donors, introduced at the moment of polymerization, seem to affect the environment around Ti centers, but not by direct interfering on the metal centers. Their contribution seems to be due to both steric and electronic effects, but the latter results from the coordination to the support or from its interaction with the cocatalyst but not from the direct interaction of Ti species. In terms of catalyst activity, its correlation with the Ti—Cl distance and with Ti ( $2p^{3/2}$ ) BE was observed. It should be stressed that the results obtained from XPS and EXAFS give an average picture of Ti present in the catalyst. Further studies are necessary to extend the knowledge of such complex catalyst system at the atomic level.

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