



TiCl₄(THF)₂ impregnation on a flat SiO_x/Si(1 0 0) and on polycrystalline Au foil: determination of surface species using XPS

Spyridon Ntais, Vassilios Dracopoulos, Angeliki Siokou*

Foundation of Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Chemical Processes, Stadiou 18, Platani Achaïas, Patras 26504, Hellas, Greece

Received 9 February 2004; accepted 4 May 2004

Abstract

TiCl₄(THF)₂ was impregnated by spin-coating on a Si(1 0 0) wafer covered with a thin SiO_x layer and on a polycrystalline Au foil. The nature of the surface species was determined at room temperature and after annealing, by X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). A mixed Si:O:Ti interfacial layer was formed on the silicon substrate while in the case of Au, TiOCl_x and TiO_x were the main surface species at room temperature. Annealing at 723 K leads to the total desorption of the Cl atoms, and in both cases a significant amount of Ti atoms was reduced to the Ti³⁺ state. AFM measurements revealed a homogenous distribution of nano-sized TiO_x clusters with semi-ellipsoid shape and increased contact area with the underlying silica.

© 2004 Elsevier B.V. All rights reserved.

Keywords: X-ray Photoelectron Spectroscopy; Titanium chloride; SiO_x/Si substrate; Surface species

1. Introduction

The surface reactions of TiCl₄ or TiCl_x(THF)_y complexes with silica are of particular interest in studies of olefin polymerization catalysts. In a latest generation of Ziegler-Natta catalysts, [Mg₂(μ-Cl)₃(THF)₆]⁺[TiCl₅(THF)]⁻ supported on SiO₂ together with an organometallic co-catalyst is used for commercial ethylene polymerization [1]. Furthermore, impregnation of silica with TiCl₄ or organic titanium-containing compounds followed by calcination at high temperatures is a common method for the preparation of well dispersed titania supported on SiO₂, which is both a catalyst and a catalyst support [2]. Transition metals, which are supported on it, develop higher activities than when supported on unmodified silica.

Generally, it has been found that during the reaction of silica with TiCl₄, the nature of the surface titanium species are determined by the surface hydroxyl groups on silica. Thus, the pre-treatment temperature and the reaction temperature of TiCl₄ with the support are the main factors influencing the formed species [3].

In this work, TiCl₄(THF)₂ is impregnated by spin-coating on the native SiO_x overlayer of a Si(1 0 0) wafer, and the surface species that are formed at room temperature and after annealing are studied by X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). The final target of this project is to prepare a model Ti-based Ziegler-Natta catalyst supported on silica. Instead of porous high surface area silica, a flat substrate is used in order to allow the surface characterization in an atomic level without the complications induced by porous and non-conductive supports.

The same study was performed using an inert substrate, a sputter-cleaned polycrystalline Au foil. The outcome of the studies is of great importance in the course of understanding the surface chemistry of the real catalytic systems.

2. Experimental

The photoemission measurements were carried out in an Ultra High Vacuum (UHV) system, which has been described in detail elsewhere [4]. 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 Au4f_{7/2} peak, were used in all XPS mea-

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

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, we estimate that for a good signal-to-noise ratio, errors in peak positions can be ± 0.1 eV. In the case of the Au foil, the binding energy (BE) scale was calibrated by assigning the Au4f signal at 84 eV, while in the case of the Si substrate, the reference was the Si2p peak at 99.8 eV. The C1s XPS peaks were analyzed by the use of doublets with a spin orbit splitting separation of 1.65 eV and full width at half maximum equal to 2 eV.

A p-doped Si(100) crystal and an Au foil were used as the conducting flat substrates. In order to remove the organic contaminants, the Si crystal was dipped in a 5:1:1 mixture of H₂O/H₂O₂/NH₄OH at 353 K for 10 min [5]. The crystal was then transferred into the UHV system where it was further cleaned from the carbon contamination with mild Ar⁺-sputtering. After cleaning, X-ray Photoelectron Spectroscopy measurements showed the existence of a thin native oxide layer. The Si substrate was then heated at 873 K under oxygen atmosphere (4×10^{-6} mbar) for 30 min. After this treatment, the thickness of the oxide was calculated to be ~ 3 nm. The Au foil after its introduction in the UHV system was cleaned with Ar⁺-sputtering for 20 min.

The deposition was performed into a glove bag filled with dry nitrogen, attached to the fast entry chamber of the UHV system. The use of the glove bag is critical since titanium chloride is sensitive to oxygen and moisture of the atmosphere. The substrate was mounted on the spin-coater and a tetrahydrofuran (THF) solution of TiCl₄(THF)₂ with concentration 1.5×10^{-2} M was applied. The same procedure was followed for both substrates. The rotation speed was 3000 rpm. After spinning, the samples were immediately introduced in the UHV chamber for surface analysis. Annealing up to 723 K under UHV conditions took place in order to study the behavior of the deposit and the modification of the surface during annealing. All spectra were recorded at room temperature.

The morphology of the surface after annealing was investigated by Atomic Force Microscopy (Topometrix Explorer) operating in contact mode. Silicon nitride cantilevers were used for imaging with tip radius less than 50 nm. The measurements were performed in air.

3. Results and discussion

3.1. Deposition on Si(100)/SiO₂

Before deposition, Si, O and C are the only elements detected on the surface. Fig. 1 shows the evolution of the O1s, Si2p and C1s peaks before and after a 1.5×10^{-2} M solution of TiCl₄(THF)₂ in THF was spin-coated on the SiO_x/Si substrate. Before deposition, the analysis of the C1s peak reveals a small carbon contamination in the C–C (BE = 284.6 eV) and C–O (BE = 286 eV) form. The BE of the O1s peak is characteristic of the oxygen atoms in silicon oxide (533.1 eV) [6], but the peak is broad (FWHM ~ 2.6 eV) due to the existence of –OH groups and C–O species on the surface. The thickness of the oxide layer on top of the silicon surface is calculated to be ~ 3 nm. The calculation was done using the XPS intensity ratio of the Si2p peaks that correspond to the different oxides (Si^I at 100.5 eV, Si^{II} at 102.6 eV and Si^{III} at 103.6 eV) and the Si2p peak from the substrate (Si⁰ at 99.8 eV) [6], considering a uniform oxide layer and an atomic sensitivity ratio for Si2p(SiO₂)/Si2p(bulk Si) = 0.8 [7]. The SiO_x stoichiometry was calculated from the intensity ratio of the Si2p peaks that correspond to the different oxides (Si^I, Si^{II} and Si^{III}) and the O1s peak at ~ 533.1 eV using the atomic sensitivities for Si2p (in SiO_x) and O1s being 0.22 and 0.66, respectively [7]. It was found to be $x = 2.2$ as expected due to the excess of oxygen on the surface in absorbents such as –OH and C–O groups.

After deposition, the Si2p and O1s spectra changed significantly. The total intensity of Si2p peak decreases because the SiO_x/Si substrate is now covered by the deposit. Furthermore, the shape of the peak changes as a result of the

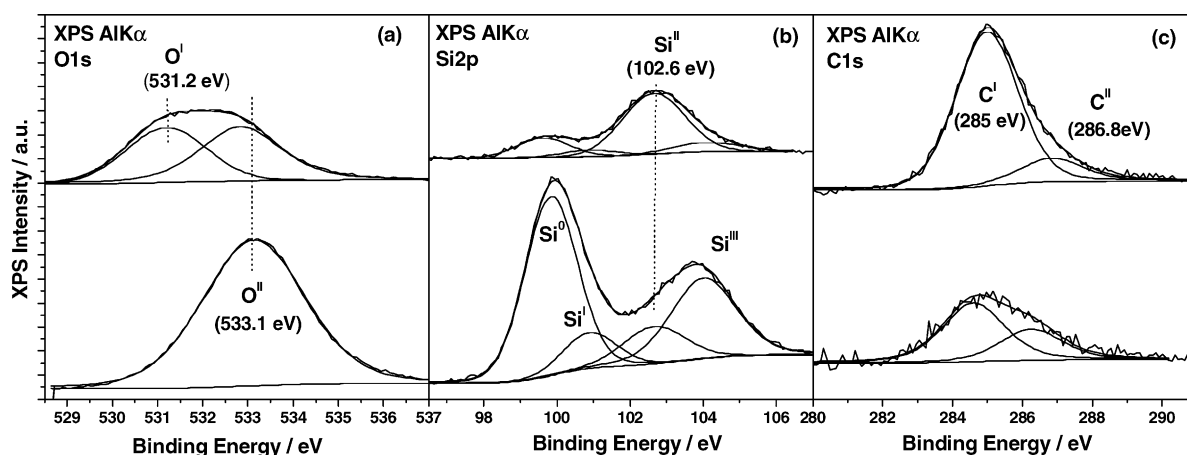


Fig. 1. O1s, Si2p and C1s XPS peaks before (bottom) and after (top) deposition of TiCl₄(THF)₂ on the SiO_x/Si(100) substrate.

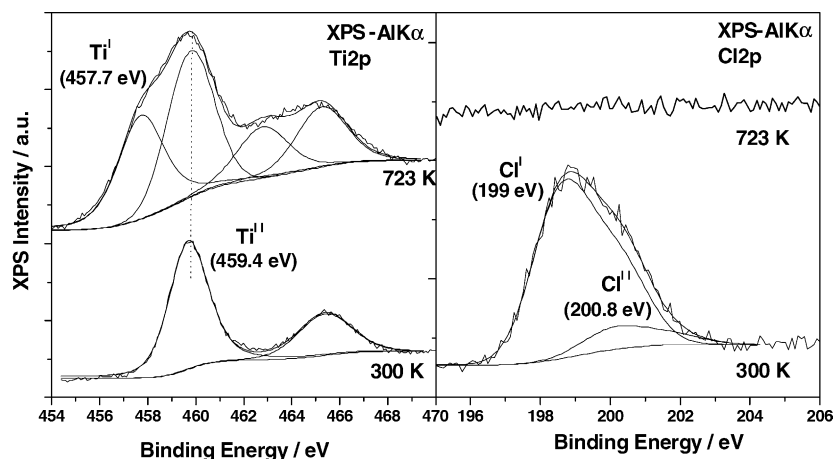


Fig. 2. Ti2p and Cl2p XPS after deposition of $\text{TiCl}_4(\text{THF})_2$ on the $\text{SiO}_x/\text{Si}(1\ 0\ 0)$ substrate at room temperature (300 K) and after annealing at 723 K.

interaction of the oxide layer with the deposited species. It is interesting that the intensity ratio of the XPS Si2p peaks attributed to the SiO_x ($x \leq 2$) layer (Si^{I} , Si^{II} and Si^{III}), and the silicon substrate Si^0 increases from 1 before deposition to 4.9 after deposition. This can be translated as an increment of the reactive layer's thickness from 3 nm before to 7 nm after deposition, indicating diffusion of Si atoms to the surface or close to the surface where they can be expected to bond in a Si:O:Ti matrix. Furthermore, while the intensity ratio $\text{Si}^{\text{III}}/\text{Si}^0$ remains constant before and after deposition (~ 0.6), the intensity ratio $\text{Si}^{\text{II}}/\text{Si}^0$ increases from 0.25 before to 3.5 after deposition. At the O1s spectrum, apart from the pre-existed peak at BE = 533.1 eV (O^{II}), a new component appears at BE = 531.2 eV (O^{I}). The intensity of the C1s peak increases due to molecular THF that remained attached on Ti species, or/and THF dissociation products [8].

The Cl2p and Ti2p overlayer XPS peaks before and after annealing at 723 K are presented in Fig. 2. The Cl2p XPS peak exhibits two components. One at BE = 199.1 eV (Cl^{I}) and the other at 200.8 eV. This last peak is attributed to Cl atoms attached to hydrocarbons [9,10] and their percentage is very small in this case. The center of the $\text{Ti}2p_{3/2}$ peak is at BE = 459.4 eV. The higher BE of $\text{Ti}2p_{3/2}$ as compared to that in TiO_2 or TiCl_4 [11,12] is a characteristic feature of the Ti–O–Si bond formation. Its higher value is attributed to the decrease of the electron density around the Ti atoms due to the higher electronegativity of Si as compared to that of Ti [13]. For the same reason, the new O1s peak (O^{I}) which has lower BE than that in Si–O–Si bonds and higher than that in Ti–O–Ti (530–530.5 eV) is attributed to O atoms in Ti–O–Si bonds. Nevertheless, a percentage of this particular O1s peak may also represent oxygen atoms in TiO_x or TiOCl_x species attached on the silicon oxide layer. This hypothesis is confirmed by the XPS results from the study of the same deposit on Au foil, as it will be discussed in detail below.

After annealing at 723 K, all the Cl atoms desorb with the contemporaneous reduction of a significant amount of tita-

nium atoms (Fig. 2). The analysis of the $\text{Ti}2p$ peak gave two components characteristic of Ti^{3+} and Ti^{4+} . At the same time, only a small amount of the initially detected carbon species remain on the surface indicating desorption of organic species which is also revealed by the increase of the total Si2p peak intensity. The thickness of the SiO_x layer appears to decrease from 7 to 5.4 nm. The $\text{Si}^{\text{III}}/\text{Si}^0$ intensity ratio increases to 1 (from ~ 0.6 at 300 K) while the $\text{Si}^{\text{II}}/\text{Si}^0$ intensity ratio decreases from 3.5 (at 300 K) to 1.5 after annealing.

The AFM image of the surface after annealing (Fig. 3b) reveals a homogenous distribution of nano-sized particles on the silica layer. Their shape is semi-ellipsoid with height between 7 and 15 nm. Two dimensional agglomerations of these particles are also observed clearly, resulting to clusters of the same height and with a maximum diameter of ~ 300 nm. These formations offer an increased contact area with the underlying silica through Si–O–Ti linkages. The existence of these bonds even after annealing is revealed by the binding energy of the XPS O1s peak which is still 0.5 eV higher from the energy of the oxygen in TiO_x . It is also worth to mention that even after annealing, the high BE component of the $\text{Ti}2p_{3/2}$ peak is at BE = 459.4 eV, a value of about 0.5 eV higher than that of Ti in TiO_2 .

3.2. Deposition on Au foil

A polycrystalline Au foil was used as a flat conductive and inert substrate for the TiCl_4 deposition, by spin-coating a $\text{TiCl}_4(\text{THF})_2/\text{THF}$ solution. The XPS measurements showed that after sputtering at room temperature, the Au surface was free from oxygen contamination, but traces of carbon were still present (about one monolayer). After deposition, the energy position (BE = 84 eV) and the shape of Au4f peak did not change indicating that there is no significant chemical interaction with the deposit.

Fig. 4 shows the XPS O1s and C1s peaks at room temperature and after annealing the sample at 723 K. The XPS

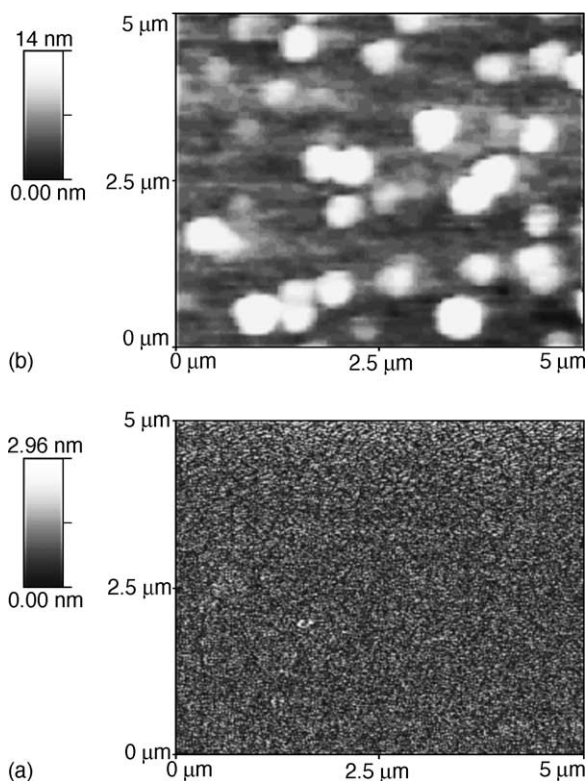


Fig. 3. AFM images (a) of the SiO₂ surface before deposition and (b) after deposition and annealing at 723 K.

O1s peak has been analyzed into two components; one at 531.1 eV and the other at 532.8 eV, both of them having FWHM = 2 eV. Since no traces of oxygen were detected on the Au surface before deposition, the total intensity of O1s peak after deposition originates from the deposit. The intensity of C1s spectrum increases after deposition, and the peak consists of two components; one at 284.9 eV and the other at 286.8 eV. These are features of either molecular THF or/and THF-dissociation products. After annealing at 723 K, the C1s peak loses a significant amount of its intensity due to desorption of organic species. The Au4f peak retains its shape but gains intensity. The intensity of the O^I component

of the O1s spectrum increases significantly while the other component (O^{II}) decreases slightly.

Fig. 5 shows the Cl2p, Ti2p XPS peaks before and after annealing. The Cl2p peak at room temperature has been analyzed into two doublets, the first at BE = 198.8 eV (Cl2p_{3/2}) and the second at BE = 199.8 eV. The BE of the Ti2p_{3/2} peak is at 459.4 eV. The FWHM of this peak is 2.12 eV, which is wide enough to imply the existence of a small percentage of titanium atoms at a more electron rich environment. After annealing at 723 K, the total amount of chlorine desorbs from the surface. The Ti2p peak exhibits now, a second well-resolved component at 457.4 eV (Ti2p_{3/2}) which is characteristic of the Ti³⁺.

The (%) atomic composition on both (Au and SiO_x/Si(1 0 0)) surfaces was calculated from the intensities of the XPS Si2p, C1s, Cl2p, O1s and Ti2p peaks using the atomic sensitivity factors that are 0.22, 0.25, 0.73, 0.66 and 1.8, respectively [7]. The results are presented in Table 1 that contains also the exact binding energy position of each peak.

It is well known that titanium tetrachloride and its THF complexes such as TiCl₄(THF)₂ are very sensitive to moisture and can decompose towards TiOCl_x or TiO_x even at room temperature [14]. The results of the present study clearly indicate the existence of TiO_x and TiOCl_x after deposition on the Au surface. The evidence for this conclusion is the presence of the O1s peak at BE = 531.2 eV in combination with the deficiency of chlorine atoms even at room temperature. The energy of the chlorine atoms in TiOCl_x is 198.8 eV (Cl2p_{3/2}) [4]. The quantitative results in Table 1 can give some clear information concerning the surface composition on Au. First of all, it is reasonable to consider that the Ti atoms that appear to be reduced after annealing are practically the only Ti atoms bonded to chlorine at room temperature. In the case of the Au substrate, these are only 28% of the total amount of Ti atoms. The logic behind this consideration is based on the fact that the TiO_x surface species would not undergo any reduction up to the annealing temperature of 723 K [15,16]. Having said that and considering the calculated atomic ratios in Table 1 (two Cl atoms for one Ti atom that undergo reaction after

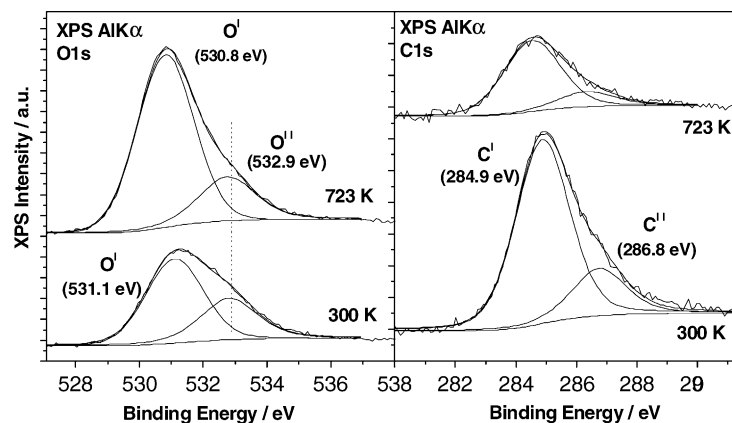


Fig. 4. O1s, and C1s XPS peaks after deposition of TiCl₄(THF)₂ on the Au foil at room temperature (300 K) and after annealing at 723 K.

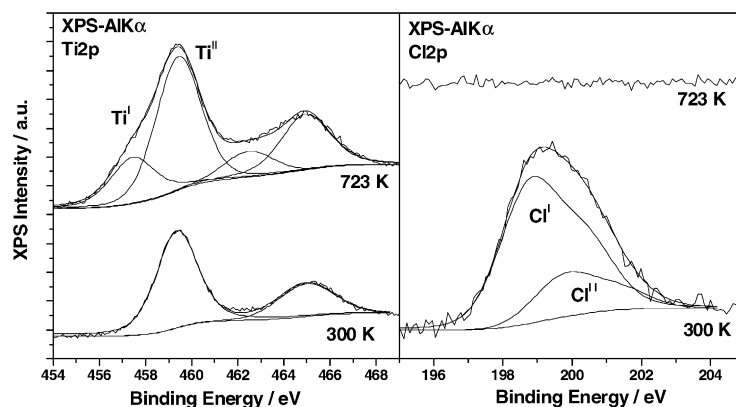


Fig. 5. Ti2p and Cl2p XPS peaks after deposition of $\text{TiCl}_4(\text{THF})_2$ on the Au foil at room temperature (300 K) and after annealing at 723 K.

annealing), we conclude that at room temperature, the most possible Cl-containing Ti compound is the titanium oxychloride TiOCl_2 , while the rest of the Ti atoms are in the form of TiO_x . Although the BE of the Ti2p XPS peak is that for completely oxidized Ti, the larger than normal width of this peak indicates the not well-defined stoichiometry of these compounds. The fact that the BE value is about 0.6 eV higher than the BE of Ti2p in TiO_x , is an indication of well dispersed small sized particles [13] on the Au surface. The Cl2p peak at higher BEs (199.8 eV) represent Cl atoms bonded to hydrocarbon species. One possible compound is 1,4-dichlorobutane which is the result of the substitution of the oxygen atom by two chlorine atoms in the THF molecule when the THF solution of $\text{TiCl}_4(\text{THF})_2$ is heated above 400 K [17]. In this work, the THF solution was only heated up to 335 K before spin-coating, in order to increase the solubility of the $\text{TiCl}_4(\text{THF})_2$. Thus, 1,4-dichlorobutane is not expected to be formed in the solution, but most probably on the surface after deposition.

The XPS O1s peak at BE = 532.8 eV is due to THF dissociation products or even due to some intact THF on the surface. It has to be mentioned here that the present experi-

mental results give no evidence of TiCl_4 or $\text{TiCl}_4(\text{THF})_x$ on the Au surface. Only decomposition products are observed, although all the experimental procedure took place under dry N_2 atmosphere and the sample was transferred into the UHV chamber without any contact with air or humidity. A possible explanation for this is that decomposition of TiCl_4 and its complexes is facilitated on the Au surface at room temperature and under UHV conditions. Nevertheless, the existence of titanium oxychlorides and mainly of TiO_x can also be expected in the solution due to some contamination of the $\text{TiCl}_4(\text{THF})_2$ powder. It is worthwhile to mention that the amount of Cl atoms attached to hydrocarbons on the Au surface is 3.5 times larger as compared to that on the SiO_x substrate. Furthermore, the percentage of Ti atoms which are attached to Cl is 28% while in the case of the SiO_x substrate is 46%. These two facts are indications that the Au substrate facilitates the TiCl_4 dissociation from the oxygen containing ligands which in this case are the THF molecules.

In the case of $\text{SiO}_x/\text{Si}(100)$ substrate, about 46% of the total amount of Ti atoms are reduced after annealing, indicating that these were Ti atoms bonded to Cl at room temperature. The energy of the corresponding chlorine atoms is

Table 1

Surface composition (%) on the $\text{SiO}_x/\text{Si}(100)$ and Au substrates after $\text{TiCl}_4(\text{THF})_2$ deposition, at 300 K and after annealing at 723 K

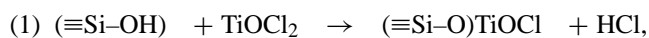
| Substrate | $\text{SiO}_x/\text{Si}(100)$ | | | | | | | | |
|------------------------|-------------------------------|-----------------|----------------|-----------------|---------------------|------------------|---------------------|------------------|--|
| | O1s | | C1s | | Ti2p _{3/2} | | Cl2p _{3/2} | | Si2p |
| | O ^I | O ^{II} | C ^I | C ^{II} | Ti ^I | Ti ^{II} | Cl ^I | Cl ^{II} | Si ^I , Si ^{II} , Si ^{III} |
| Substrate BE (eV) | – | 533.1 | 284.6 | 286.3 | – | – | – | – | 100.5, 102.6, 103.6 |
| Atomic composition (%) | – | 63 | 7 | 3 | – | – | – | – | 27 |
| 300 K BE (eV) | 531.2 | 533.1 | 285 | 286.8 | – | 459.4 | 199.1 | 200.8 | 100.5, 102.6, 103.6 |
| Atomic composition (%) | 18.3 | 20.5 | 32.2 | 7 | 0 | 7.3 | 3.4 | 0.3 | 11 |
| 723 K BE (eV) | 531.1 | 532.8 | 285 | 286.3 | 457.7 | 459.4 | – | – | 100.5, 102.6, 103.6 |
| Atomic composition (%) | 33.3 | 27.6 | 9.3 | 2.2 | 6.7 | 7.8 | 0 | 0 | 13.1 |
| | <u>Au foil</u> | | | | | | | | |
| 300 K BE (eV) | 531.1 | 532.8 | 284.9 | 286.8 | – | 459.4 | 198.8 | 199.8 | – |
| Atomic composition (%) | 23 | 12.6 | 35.6 | 9.8 | – | 11 | 6.3 | 1.7 | – |
| 723 K BE (eV) | 530.8 | 532.8 | 284.6 | 286.3 | 457.4 | 459.4 | – | – | – |
| Atomic composition (%) | 37.6 | 10.9 | 28.9 | 3.7 | 5.3 | 13.5 | 0 | 0 | – |

The binding energy (BE) values of the peaks are also presented.

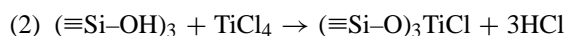
199 eV (Cl2p_{3/2}). All the experimental observations indicate the anchoring of TiCl_x on the SiO_x substrate through the interaction with the surface –OH species and the formation of a mixed Si:O:Ti oxide layer at the interface. As shown in Table 1, the atomic ratio Si:Ti in the reactive layer is 1.5.

The hydroxyls generally act as the reactive sites on the silica surface [3]. The interaction of TiCl₄ and its THF complexes with the surface hydroxyls is either mono-functional (one TiCl₄ molecule titrating one –OH group) or bi-functional (one TiCl₄ titrating two –OH groups) depending on the surface pre-treatment and the reaction temperature [3,18]. Thus, the titanium atoms bind to the silica surface via oxygen bridges. Two types of Ti-species, highly dispersed surface TiO_x species and TiO₂ crystallites are possibly present on the silica surface depending on the preparation conditions [19]. The dispersion capacity is closely related to the concentration of hydroxyls on the silica surface. As the temperature of silica pre-treatment becomes higher than 723 K, removal of isolated groups and loss of the hydrogen bonded ones occurs. In this study, the silicon substrate has been annealed at 823 K, and thus the main species on the oxide surface are expected to be isolated OH groups and siloxanes. It has already been shown in our previous studies [4] that the reaction of TiCl₄ with the SiO_x/Si(100) surface after the above mentioned treatment would lead to species such as (≡Si–O)_xTiCl_{4–x}.

The quantitative estimations of Table 1 show that one Cl atom corresponds to one Ti atom (that undergo reaction after annealing). Thus, the most possible Cl-containing species on the surface are either (≡Si–O)TiOCl as a product of the reaction:



or (≡Si–O)₃TiCl as a product of the reaction [18]:



The rest of the Ti atoms are in the form of TiO_x and also (≡Si–O)₂TiO, always in the completely oxidized state at room temperature. When the Si–O–Ti linkages are formed, the BE of Si2p peak for the corresponding Si atoms is ~102.6 eV, which is lower from that of the Si atoms in SiO₂ (103.6 eV) due to the decrease in the effective positive charge on the Si atoms. This explains the increase at the percentage of the Si^{II} peak in the Si2p spectrum after deposition (Fig. 1).

Annealing the samples at 723 K leads to the total desorption of the Cl atoms due to dissociation of Ti–Cl bonds. In the case of the Au substrate, after annealing the energy of the low BE component of the O1s peak undergoes a downward shift of 0.3 eV, from 531.1 to 530.8 eV. This occurs because after the total desorption of chlorine atoms, the surface contains only TiO_x formations, while the electronic environment around the oxygen atoms is richer. Thus, the corresponding oxygen atoms have lower binding energy. One would expect to observe the same downward shift at the BE of Ti2p_{3/2} peak which originates from the Ti⁴⁺

species (459.4 eV). Nevertheless, no such shift is observed, leading us to the conclusion that the TiO_x species are highly dispersed on the Au surface even after annealing.

In the case of the Si substrate, the O1s component at 531.2 eV represents oxygen atoms that bridge silicon and titanium atoms in (≡Si–O)₃TiCl as well as those in (≡Si–O)TiOCl species. After annealing, the BE of this O1s component does not undergo any significant shift as in the case of Au. This, in combination with the fact that the BE of Ti2p_{3/2} peak which originates from the Ti⁴⁺ species remains as high as 459.4 eV, indicates that a considerable amount of Si–O–Ti linkages still exists on the surface, but it could also mean that the TiO_x clusters are very well dispersed on the Si:O:Ti matrix. The good dispersion of the TiO_x is also confirmed by the AFM measurements where flat-based nano-sized clusters are observed.

4. Conclusions

A THF solution of TiCl₄(THF)₂ was impregnated by spin-coating on a Si(100) wafer covered with a 3 nm thick SiO_x layer and on a polycrystalline Au foil. It was found that the TiCl_x or TiOCl_x species from the solution anchor on the oxide's surface by reacting with the surface hydroxyl groups. A mixed Si:O:Ti interfacial layer is formed while there is strong spectroscopic evidence for the existence of Si–O–Ti linkages.

Impregnation of the same deposit on the Au foil verified the existence of some TiCl₄ decomposition species such as TiOCl_x in the THF solution. In this case, there was no evidence of strong interaction with the substrate, but TiCl₄ dissociation occurred readily.

Annealing the samples at 723 K lead to the total desorption of the Cl atoms by breaking Ti–Cl bonds and by the complete desorption of Cl-containing hydrocarbons. In both cases, a significant amount of Ti atoms is reduced to the Ti³⁺ state. AFM measurements revealed a homogenous distribution of nano-sized clusters with semi-ellipsoid shape and increased contact area with the underlying silica.

References

- [1] P. Sobota, Chem. Eur. J. 9 (2003) 4854–4860.
- [2] A. Muñoz, G. Muñera, Studies in surface science and catalysis, in: G. Poncelet, P.A. Jacobs, P. Grange, B. Delmon (Eds.), Preparation of Catalysts V, vol. 63, Elsevier, Amsterdam, 1991, p. 627.
- [3] S. Srinivasan, A.K. Datye, M.H. Smith, C.H.F. Peden, J. Catal. 145 (1994) 565.
- [4] A. Siokou, S. Ntais, Surf. Sci. 540 (2003) 379.
- [5] R.K. Iler, The chemistry of silica: solubility, polymerization, colloid and surface properties and biochemistry, Wiley-Interscience, Chichester, 1979.
- [6] S. Iwata, A. Ishizaka, Appl. Phys. Rev. 79 (9) (1996) 6653.
- [7] D. Briggs, M.P. Seah, Practical Surface Analysis, 2nd ed., vol. 1, Wiley, New York, 1996.
- [8] G. Zhuang, K. Wang, P.N. Ross Jr., Surf. Sci. 387 (1997) 199.

- [9] X.D. Huang, S.H. Goh, *Polymer* 43 (2002) 1417.
- [10] J.M. Lannon Jr., Q. Meng, *Surf. Sci. Spectra* 6 (2) (1999) 131.
- [11] E. Magni, G.A. Somorjai, *Surf. Sci.* 345 (1996) 1.
- [12] K. Hasebe, H. Mori, M. Terano, *J. Mol. Catal. A: Chem.* 124 (1997) L1–L3.
- [13] A. Yu Stakheev, E.S. Sphiro, J. Apijok, *J. Phys. Chem.* 97 (1993) 5668.
- [14] R.J.H. Clark, *Comprehensive Inorganic Chemistry*, vol. 3, Pergamon Press Ltd., 1973, p. 409.
- [15] R. Castillo, B. Koch, P. Ruiz, B. Delmon, *J. Catal.* 161 (1996) 524.
- [16] Y. Masuda, W.S. Seo, K. Koumoto, *Langmuir* 17 (2001) 4876.
- [17] H.K. Choi, D.W. Chung, T.K. Han, S.I. Woo, *Macromolecules* 26 (1993) 452.
- [18] S. Haukka, E.L. Lakomaa, A. Root, *J. Phys. Chem.* 97 (1992) 5085.
- [19] N. Hüsing, B. Launay, D. Doshi, G. Kickelbick, *Chem. Mater.* 14 (6) (2002) 2429.