

# An XPS investigation of the interaction mechanism between $\text{AlEt}_3$ and $\text{TiCl}_4$ supported on sputtered native $\text{SiO}_x$ layer

Spyridon Ntais, Angeliki Siokou\*

Foundation of Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Chemical Processes (FORTH/ICE-HT),  
18 Stadiou Str, Platani Achaïas, GR-26504 Patras, Greece

Received 11 April 2005; received in revised form 31 August 2005; accepted 16 September 2005

Available online 27 October 2005

## Abstract

$\text{TiCl}_4$  supported on silicon oxide or magnesium halides is widely used as catalyst for olefin polymerization from the gas phase. These catalysts are usually activated with organoaluminum compounds such as triethylaluminum ( $\text{AlEt}_3$ ). In the present study, the interaction mechanism between  $\text{AlEt}_3$  and titanium chloride supported on a  $\text{SiO}_x$  layer was investigated using X-ray photoelectron spectroscopy (XPS). A flat conductive Si wafer covered with a thin native  $\text{SiO}_x$  layer, was used as support, in order to eliminate electrostatic charging effects during the XPS measurements and allow a more reliable identification of surface chemical species. It was found that the  $\text{TiCl}_4$  vapors react with the sputtered oxide layer mainly through isolated surface Si–OH species leading to formation of Si–O– $\text{TiCl}_3$ . There was no evidence of Ti reduction after the interaction with  $\text{AlEt}_3$  vapors but only a small downward BE shift of the Ti  $2p_{3/2}$  peak. This behavior was attributed to the effect of alkylation of the titanium oxychloride species. On the basis of the present results it is proposed that the alkylation takes place by means of surface complex formation with  $\text{AlEt}_x$  that may or may not be chemically bonded on the  $\text{SiO}_x$  surface.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Titanium chloride; Triethylaluminum; X-ray photoelectron spectroscopy;  $\text{SiO}_x/\text{Si}$

## 1. Introduction

The interaction of titanium halides with organoaluminum compounds has been the subject of several studies in the last 4 decades because of the wide use of these materials in the Ziegler-Natta olefin polymerization catalysts. In the fourth generation of Ziegler-Natta catalysts  $\text{TiCl}_4$  is anchored on  $\text{MgCl}_2$  and/or  $\text{SiO}_2$  while an organometallic compound, usually  $\text{AlEt}_3$  or  $\text{AlMe}_3$  is used as the co-catalyst that activates the system [1,2]. Despite the number of investigations performed on these systems, there are still no definite answers on questions related to the structure and oxidation state of the active sites, the role of the support and the role of the co-catalyst. Controversial results have been reported concerning these properties as well as how the catalyst preparation method influences the stereospecificity and stereoselectivity of the produced polymer. The difficulties in these studies are related to the existence of only a low con-

centration of active sites in a relatively disordered environment. At the same time, conventional surface sensitive spectroscopies run into problems due to the insulating nature of  $\text{MgCl}_2$  or  $\text{SiO}_2$  which leads to electrostatic charge built up.

Somorjai et al. have performed a series of studies on model Ziegler-Natta catalysts supported on Au foil and prepared under UHV conditions, by  $\text{MgCl}_2$  evaporation followed by exposure to  $\text{TiCl}_4$  vapors. They showed that activation of the precatalyst with  $\text{AlEt}_3$  provokes reduction of titanium atoms [3]. On the other hand, Fregonese et al. [4] have shown that the activation of the  $\text{MgCl}_2/\text{TiCl}_4$  system with  $\text{AlEt}_3$  shifted the Ti 2p XPS peak toward higher binding energies (BEs). If reduction had occurred then the peak should shift to the opposite direction (lower BE). They attributed this behavior to electron deficient catalytic species where the Ti atom is trapped into cage structures formed from Al-alkoxy species.

The mechanism of olefin polymerization on titanium based silica supported catalysts has often been approached and variously interpreted. Generally, it is supposed that the titanium atoms anchored by a covalent bond on the silica surface can be extracted by metal alkyl compounds via an exchange reaction.

\* Corresponding author. Tel.: +30 2610 965263; fax: +30 2610 965223.  
E-mail address: [siokou@iceht.forth.gr](mailto:siokou@iceht.forth.gr) (A. Siokou).

TiCl<sub>3</sub> clusters will be formed in this way and with further alkylation they become active for the polymerization reaction. Kovaleva et al. [5] have shown using EPR and polarography measurements that alkylated and separately located Ti<sup>3+</sup> compounds are formed chemically bonded with the silica (aerosil) support, giving rise to a number of atactic active centres for propylene polymerization. However, Ti<sup>2+</sup> and Ti<sup>4+</sup> ions are not ESR active, and thus it is still not clear which oxidation state is active in the polymerization process [6].

In the present work, we attempt to elucidate the mechanism of the interaction between AlEt<sub>3</sub> and titanium chloride supported on a flat SiO<sub>x</sub> layer using the surface sensitive X-ray photoelectron spectroscopy. The flat conductive Si wafer covered with a thin native SiO<sub>x</sub> layer, was used as support, in order to avoid electrostatic charging effects during the XPS measurements. The lack of charging effects makes the detection of chemical shifts of the XPS peaks less complicated, allowing a more accurate identification of surface chemical species.

The sample was prepared by exposure of the SiO<sub>x</sub>/Si(1 0 0) surface to TiCl<sub>4</sub> vapors in the UHV chamber, followed by exposure to AlEt<sub>3</sub> vapors. X-ray photoelectron spectroscopy was used in order to identify the surface species at each stage.

## 2. Experimental

The photoemission measurements were carried out in an ultra high vacuum (UHV) system, which has been described in detail elsewhere [7]. The unmonochromatized Al Kα line at 1486.6 eV and constant analyzer pass energy of 97 eV, giving a full width at half maximum (fwhm) of 1.7 eV for the Au 4f<sub>7/2</sub> peak, were used in all XPS measurements. The XPS core level spectra were analyzed with a fitting routine, which decomposes each spectrum into individual mixed Gaussian–Lorentzian peaks after a Shirley background subtraction. Regarding the measurement errors, for the XPS core level peaks it was estimated that for a good signal to noise ratio, errors in peak positions can be ±0.05 eV. The Cl 2p XPS peaks were analyzed by the use of doublets with a spin orbit splitting separation of 1.65 eV.

A p-doped Si(1 0 0) crystal was used as the conducting flat substrate. In order to remove the organic contaminants, the Si

wafer was dipped in a 5:1:1 mixture of H<sub>2</sub>O/H<sub>2</sub>O<sub>2</sub>/NH<sub>4</sub>OH at 353 K for 10 min followed by mild Ar<sup>+</sup>-sputtering in UHV in order to remove excess carbon contamination from the native surface oxide layer [8]. The gas deposition was performed using a leak valve through which TiCl<sub>4</sub> vapors were introduced into the UHV chamber. AlEt<sub>3</sub> was dosed from the gas phase as well and the total exposure was 3.6 × 10<sup>7</sup> L. Both TiCl<sub>4</sub> and AlEt<sub>3</sub> were purified right before use by cycles of freezing at liquid N<sub>2</sub> temperature followed by evacuation in the region of 10<sup>−6</sup> mbar and then warming to room temperature (RT). During the deposition procedures the substrate was kept at RT.

## 3. Results

### 3.1. The substrate

After the chemical cleaning procedure and the mild sputtering, traces of carbon contaminants could still be detected on the surface. Fig. 1 shows the C 1s, O 1s and Si 2p peaks at this stage. The C 1s peak is analyzed into two components at binding energies 282.8 eV (C<sup>I</sup>) and 284.6 eV (C<sup>II</sup>), attributed to carbide (SiC) and graphite contamination, respectively. The Si 2p peak consists of two components as well, one at 99.1 eV originating from elemental Si<sup>0</sup> and one at 100.7 eV (Si<sup>I</sup>), characteristic of silicon atoms in SiC or SiO<sub>x</sub> (x ≤ 1). Using the XPS intensities of the C 1s and Si 2p peaks corrected by the atomic sensitivity factors which are 0.25 and 0.27, respectively, and assuming a layered distribution of carbon, its amount was found to be ~80% of a monolayer [9]. The O 1s peak is analyzed into two components one at 531.1 eV (O<sup>I</sup>) and another at 532.6 eV (O<sup>II</sup>). The O<sup>I</sup>/O<sup>II</sup> intensity ratio is 3.7. The first peak is characteristic for oxygen atoms in the silicon sub-oxide layer [10]. The second peak has the characteristic energy of O 1s originating from SiO<sub>2</sub> or Si–OH species. Nevertheless, the Si 2p peak does not contain components corresponding to SiO<sub>x</sub> with x > 1 and it is thus concluded that the O<sup>II</sup> peak represents mainly silanol (Si–OH) groups on the oxide's surface. The binding energy of oxygen in silanols has been reported to be between 532.4 and 533 eV [9,11].

The average oxide thickness (*d*) can be calculated from the intensity ratio of the XPS Si 2p peaks attributed to SiO<sub>x</sub> (x ≤ 1)

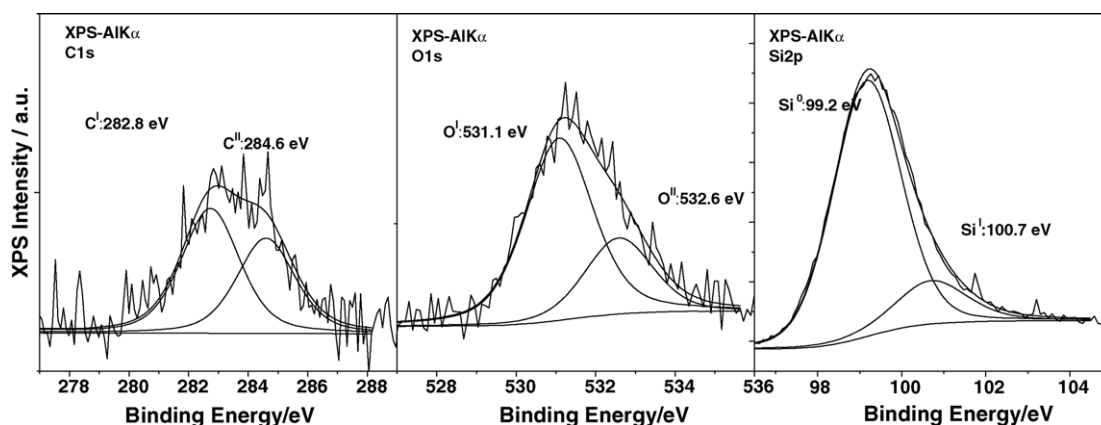


Fig. 1. C 1s, O 1s and Si 2p XPS peaks for the bare SiO<sub>x</sub>/Si(1 0 0) substrate.

Table 1  
Binding energy (BE) and full width at half maximum (fwhm) values of the XPS peaks C 1s, O 1s, Cl 2p<sub>3/2</sub>, Ti 2p<sub>3/2</sub>, Al 2p and Si<sup>I</sup> 2p

XPS peaks	C 1s			O 1s		Cl 2p <sub>3/2</sub>	Ti 2p <sub>3/2</sub>	Al 2p	Si 2p
	C <sup>I</sup>	C <sup>II</sup>	C <sup>III</sup>	O <sup>I</sup>	O <sup>II</sup>	Cl	Ti	Al	Si <sup>I</sup>
Substrate									
BE (eV)	282.8	284.6		531.1	532.6				100.7
fwhm (eV)	2.3	2.3		2.3	2.3				2
+TiCl <sub>4</sub>									
BE (eV)	282.8	284.6		531.1	532.6	199.3	458.7		100.8
fwhm (eV)	2.3	2.3		2.3	2.3	2.3	3.4		2
+AlEt <sub>3</sub>									
BE (eV)	282.8	284.6	286.4	531.4	533.2	199.5	458.3	74.5	100.8
fwhm (eV)	2.3	2.3	2.3	2.3	2.3	2.6	3.1	2	2

and the silicon substrate, assuming that the attenuation of the substrate (Si<sup>0</sup>) and the oxide overlayer (Si<sup>I</sup>) signals – for a uniform oxide film – follow the exponential relations [9]:

$$\frac{I_{\text{Si}^0}}{I_{\text{Si}^I}^\infty} = \exp\left(\frac{-d}{\lambda_{\text{Si}^0}^{\text{SiO}_x}}\right) \quad (1)$$

$$\frac{I_{\text{Si}^I}}{I_{\text{SiO}_x}^\infty} = 1 - \exp\left(\frac{-d}{\lambda_{\text{SiO}_x}^{\text{SiO}_x}}\right) \quad (2)$$

where  $I_{\text{Si}^0}^\infty$  and  $I_{\text{SiO}_x}^\infty$  are the peak intensities measured independently in our system for the clean silicon crystal and the bulk oxide surface, giving a ratio  $I_{\text{Si}^0}^\infty/I_{\text{SiO}_x}^\infty = 1.67$  and the inelastic mean free paths are  $\lambda_{\text{Si}^0}^{\text{SiO}_x} \cong \lambda_{\text{SiO}_x}^{\text{SiO}_x} = 3.49$  nm [10].

In the present experiment, the Si<sup>I</sup> peak contains a contribution from SiC, as indicated from the C 1s component at BE = 282.8 eV. From independent measurements on bulk C-faced SiC samples in our system, it has been found that the intensity ratio of the C 1s and Si 2p peaks is  $I_{\text{C}1s}/I_{\text{Si}2p} = 1.1$ . Using this relationship and knowing the intensity of the C 1s component corresponding to SiC, the percentage of the Si<sup>I</sup> signal that originates from the surface SiC layer can be calculated. This is found to be 33% of the total Si<sup>I</sup> intensity and must be subtracted from the intensity of the Si<sup>I</sup> peak in order to make a

correct calculation of the oxide thickness. Following the above procedure and using Eqs. (1) and (2) the oxide thickness was found to be  $d = 0.7 \pm 0.05$  nm. The error at the present thickness estimation is mainly related to the value of the  $I_{\text{C}1s}/I_{\text{Si}2p}$  intensity ratio in the SiC that has been found experimentally to depend on the carbides structure.

The BEs and the fwhm of all the XPS peaks detected and analyzed in this work are shown in Table 1. The table also contains the features of the components into which the detected peaks have been analyzed, whenever it was necessary, using the fitting procedure described in Section 2.

### 3.2. Exposure to TiCl<sub>4</sub> vapors

The next step was the deposition of TiCl<sub>4</sub> from the gas phase. The intensity of the O 1s XPS peak (Fig. 2) undergoes a 20% reduction while it exhibits again two components at 531.1 eV (O<sup>I</sup>) and 532.6 eV (O<sup>II</sup>). The O<sup>I</sup>/O<sup>II</sup> intensity ratio is calculated to be 4.8. The intensity of the Si 2p peak drops as well and the Si<sup>I</sup>/Si<sup>0</sup> XPS intensity ratio does not change, indicating that there is no further Si oxidation after exposure to TiCl<sub>4</sub> vapors.

In the bottom spectra of Fig. 3, the Cl 2p and Ti 2p XPS peaks after TiCl<sub>4</sub> deposition are presented. The Ti 2p<sub>3/2</sub> peak is at 458.7 eV characteristic for titanium atoms in the 4+ oxidation

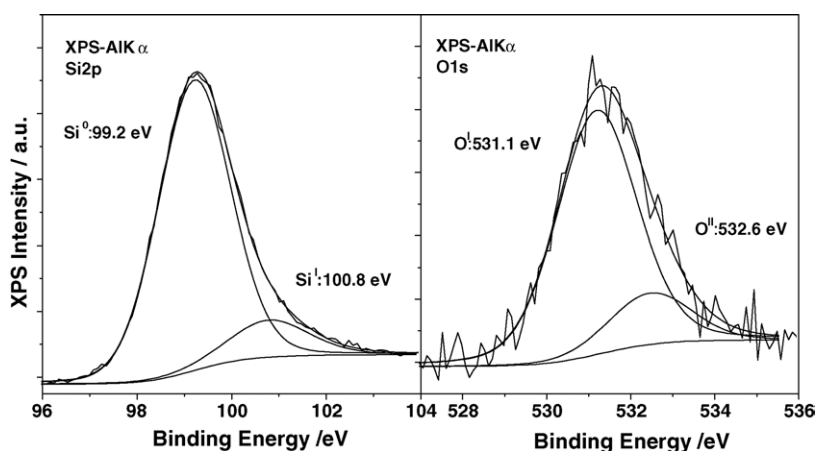


Fig. 2. Si2p and O1s XPS peaks after deposition of TiCl<sub>4</sub> on the SiO<sub>x</sub>/Si(100) substrate.

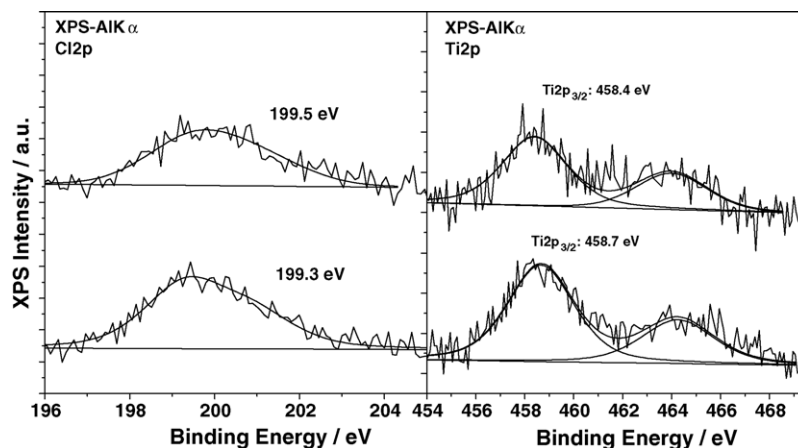


Fig. 3. Ti 2p and Cl 2p XPS after deposition of  $\text{TiCl}_4$  on the  $\text{SiO}_x/\text{Si}(100)$  substrate (bottom) and after the reaction with  $\text{AlEt}_3$  (top).

state. The peak is quite broad with  $\text{fwhm} = 3.4$  eV. The corresponding Cl 2p peak is at  $\text{BE} = 199.3$  eV ( $\text{Cl } 2p_{3/2}$ ) characteristic for chlorine atoms in  $\text{TiCl}_x$  [12]. The Cl:Ti surface atomic ratio was calculated using the intensity ratio of the Cl 2p and Ti 2p peaks corrected by the atomic sensitivity factors (0.73 and 1.8, respectively [9]) and it was found to be  $\sim 2.7:1$ .

Assuming an exponential attenuation of the Si 2p peak signal after  $\text{TiCl}_4$  deposition the thickness “ $t$ ” of the deposit was calculated and found to be  $t \sim 0.27$  nm that is equivalent to about 0.5 monolayer of  $\text{TiCl}_x$ . The exponential equation that was used is the following:

$$\frac{I_{\text{Si } 2p}^{\text{after}}}{I_{\text{Si } 2p}^{\text{before}}} = \exp\left(\frac{-t}{\lambda}\right) \quad (3)$$

where the value of the inelastic mean free path  $\lambda$  for Si 2p electrons through the deposit is 3.57 nm.

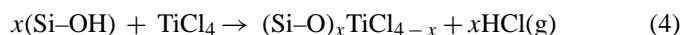
### 3.3. Exposure to $\text{AlEt}_3$ vapors

Fig. 4 shows the C 1s, Si 2p and Al 2p XPS peaks after  $\text{AlEt}_3$  exposure. The intensity of the C 1s peak increases considerably due to the insertion of the alkyl groups. The shape of the Si 2p peak does not change but its intensity decreases. Aluminum is also detected on the surface and the Al 2p XPS peak is detected

at 74.5 eV. A small increment is also observed at the O 1s peak probably due to oxygenated contaminants in the chamber. The intensity of the Ti  $2p_{3/2}$  peak decreases and its binding energy undergoes a 0.4 eV downward shift. The Cl  $2p_{3/2}$  XPS peak shifts 0.2 eV towards higher binding energies and becomes broader with  $\text{fwhm} = 2.6$  eV (Fig. 3, top spectra). The shifts observed at both Ti 2p and Cl 2p peaks indicate changes at the electronic environment around the Ti and Cl atoms and they will be discussed later. The Al:Ti atomic ratio is 4.5:1. It is worth noticing that no loss of Cl atoms is detected since the Cl:Ti atomic ratio remains the same ( $\sim 2.9$ ) within the experimental error, while the carbon uptake after  $\text{AlEt}_3$  deposition (for carbon that corresponds to C–H and C–C species, i.e. with the C 1s peak at 284.6 eV) is calculated to be 3.5  $\text{C}^{\text{II}}$  atoms per Al atom.

## 4. Discussion

It is well known that  $\text{TiCl}_4$  chemisorbs on the silicon oxide’s surface by interacting with Si–OH groups via the following reaction [13,14]:



The interaction of  $\text{TiCl}_4$  with the surface hydroxyls can be mono-functional (one  $\text{TiCl}_4$  molecule titrating one –OH group)

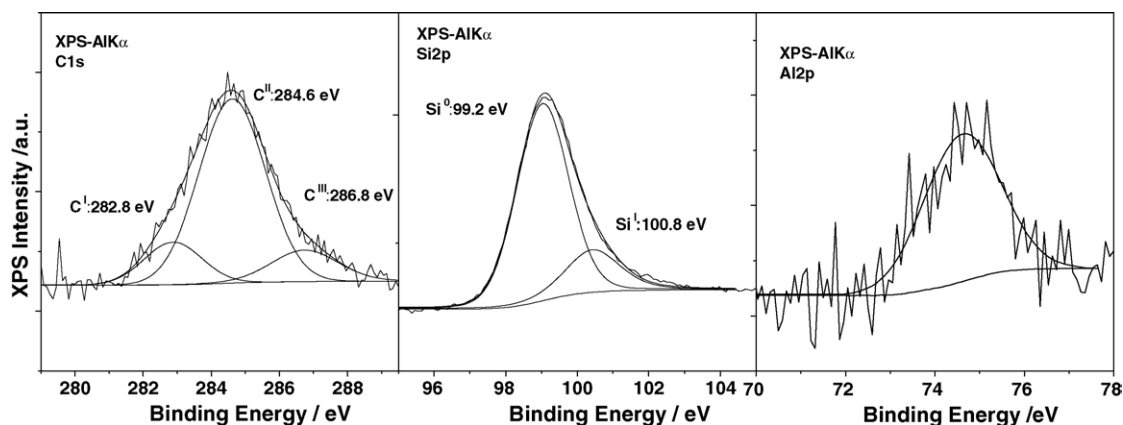


Fig. 4. C 1s, Si 2p and Al 2p XPS peaks after the reaction with  $\text{AlEt}_3$ .

bi- or tri-functional (one  $\text{TiCl}_4$  titrating two or three  $-\text{OH}$  groups, respectively) depending on the concentration of hydroxyls on the silica surface. The calculated atomic ratio  $\text{Cl}:\text{Ti} = 2.7:1$  indicates that  $\text{TiCl}_4$  interacts mainly with isolated  $\text{Si}-\text{OH}$  groups. In other words the value of the factor “ $x$ ” in reaction (4) is  $x \sim 1$ . Indeed, isolated  $\text{Si}-\text{OH}$  groups are the most probable species to be present on the surface after the mild  $\text{Ar}^+$  sputtering during its preparation. If reaction (4) occurs at the surface then  $\text{Si}-\text{O}-\text{Ti}$  bonds will be formed. The binding energy of oxygen atoms in these bonds has been found to lie between the value that represents oxygen atoms in  $\text{Si}-\text{O}-\text{Si}$  bonding (532.6–533 eV) and the value for oxygen atoms in  $\text{Ti}-\text{O}-\text{Ti}$  (530.5 eV) [12,15]. In the present experiment, an increase at the  $\text{O}^{\text{I}}/\text{O}^{\text{II}}$  intensity ratio is observed at the O 1s spectra, from 3.7 before, to 4.8 after  $\text{TiCl}_4$  deposition. Furthermore there is no evidence of further silicon oxidation after the  $\text{TiCl}_4$  evaporation, because the  $\text{Si}^{\text{I}}/\text{Si}^{\text{0}}$  intensity ratio of the Si 2p components remains constant, and there is no oxygen contamination during the  $\text{TiCl}_4$  dosing procedure because the total intensity of the O 1s peak decreases. Thus, the increase of  $\text{O}^{\text{I}}/\text{O}^{\text{II}}$  ratio is mainly attributed to the transformation of surface silanols to  $\text{Si}-\text{O}-\text{Ti}$  linkages. The chemical shift and the fwhm of the Ti 2p XPS peak indicate the electron density of the titanium species, namely the oxidation state, and its distribution, respectively. The large fwhm value (3.4 eV) observed at the Ti  $2p_{3/2}$  peak after  $\text{TiCl}_4$  deposition may be due to the broad distribution of the titanium species while their binding energy indicates that their main oxidation state is  $\text{Ti}^{4+}$ .

The mechanism proposed by Kovaleva et al. [5] for the interaction of  $\text{AlEt}_3$  with  $\text{SiO}-\text{TiCl}_3$ , involves the replacement of Ti atoms from the  $\text{Si}-\text{O}-\text{Ti}$  linkages by Al and creation of  $\text{Ti}^{3+}$  clusters chemically bonded to the oxide substrate. At the present results, there is no evidence for  $\text{Ti}^{3+}$  species that should shift the Ti  $2p_{3/2}$  peak to  $\text{BE} \sim 457.5$  eV [12]. Instead, only a small (0.4 eV) downward BE shift of this peak is observed after the reaction with  $\text{AlEt}_3$  followed by a decrease at the fwhm. Generally, electron donation to the titanium atoms is expected to cause a peak shift to a lower binding energy region. Thus, alkylation of  $\text{SiO}-\text{TiCl}_3$  is expected to cause a small shift of the Ti  $2p_{3/2}$  peak towards lower BE, since chlorine atoms bonded to Ti are substituted by the less electronegative ethyl groups. Nevertheless, a direct ligand replacement mechanism would lead to the formation of  $\text{AlEt}_2\text{Cl}$  that would easily desorb from the surface leaving a deficiency in Cl atoms. This is not supported here, since the amount of Cl atoms remains practically the same after  $\text{AlEt}_3$  deposition. Based on this fact and taking into account that a considerable amount of Al is detected on the surface, it is proposed that the alkylation mechanism involves the formation of surface complexes between the  $\text{SiO}-\text{TiCl}_3$  surface species and the incoming  $\text{AlEt}_3$  molecules. The formation of such intermediate complexes has been proposed in many studies on Z-N catalysts, nevertheless there is no direct spectroscopic evidence confirming their existence [16,17].

The mechanism of  $\text{AlEt}_3$  reaction with  $\text{Si}-\text{OH}$  groups is well known and could be described by the following reaction [18]:

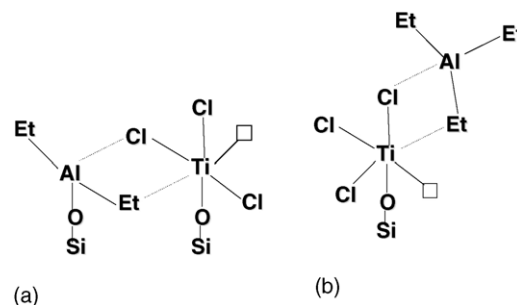
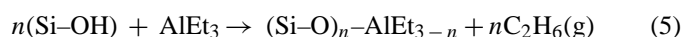


Fig. 5. Plausible structures of surface complexes formed between  $\text{SiO}-\text{TiCl}_3$  and  $\text{AlEt}_x$  that (a) may or (b) may not be chemically bonded on the  $\text{SiO}_x$  surface.

This reaction can take place in the present procedure, between the  $\text{AlEt}_3$  vapors and the remaining  $\text{Si}-\text{OH}$  species on the oxide's surface. It was mentioned earlier that after exposure to  $\text{AlEt}_3$  vapors the carbon uptake is of about 3.5 carbon atoms originating from C–H species ( $\text{C}^{\text{II}}$  component at the C 1s peak) per Al atom (i.e. about two ethyl groups per Al atom). This indicates that the value of the factor “ $n$ ” in reaction (5) is  $n \sim 1$  leading mainly to the formation of  $\text{SiO}-\text{AlEt}_2$ . The interaction with neighboring  $\text{SiO}-\text{TiCl}_3$  by sharing Cl and Et groups, is favored thermodynamically [19], and the complexes that can be formed in this way are shown schematically in Fig. 5a. If there are no residual  $\text{Si}-\text{OH}$  groups on the surface or if additional  $\text{AlEt}_3$  molecules arrive, they will interact directly with the surface  $\text{SiO}-\text{TiCl}_3$  species in the same way, forming complexes like those shown in Fig. 5b. In agreement with recent theoretical predictions and experimental results obtained by XPS and X-ray adsorption [4,20,21], the dominant oxidation state of Ti in these species is  $\text{Ti}^{4+}$ . Nevertheless, a more accurate structural identification of the surface complexes lies beyond the limitations of XPS. The present results give an additional evidence for the formation of such complexes: the Cl atoms that act as bridges between Ti and Al atoms should give XPS peaks at slightly higher binding energy as compared to the peaks originating from terminal chlorine atoms at the  $(\text{Si}-\text{O})_x-\text{TiCl}_{4-x}$  species [22]. This behavior is apparent here since the Cl 2p peak broadens and shifts towards higher BEs.

Ti-species like those shown in Fig. 5 cannot be necessarily considered as an alternative to the formation of species where direct bond  $\text{Ti}-\text{C}$  is present, but they could be precursor complexes that in the presence of olefins, during polymerization reaction, can evolve towards species where a  $\text{Ti}-\text{C}$  bond is present. Further experiments, where the entire reaction path is studied, are expected to clarify this point.

## 5. Conclusions

The interaction mechanism between  $\text{AlEt}_3$  and titanium chloride supported on a  $\text{SiO}_x$  layer was studied using X-ray photoelectron spectroscopy. A flat conductive Si wafer covered with a thin native  $\text{SiO}_x$  layer, was used as support, eliminating charging effects and allowing a more reliable identification of surface chemical species. The  $\text{TiCl}_4$  vapors reacted with the sputtered oxide layer mainly through isolated  $\text{Si}-\text{OH}$  species leading to formation of  $\text{SiO}-\text{TiCl}_3$ . There was no evidence of Ti reduction

after the interaction with  $\text{AlEt}_3$  vapors. The alkylation of the titanium oxychloride species takes place by means of surface complex formation with ethylaluminum species that may or may not be chemically bonded on the  $\text{SiO}_x$  surface. In the alkylated complexes  $\text{Ti}^{4+}$  is found to be the dominant oxidation state of Ti.

## References

- [1] T. Xie, K.B. McAuley, J.C. Hsu, D.W. Bacon, *Ind. Eng. Chem. Res.* 33 (1994) 449.
- [2] P. Sobota, S. Szafert, *Inorg. Chem.* 35 (1996) 1778–1781.
- [3] E. Magni, G.A. Somorjai, *Surf. Sci.* 377–379 (1997) 824.
- [4] D. Fregonese, A. Glisenti, S. Mortara, G.A. Rizzi, E. Tondello, S. Bresadola, *J. Mol. Catal. A: Chem.* 178 (2002) 115.
- [5] N.Yu. Kovaleva, Yu.A. Gavrillov, L.A. Novokshonova, *Polymery* 42 (1997) 616.
- [6] P. Brant, A.N. Speca, *Macromolecules* 20 (1987) 2740.
- [7] A. Siokou, S. Ntais, *Surf. Sci.* 540 (2003) 379.
- [8] R.K. Iler, *The Chemistry of Silica: Solubility, Polymerization Colloid and Surface Properties and Biochemistry*, Wiley, Chichester, 1979.
- [9] D. Briggs, M.P. Seah, *Practical Surface Analysis*, vol. 1, second ed., Wiley, New York, 1996.
- [10] S. Iwata, A. Ishizaka, *Appl. Phys. Rev.* 79 (9) (1996) 6653.
- [11] J. Viard, E. Beche, D. Perarnau, R. Berjoan, J. Durand, *J. Eur. Ceram. Soc.* 17 (1997) 2025.
- [12] S. Ntais, V. Dracopoulos, A. Siokou, *J. Mol. Catal. A: Chem.* 220 (2004) 199.
- [13] S. Haukka, E.L. Lakomaa, A. Root, *J. Phys. Chem.* 97 (1992) 5085.
- [14] D. Damianov, M. Velikova, Iv. Ivanov, L. Vlaev, *J. Non-Cryst. Solids* 105 (1988) 107.
- [15] A. Yu Stakheev, E.S. Sphiro, J. Apijok, *J. Phys. Chem.* 97 (1993) 5668.
- [16] Y.I. Yermakov, B.N. Kuznetsov, V.A. Zacharov, *Studies in Surface Science and Catalysis*, vol. 8, *Catalysis by Supported Complexes*, Elsevier, Amsterdam, 1981.
- [17] B. Liu, T. Nitta, M. Terano, *Macromol. Chem. Phys.* 203 (2002) 2412.
- [18] J.B. Kinney, R.H. Staley, *J. Phys. Chem.* 87 (1983) 3735.
- [19] D.R. Lide, *CRC Handbook of Chemistry and Physics*, vol. 1, 72nd ed., CRC Press, Boston, 1991–1992, pp. 5–18.
- [20] M. Boero, M. Parrinello, S. Huffer, H. Weiss, *J. Am. Chem. Soc.* 122 (2000) 501.
- [21] P.J.V. Jones, R.J. Oldman, W. Kaminsky, in: H. Sinn (Ed.), *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, Springer, Berlin, 1988, p. 223.
- [22] S. Srivastava, *Appl. Spectr. Rev.* 22 (1986) 401.