

# XPS study of metallocene based catalysts for the polymerization of ethylene

F. Garbassi \*, L. Gila, A. Proto

EniChem S.p.A., Istituto Guido Donegani, Via Fauser 4, 28100 Novara, Italy

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## Abstract

X-ray photoelectron spectroscopy (XPS) has been applied to the study of a series of metallocene catalysts, containing Zr, Ti or Hf, for the polymerization of ethylene. Surface atomic compositions, binding energies and valence band (VB) spectra have been measured. Surface compositions were found to be more or less similar to the expected values on the basis of molecular structure depending on the stability of compounds vs. air contact. XPS analyses after air exposure showed a marked tendency of metal–Cl bonds to be substituted by metal–O bonds. Binding energy of zirconium was found to be rather sensitive on the overall electron-attractive effect of ligands, with the following energy scale:  $ZrCl_4 > Cp_2ZrF_2 > CpZrCl_3 > Cp_2ZrCl_2 = (Cp_2ZrCl)_2O > Cp_2Zr(NEt_2)_2$ . A relationship was found with catalytic activity, which seems to be favoured by a low binding energy value of Zr. VB spectra have been discussed, showing peculiar features depending on the molecular structure.

**Keywords:** Ethylene; Hafnium; Metallocenes; Photoemission; Polymerization; Titanium; XPS; Zirconium

## 1. Introduction

In the early 1980s, high yield polymerization of ethylene was achieved by using a mixture of bis(cyclopentadienyl) zirconium dichloride,  $Cp_2ZrCl_2$  and methylalumoxane (MAO) [1]. Later, experimental results were extended to other metals, mainly Ti but also Hf [2] and other ligands. Different polymers were obtained using catalysts of the same family, like syndiotactic polystyrene [3], stereospecific polypropylene [4] and ethylene–propylene copolymers [5].

It is believed, though it is still controversial, that the true catalyst is a  $Cp_2ZrMe^+$  cation, able to coordinate the olefin and to proceed by successive insertions to lengthen the chain. For this rea-

son, chlorine atoms are considered as ‘mobile’ ligands. Especially when stereospecificity is important, a complex but well established link between catalyst structure and polymer structure was observed [2]. Also the activity is strongly influenced by the catalyst structure, for instance bis(pentamethyl cyclopentadienyl) zirconium dichloride, was found to be less active than  $Cp_2ZrCl_2$  [6].

X-ray photoelectron spectroscopy (XPS) was used to study the effect of the nature of ligands on the binding energy of the metal. In particular, the replacement of hydrogen atoms of the Cp rings by methyl groups was studied in the case of Ti, Zr and Hf, observing a lowering of the Zr 3d binding energy around 0.06–0.08 eV per methyl group [7]. The electron-withdrawing power of some

\* Corresponding author.

substituents at the ring were also assessed [8], as well as the effect of maintaining the two Cp rings and changing the mobile ligands L. Binding energy variations for  $\text{Cp}_2\text{ZrL}_1\text{L}_2$  compounds in a range of 1.7 eV were observed [9]. The equivalent effects were studied in the case of titanocene dichloride catalysts, observing variations up to 0.8 eV for Ti 2p and 0.4 eV for Cl 2p photoemission peaks [10].

By performing the XPS analysis of several  $\text{Cp}_x\text{ML}_y$  catalysts (where  $\text{M} = \text{Zr, Ti or Hf}$ ;  $x = 1$  or 2 and  $y = 2$  or 3,  $x + y = 4$ ), aim of this work was to gain a better assessment of the potentiality of such a spectroscopy in the study of polymerization catalysts, combining the measurement of binding energies with the determination of elemental composition and with the study of the valence band region of the spectrum.

## 2. Experimental

### 2.1. Preparation of complexes

$\text{Cp}_2\text{ZrCl}_2$  (purity >98%) and  $\text{Cp}_2\text{TiCl}_2$  (purity 97%) were purchased from Fluka.  $\text{Cp}_2\text{HfCl}_2$  (purity 98%) and zirconium tetrachloride  $\text{ZrCl}_4$  (purity 99.5%) were purchased from Aldrich.

$\text{Cp}_2\text{ZrF}_2$  was synthesized by a method described in the literature [11], involving the transformation of dichloride in the corresponding di-tert-butoxy complex and its subsequent fluorination.  $\text{CpZrCl}_3$  was prepared by photochemical chlorination of dichloride with gaseous chlorine [12].  $(\text{Cp}_2\text{ZrCl})_2\text{O}$  was prepared by oxidation of dichloride with water in dichloroethylene in the presence of aniline [13,14].  $\text{Cp}_2\text{Zr}(\text{NEt}_2)_2$  was prepared by reaction of cyclopentadiene with zirconium tetramide [15,16].

Elemental compositions of all complexes purchased and prepared were checked by chemical analysis and  $^1\text{H-NMR}$ .

### 2.2. Catalytic activity

Polymerization runs were carried out in slurry conditions in a glass reactor of 500  $\text{cm}^3$  (Buchi) equipped with mechanical stirrer, thermocouple and introduction valves for reagents. After three consecutive dry  $\text{N}_2$ /vacuum washing runs, 250  $\text{cm}^3$  of anhydrous toluene and a suitable amount of methylalumoxane (MAO) (Schering) were introduced in the reactor and the temperature increased to 70°C. After 5 min aging, ethylene was introduced at a partial pressure of  $2 \times 10^5$  Pa, together with  $10^{-3}$  mmol of catalyst previously dissolved in toluene. In all experiments the atomic ratio between aluminum (from MAO) and metal (of the metallocene complex) was taken to be at 2500.

During catalytic runs, temperature and pressure were maintained constant. After 30 min, the reaction was stopped and the polymer precipitated in acidified methanol. Polyethylene was washed accurately with acetone, dried overnight in an oven at 50°C, then characterized by gel permeation chromatography (GPC) using a GPC System (Waters 150CV) operating at 135°C with trichlorobenzene as a solvent and differential refractive index detector.

### 2.3. XPS analysis

XPS analysis was performed with a Physical Electronics Inc. (PHI) 5500 ESCA system. The instrument was equipped with a monochromatic X-ray source (Al  $K\alpha$  anode) operating at 14 kV and 200 W. Powder samples were pressed onto a clean In foil under  $\text{N}_2$  atmosphere and transferred to the analysis chamber using a sample transfer vessel Model 04-110 (PHI, Eden Prairie), in order to avoid contact with air atmosphere. The diameter of the analysed spot was 400  $\mu\text{m}$ . The pressure of the analysis chamber was maintained at  $10^{-8}$  Pa. The electron take-off angle was generally maintained at 45°.

After measuring general XPS spectra, single photoemission peaks were collected in high resolution mode. In order to examine the valence

band features, the 0–35 eV binding energy range was also collected. Surface atomic concentrations were derived from integrated peak intensities corrected for the elemental sensitivity factors provided by Physical Electronics. A low energy flood electron gun was used for compensating electrostatic charging effects. The binding energy scale was regulated by setting the C 1s peak at 285.0 eV.

Because several of the analysed substances are very sensitive toward air exposure, samples were extracted from the spectrometer after XPS analysis, exposed to air for a given time (10 min), then analysed again. This procedure was made for two reasons, firstly to check the efficiency of the transfer operations under controlled atmosphere and secondly to observe the effects of the air exposure itself.

### 3. Results

#### 3.1. Binding energies

Binding energies of elements constituting the molecules and complexes considered are reported in Table 1. Measured values are compared with available literature data [7,8,10]. As  $\text{Cp}_2\text{MCl}_2$  ( $\text{M} = \text{Zr, Ti or Hf}$ ) are concerned, good agreement with literature was found [7,10]. In the case of zirconocene oxychloride, because the carbon reference value is not reported in Ref. [8], the same value of Ref. [7] was assumed. With this procedure, agreement with our data is again satisfactory.

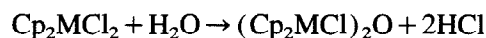
In all metallocene complexes containing chlorine as a ligand, Cl 2p binding energies are similar, at  $199.0 \pm 0.2$  eV. On the contrary, a value 1 eV higher was found in  $\text{ZrCl}_4$ . The latter result is consistent with the value of 199.6 eV obtained by Nefedov [17].

Taking into account the binding energies of zirconium, they were found quite sensitive to the nature of 'mobile' ligands, in fact values ranged between 181.6 eV for the diethylamide complex and 182.8 eV for  $\text{Cp}_2\text{ZrF}_2$ . No literature data were

found for the latter compound, however it is interesting to note that passing from dichloride to difluoride the corresponding Ti complexes showed an increase of 0.6 eV of the metal binding energy [7], very similar to the 0.8 eV here observed for zirconium. The highest Zr binding energy value was measured, among the compounds considered, for zirconium tetrachloride.

#### 3.2. Surface compositions

Surface compositions are reported in Table 2 and compared with values calculated considering the chemical formulas. Dichlorides and the difluoride show only minor deviations from expected values, mainly due to a slight uptake of oxygen (around 2–3 at.%) and to a limited excess of carbon (carbon-to-metal ratios are always higher than the expected value of 10). Some adventitious carbon contamination is likely at the origin of these results. The presence of oxygen is due to the unwanted exposure to air of the powder samples, either leakage of their sealed storage flasks (maintained under inert atmosphere) after preparation or, more likely, during the insertion procedure in the analysis chamber. The effect of humidity of air atmosphere can be sketched as follows:



The exposure to air of analysed samples for some minutes, followed by a second XPS analysis, has the effect of increasing 2–3 times the oxygen concentration. Considering the halogen-to-metal ratios, this seems to occur more at the expenses of halogens than of the other elements, in agreement with the above reaction, even if the high amount of oxygen suggests that further Cl atoms are substituted in the complex, probably by hydroxyl groups. This further oxygen uptake is also a confirmation that the insertion procedure of samples into the XPS analysis chamber is at least partially suitable. It is finally interesting to note that only in the case of difluoride the oxygen increase after air exposure seems to occur not at the expenses of the mobile ligands, but of cyclopentadienyl ring,

Table 1  
Binding energies of compounds examined and comparison with literature data

Compound	Binding energies (eV)							
	C	Cl	F	Zr	Ti	Hf	O	N
Cp <sub>2</sub> ZrCl <sub>2</sub>	284.9	198.8	–	182.0	–	–	–	–
Cp <sub>2</sub> TiCl <sub>2</sub>	285.0	198.7	–	–	457.5	–	–	–
Cp <sub>2</sub> HfCl <sub>2</sub>	285.0	199.2	–	–	–	17.6	–	–
Cp <sub>2</sub> ZrF <sub>2</sub>	285.0	–	687.6	182.8	–	–	–	–
CpZrCl <sub>3</sub>	285.0	198.9	–	182.6	–	–	–	–
(Cp <sub>2</sub> ZrCl) <sub>2</sub> O	285.0	199.2	–	182.1	–	–	530.4	–
Cp <sub>2</sub> Zr(NEt <sub>2</sub> ) <sub>2</sub>	284.9	–	–	181.6	–	–	–	399.1
ZrCl <sub>4</sub>	285.0	200.1	–	183.9	–	–	531.8	–
Cp <sub>2</sub> MCl <sub>2</sub> <sup>a,b</sup> [7]	285.0	–	–	182.3	457.5	17.5	–	–
Cp <sub>2</sub> TiCl <sub>2</sub> <sup>b</sup> [10]	285.0	198.5	–	–	457.5	–	–	–
(Cp <sub>2</sub> ZrCl) <sub>2</sub> O <sup>c</sup> [9]	–	–	–	182.1	–	–	–	–

<sup>a</sup> M = Zr, Ti, Hf.

<sup>b</sup> Values increased by an amount of +0.4 eV, because the reference peak C 1s was fixed at 284.6 eV.

<sup>c</sup> Value increased by analogy with ref. [7], because the reference is not given.

suggesting a larger stability of Zr–F bonds with respect of Zr–Cl bonds.

Some XPS analysis runs of air-exposed complexes were carried out at low take off angle (15°), in order to check the depth of composition variations: no substantial changes were observed (an example is reported in Table 2), suggesting that several layers of molecules are involved in the reaction.

Coming back to the examination of other complexes, the trichloride appears to contain more oxygen than dichlorides, while the surface composition of oxychloride is very close to the calculated one. In the former case it can be argued that the compound is more reactive towards air, for instance partially reacting as follows:



while in the latter case the complex is confirmed to be rather stable.

Also zirconium tetrachloride was found very sensitive to air exposure and contamination, showing a high surface concentration of both oxygen and carbon.

A particular case is that of diethylamide complex. Its high reactivity was recognized early during preparation and was confirmed by the XPS analysis, notwithstanding the accurate precautions

Table 2  
Surface compositions from XPS intensity values. Calculated values are drawn from chemical formulas

Compound	<sup>a</sup>	Surface composition (at.%)						
		C	Halogen	Metal	O	C/M	Hal/M	O/M
Cp <sub>2</sub> ZrCl <sub>2</sub>		78.0	12.8	6.2	3.0	12.6	2.1	0.5
	(1)	76.3	9.4	6.4	7.9	11.9	1.1	1.2
	(2)	76.8	10.7	6.3	6.2	12.3	1.7	1.0
Cp <sub>2</sub> TiCl <sub>2</sub>		78.0	14.0	5.6	2.4	13.9	2.5	0.4
Cp <sub>2</sub> HfCl <sub>2</sub>		77.3	13.0	6.8	2.9	11.3	1.9	0.4
	(1)	76.4	9.4	6.6	6.6	11.8	1.4	1.0
Cp <sub>2</sub> ZrF <sub>2</sub>		75.0	16.0	7.0	2.0	10.7	2.3	0.3
	(1)	65.7	19.8	8.1	6.3	8.1	2.4	0.8
	calc.	76.9	15.4	7.7	–	10	2	–
CpZrCl <sub>3</sub>		47.5	25.8	11.8	13.4	4.0	2.2	1.1
	(1)	50.0	23.8	10.8	13.3	4.6	2.2	1.2
	calc.	55.6	33.3	11.1	–	5	3	–
(Cp <sub>2</sub> ZrCl) <sub>2</sub> O		80.4	8.1	7.3	4.2	11.0	1.1	0.6
	(1)	80.6	7.6	7.2	4.6	11.2	1.1	0.6
	calc.	80.0	8.0	8.0	4.0	10	1	0.5
Cp <sub>2</sub> Zr(NEt <sub>2</sub> ) <sub>2</sub>		84.7	2.0 <sup>b</sup>	6.8	5.5	11.0	1.1	0.6
	calc.	82.3	11.8 <sup>b</sup>	5.9	–	14	2 <sup>c</sup>	–
ZrCl <sub>4</sub>		33.3	31.9	13.1	21.7	1.0	2.4	0.7
	calc.	–	80.0	20.0	–	–	4	–

<sup>a</sup> (1) exposed to air atmosphere; (2) exposed to air and take off angle 15°.

<sup>b</sup> Nitrogen.

<sup>c</sup> N/M.

during handling. Indeed the experimental nitrogen amount is less than 20% of that expected, while a remarkable quantity of oxygen was detected. A nucleophilic attack of water on the Zr–N bond can be envisaged, with formation of volatile diethylamine. Carbon and zirconium appear less affected. It must be remembered that the diethylamide complex was the most reactive molecule of the series that we were able to analyse; in other cases we failed to obtain an analysis, for instance in the case of the analogous dimethylamide complex, due to its sublimation tendency. This is a real limit of the technique, which can be overcome only by more sophisticated handling procedures or sample holders (i.e. low temperature freezing).

### 3.3. Valence band spectra

In the literature, valence band (VB) studies by photoemission have been widely used to study the electronic structure of complexes [18]. HeI (21.2 eV) or HeII (40.8 eV) sources and, more recently, synchrotron light radiation in the range 0–100 eV, have been widely used in ultraviolet photoemission spectroscopy (UPS) experiments [19]. In such studies, a comparison between experimental spectra and theoretical band structures are usually attempted [20]. XPS has found less application in this field, mainly because of the inadequacy of instruments (energy resolution and/or intensity). Also the fact that XPS valence bands are more representative of the bulk than of the surface of the specimen played a role in such a scarcity. Recently, XPS valence band studies have been published on organic solids like polymers using a ‘fingerprint’ approach, i.e. considering when possible the spectrum features as specific to the substance under investigation, for a better identification [21]. Spectra presented here constitute a first attempt to establish whether and to what extent a similar approach can be used for this class of complexes, on the expectation that in time computational chemistry can simulate and fully interpret all spectral features.

In Fig. 1a–c valence band spectra of  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Cp}_2\text{HfCl}_2$  are reported in the range

0–35 eV. In Fig. 1a the peak at 30 eV represents the contribution of Zr 4p, while the peaks at 6 and 16 eV can be tentatively assigned to Cl 3p and Cl 3s, respectively. It is likely that their asymmetric profiles contain some hybridization contribution. Some low structures are also visible at 12 eV and 22 eV. In the VB spectrum of the titanium complex (Fig. 1b), Ti 3p is out of the energy range, at 38 eV. The peaks attributed to chlorine are visible, as well as the peak at 12 eV and some small structures at 22 and 26 eV. Finally, in the hafnium complex (Fig. 1c), the spectrum is dominated by Hf 4f at 17 eV, while Hf 5p, less intense, occurs near 32 eV. The Cl 3p peak is present (Hf 4f transition overlaps Cl 3s) as well as the peak at 12 eV.

In Fig. 2a the VB spectrum of zirconocene oxychloride ( $\text{Cp}_2\text{ZrClO}_2$ ) is reported and compared with that of dichloride. They are very similar, except that the intensity of the peak at 22 eV is larger in the case of the oxychloride. It is reasonable to attribute this peak at O 2s, even if in other compounds, like polymers and oxides, it appears at a slightly higher energy (24–27 eV) [21,22]. The VB spectrum of zirconium trichloride  $\text{CpZrCl}_3$  is reported in Fig. 2b. It is similar to the spectra of Zr complexes already described, apart a lower intensity of the structure centered at 12 eV and some broadening of Cl peaks. In the solid state,  $\text{CpZrCl}_3$  is a one-dimensional polymeric species, formed by edge-shared pseudooctahedral  $\text{ZrCl}_6$  units. Zr–Cl bond lengths range from 2.42 to 2.72 Å [23]. It is possible that broadening of chlorine peaks is due to the non-equivalence of bonds involving the chlorine atoms. In the VB spectrum of  $\text{ZrCl}_4$  the structure at 12 eV is absent, suggesting its assignment in the metallocene compounds to cyclopentadienyl rings. This is in agreement with UPS HeI spectra [24], where three structures at 9, 11 and 14 eV were observed and assigned to Cp rings (with a contribution of Cl orbitals), Cp rings and Cl 3s respectively. HeI VB spectra of Ti, Zr and Hf dichloride complexes are very similar, as well as those of corresponding trichlorides [25].

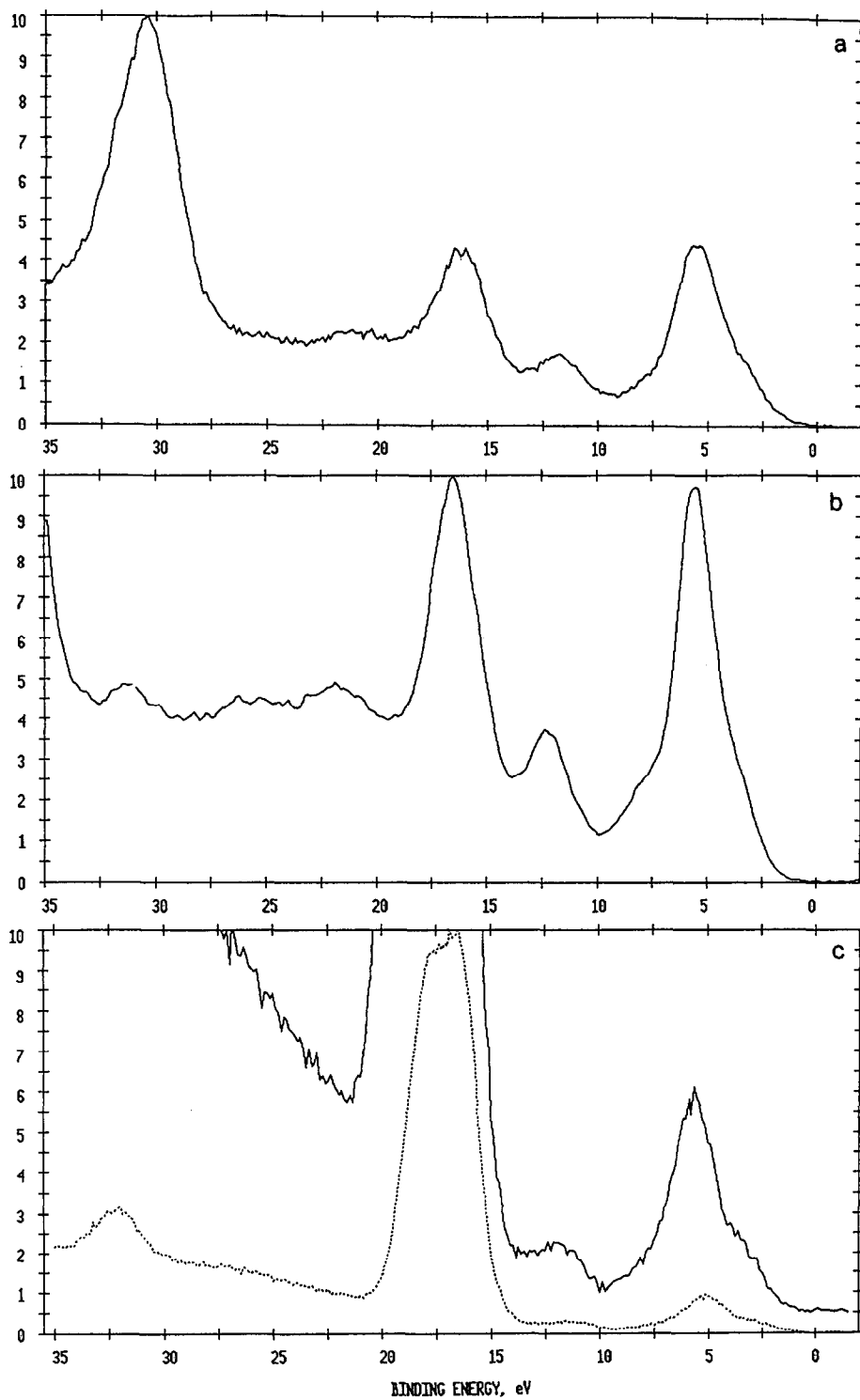


Fig. 1. Valence bands of metallocene complexes: a)  $\text{Cp}_2\text{ZrCl}_2$ ; b)  $\text{Cp}_2\text{TiCl}_2$ ; c)  $\text{Cp}_2\text{HfCl}_2$ .

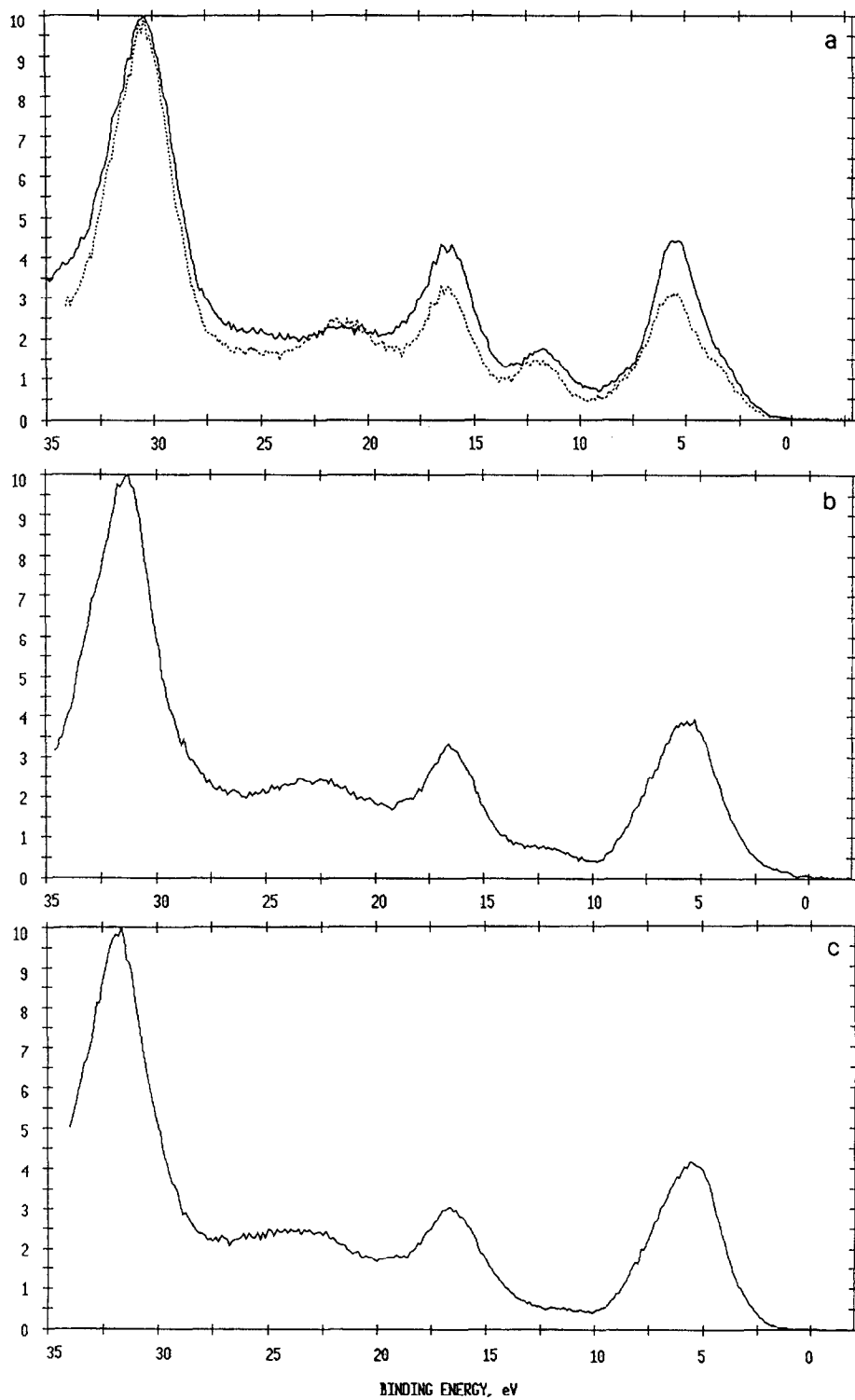


Fig. 2. Valence bands of zirconium compounds: a)  $(\text{Cp}_2\text{ZrCl})_2\text{O}$  (dotted line) and  $\text{Cp}_2\text{ZrCl}_2$  (continuous line); b)  $\text{Cp}_2\text{ZrCl}_3$ ; c)  $\text{ZrCl}_4$ .

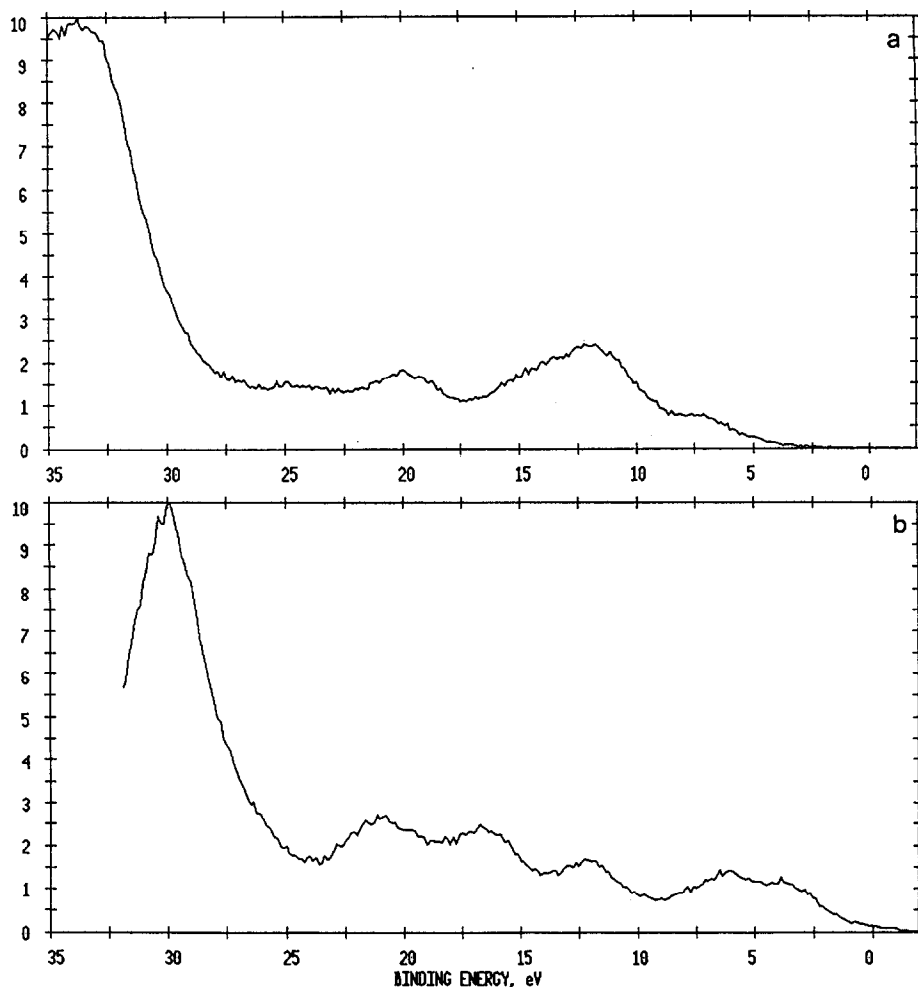


Fig. 3. Valence bands of metalocene complexes: a)  $\text{Cp}_2\text{ZrF}_2$ ; b)  $\text{Cp}_2\text{Zr}(\text{NEt}_2)_2$ .

Table 3  
Binding energies of peaks observed in the range 0–35 eV

Tentative assignment	Binding energy (eV)									
	Zr 4p	<sup>a</sup>	O 2s	<sup>a</sup>	Cl 3s	<sup>a</sup>	C	<sup>a</sup>	Cl 3p	<sup>a</sup>
	Hf 5p				Hf 4f					
	F 2s									
Compound										
$\text{Cp}_2\text{ZrCl}_2$	30.4	–	21.7	–	16.2	–	11.9	–	5.7	–
$\text{Cp}_2\text{TiCl}_2$	–	25.6	21.8	–	16.4	–	12.1	–	5.7	–
$\text{Cp}_2\text{HfCl}_2$	32.0	–	–	–	16.5	–	12.0	–	5.6	–
$\text{Cp}_2\text{ZrF}_2$	33.6	–	–	19.9	–	14.6	11.9	7.1	–	–
$\text{CpZrCl}_3$	31.4	–	22.9	–	16.6	–	11.9	–	5.5	–
$(\text{Cp}_2\text{ZrCl})_2\text{O}$	30.4	–	21.1	–	16.2	–	11.9	–	5.7	–
$\text{Cp}_2\text{Zr}(\text{NEt}_2)_2$	30.1	–	21.1	–	16.7	–	12.1	–	6.2	3.9
$\text{ZrCl}_4$	31.7	–	–	–	16.6	–	–	–	5.5	–

<sup>a</sup> Not assigned.



Table 4  
Catalytic activity of metallocene complexes

Compound	Catalytic activity ( $\text{g}_{\text{PE}}/\text{mg}_{\text{M}} \cdot \text{h} \cdot \text{atm}$ )	$M_n^a$ ( $\times 1000$ )	$M_w^b$ ( $\times 1000$ )	MWD <sup>c</sup>
$\text{Cp}_2\text{ZrCl}_2$	163	142	326	2.3
$\text{Cp}_2\text{TiCl}_2$	92	176	406	2.3
$\text{Cp}_2\text{HfCl}_2$	21	167	411	2.5
$\text{Cp}_2\text{ZrF}_2$	145	103	261	2.5
$\text{CpZrCl}_3$	96	291	626	2.1
$(\text{Cp}_2\text{ZrCl})_2\text{O}$	146	154	361	2.3
$\text{Cp}_2\text{Zr}(\text{NEt}_2)_2$	225	157	361	2.3
$\text{ZrCl}_4$	4	116	260	2.2

<sup>a</sup>  $M_n$ : number-average molecular weight.

<sup>b</sup>  $M_w$ : weight-average molecular weight.

<sup>c</sup> MWD: molecular weight distribution.

VB spectra of  $\text{Cp}_2\text{ZrF}_2$  and  $\text{Cp}_2\text{Zr}(\text{NEt}_2)_2$  are reported in Fig. 3a and b respectively. Their appearance is rather different to the previous ones, in fact, apart from the relevant peak of Zr 4p (overlapped in the case of difluoride to F 2s) only weak structures are observed. The difluoride complex exhibits signals at 7.1, 11.9, 14.6 and 19.9 eV, while the diethylamide complex has structures at 3.9, 6.2, 12.1, 16.7 and 21.1 eV. Only the structure near 12 eV can be assigned to the cyclopentadienyl rings with some confidence, while for the other peaks further studies are necessary.

Observed peaks in valence band spectra and their tentative assignments are reported in Table 3.

### 3.4. Catalytic activity

Results of catalytic test runs are reported in Table 4. Zirconium based metallocenes were found more active in the homopolymerization of ethylene than Ti catalyst, and one order of magnitude more active than hafnium catalyst, in agreement with literature [26,27]. Among Zr catalysts, the diethylamide complex is significantly more active than dichloride and analogous complexes, while trichloride is less active. Also the latter result is a confirmation of literature data, where dicyclopentadienyl compounds were found more active than the correspondent monocyclopenta-

dienyl molecules [28]. Zirconium tetrachloride exhibits a very low activity.

Molecular weight distributions (Table 4) confirm the finding that metallocene based catalyst of the family studied here have a general tendency to generate polymers with a narrow MWD of about 2 [29]. Numerical molecular weights tend to be higher in the case of less active catalysts.

Before attempting to find some relationship between XPS data and catalytic activity, it must be remembered that in our conditions the true catalyst is not the metallocene complex but a new species resulting from the fast reaction between the complex and MAO, added in very strong excess before polymerization. Following the current views [26], MAO has at least two functions, i.e. the alkylation of the metallocene compound, and the subsequent complexation of the latter compound forming the active site. For instance, in the case of  $\text{Cp}_2\text{ZrCl}_2$ , the  $\text{Cp}_2\text{ZrCl}(\text{CH}_3)$  species is formed as a first step, then the cation  $\text{Cp}_2\text{Zr}(\text{CH}_3)^+$  is supposed to be the active species.

From Table 1, the binding energy of zirconium (Zr 3d peak) appears sensitive to the nature of atoms directly bonded to it in the following order:  $\text{ZrCl}_4 > \text{Cp}_2\text{ZrF}_2 > \text{CpZrCl}_3 > \text{Cp}_2\text{ZrCl}_2 = (\text{Cp}_2\text{ZrCl})_2\text{O} > \text{Cp}_2\text{Zr}(\text{NEt}_2)_2$ . An increase of binding energy is apparently caused by the increase of the number of electron attractive ligands (like chlorine atoms) or its substitution with more electronegative atoms (F instead of Cl). In this frame it is reasonable that zirconocene dichloride and oxychloride show the same B.E. value. Diethylamide complex show a donor nature, confirmed in previous literature [30]. However, due to the heavy decomposition shown by this complex, this result should be considered with some caution. In Fig. 4, catalytic activity is plotted as a function of Zr 3d binding energy. A clear relationship was found suggesting that the catalytic activity increases when the binding energy of zirconium decreases. Among the catalysts examined, only the difluoride complex deviates from such behaviour, this can be connected to the special nature of this ligand.

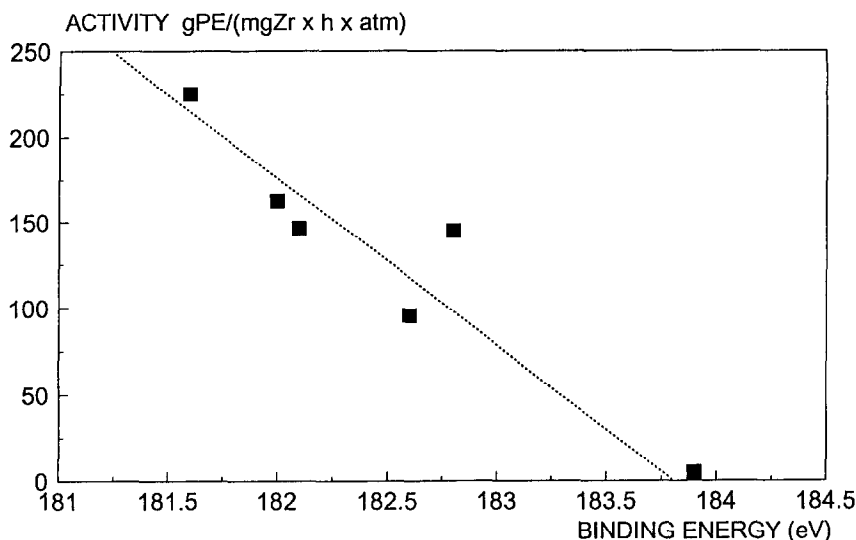
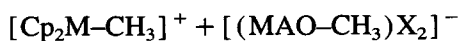
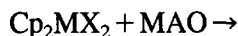


Fig. 4. Relationship between Zr 3d binding energy and catalytic activity of zirconium compounds in the polymerization of ethylene.

#### 4. Discussion

In the previous reports [7–10], XPS has been used to establish the effect of ligands on the core electronic levels of metals. Also a direct characterization of a catalyst was attempted, observing two distinct catalyst species showing small binding energy differences [9]. In this work an interesting relationship was found between Zr 3d binding energy and catalytic activity, as reported in Fig. 4. Taking into account the above considerations on the true nature of the catalytic site, this result should be considered with some caution. Further studies and confirmations are necessary before to assume such finding as a general rule. Molecular modelling studies are in progress in order to go inside this issue.

Following the current views, the activation mechanism of metallocene catalysts with MAO is as follows [31]:



Consequently, the binding energy of Zr in the precursor cannot directly influence the catalytic activity, as the relationship of Fig. 4 could suggest. Also the hypothesis that the presence of X ligands on the cocatalysts can have a significant effect on the activity is not convincing, because in

many cases the nature of X is the same, i.e. chlorine. We suggest that the nature of X can affect the kinetics of formation of the active species, i.e. the substitution of X with methyl. Because we used the same activation conditions for all catalysts (see Section 3.4 'Catalytic activity'), a different number of active centers are likely present during polymerization. If this is true, our results indicate that Zr binding energy is an important parameter for the activation step. Following the same hypothesis, this could be also an explanation for the peculiar behaviour of zirconocene difluoride, which falls out of the observed relationship. It can be the consequence of the difficulty of MAO to break the Zr–F bonds to form the active sites.

Seemingly, surface chemical composition results (Table 2) are at least partially eclipsed by some unavoidable reaction with humidity, however their deeper examination give rise to at least two interesting results. Firstly, the degree of disagreement between experimental and calculated composition is an indication of the reactivity of the complex, suggesting particular precautions in the case of the most reactive compounds. Secondly, and more important, variations observed after air exposure of samples offer interesting indications on the relative strength of bonds among metal and ligands. Consider the different behaviour of zirconocene difluoride complex with

respect to that of dichloride: in the latter case a decrease of halogen concentration was observed, indicating that the O-containing reagent makes a nucleophilic substitution on the metal–halogen bond; on the contrary, in the former case, the amount of fluorine into the molecule seems to remain constant, while the carbon content decreases, suggesting that the Zr–F bond is too strong to be substituted by Zr–O bonds, thus the Cp ligands are partially substituted.

Valence band studies find a difficult connection with previous studies carried out using UV radiation [18–20,24,25], but are promising at least as ‘fingerprints’ of complexes considered. It is also probable that VB information can be used in connection with theoretical studies, where the energy status of HOMO and LUMO orbitals are generally investigated, i.e. energy levels near to those observed in the VB spectra.

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