

MgCl₂/TiCl₄/AlEt₃ catalytic system for olefin polymerisation: a XPS study

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Abstract

A variety of techniques have been applied for 40 years in order to characterise Ziegler–Natta catalysts, however, few studies report the use of surface science technologies in an effort to understand surface structure, composition and chemical bonding in MgCl₂ supported catalytic system. In this paper, the synthesis and the characterisation of the MgCl₂/TiCl₄/AlEt₃ catalyst in controlled conditions is reported.

Our aim is to understand (1) the activation process of the magnesium chloride support; (2) the interaction between the magnesium chloride support and TiCl₄; (3) the chemical structure of the titanium active centres formed by treatment of the procatalyst, MgCl₂/TiCl₄, with the co-catalyst, TEA (triethylaluminium); (4) which Tiⁿ⁺ species is active in ethene and propene polymerisations. These experiments were performed in conditions as similar, as possible, to the ones used for laboratory synthesis and polymerisation.

The experiment consists of different steps: (1) preparation of δ-MgCl₂ under strictly inert atmosphere as previously reported [1]; (2) activation of δ-MgCl₂ in a UHV chamber by means of argon ion sputtering; (3) exposure to TiCl₄ vapours; (4) exposure to TEA. The surface composition was checked during the experimental steps by means of XPS technique. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Olefin polymerisation; Supported catalysts; Titanium oxidation states; XPS study; Ziegler–Natta catalysis

1. Introduction

More than 40 years have passed since the Ziegler–Natta catalytic system was discovered. During this time a great deal of efforts has been made to improve the catalyst performance, such as activity and stereoselectivity. The catalytic systems used at present have reached an amazing performance, which allow designing versatile, clean and economical poly-

merisation processes [2,3]. Briefly, with regard to the Ziegler–Natta catalysis, in the so-called third and fourth generation catalysts, TiCl₄ is fixed on δ-MgCl₂. The active sites are considered to be titanium species obtained by treating the supported TiCl₄ with AlEt₃ (TEA), that acts as reducing and alkylating agent of titanium. The use of both internal and external electron donors (Lewis base) are necessary in order to attain stereoselective propene polymerisation.

Although many reports have been published on the nature of the active species, only few studies were addressed to the surface characterisation of the catalysts

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[4–15]. Surface science techniques offer many opportunities in catalytic research since a variety of modern spectroscopies allow to study the surface structure and composition and to identify stable surface species. A frequent and adverse criticism to the use of these techniques to study catalytic systems is that the ultrahigh vacuum (UHV) conditions are too far from reality. Catalytic reactions are typically carried out at atmospheric (or higher) pressures. Moreover, active catalysts are usually complex systems whose modelling with thin film or single crystal surfaces may be not straightforward because structural and compositional defects can deeply influence the reactivity of real surfaces.

Recently, Somorjai and co-workers [6–9,11,12] have synthesised procatalysts made of TiCl_4 supported on MgCl_2/Au under UHV conditions. The procatalysts so prepared have been characterised by means of several surface techniques. In 1995, the same research group prepared a model catalyst by depositing TiCl_4 from gas phase on MgCl_2 . This system, once activated with AlEt_3 , resulted active in ethene polymerisation. Afterwards, Somorjai and co-workers studied the activation of MgCl_2 by irradiation with low energy electron beam (1 keV) and claimed that this support is catalytically equivalent to that obtained by chemical or mechanical activation. The use of UHV techniques working in the Ziegler–Natta catalysts characterisation has been reported since 1981 by Furuta [4], who investigated a catalyst obtained by co-milling MgCl_2 and TiCl_3 by means of XP spectroscopy and suggested a correlation between the titanium electronic parameters and the activity. This study anticipated the results reported by Gassman and Callstrom [5] concerning an XPS investigation on titanium and zirconium metallocenic catalyst.

In this paper, we propose an alternative route with the aim to take advantage of the potentialities offered by the surface science techniques (clean surface and controlled conditions) and, at the same time, using a catalyst as similar as possible to the one used in normal polymerisation process. Briefly, here we report, a preliminary study carried out on a three component Ziegler–Natta catalytic system: $\text{MgCl}_2/\text{TiCl}_4/\text{AlEt}_3$. Our aim is to understand (1) the activation process of the magnesium chloride support; (2) the interaction between the magnesium chloride support and TiCl_4 ; (3) the chemical structure of the titanium active centres formed by treatment of the procatalyst with the

co-catalyst, aluminium triethyl (TEA); (4) which Ti^{n+} species is active in ethene and propene polymerisations. These experiments were performed in conditions as similar as possible, to the ones used for the laboratory synthesis and polymerisation [1].

The experiment consists of different steps: (1) preparation of $\delta\text{-MgCl}_2$ under strictly inert atmosphere as previously reported [1]; (2) activation of $\delta\text{-MgCl}_2$ in a UHV chamber by means of argon ion sputtering; (3) exposure to TiCl_4 vapours; (4) exposure to TEA vapours; (5) exposure of the obtained surface to ethene and propene vapours. The surface composition was checked during the experimental steps by means of XPS.

2. Experimental

2.1. Reagents and instruments

Metallic magnesium (powder), 1-chlorobutane, hexane, heptane, and titanium tetrachloride were Aldrich Chemicals reagents. Propene, ethene and TEA were supplied by Montell Italia S.p.A., Ferrara (Italy).

$\delta\text{-MgCl}_2$ was synthesised by reacting magnesium metallic powder with 1-chlorobutane. The detailed conditions for the preparation are described elsewhere [1]. The reagents were purified by standard methods in order to obtain reproducible results. The solvents were purified by refluxing over Na/K alloy for 8 h. Oxygen and water were removed from propene and ethene by means of molecular sieves 4A and BASF catalyst R 3–11. Titanium tetrachloride and TEA were used without further purification.

The XRD patterns were scanned by transmission technique, using a GD-2000 diffractometer (Ital Structures, Riva Del Garda, Italy) operating in the Seemann–Bohlin geometry and equipped with a quartz-curved crystal monochromator of the Johansson-type aligned on the primary beam. The patterns were recorded by using the $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). The diffraction measurements were carried out under a strictly inert atmosphere on samples prepared in a Braun MB-150 I/II dry-box.

The catalyst preparation was carried out in a UHV system equipped with XPS, AES, ISS as well as a reaction chamber. The reaction chamber configuration allows working both in static and in flow (dynamic)

condition. In this last case, a turbomolecular pump can maintain the background pressure below 5×10^{-6} Pa. A quadruple mass spectrometer (QMS-High Vacuum) is installed in the reaction chamber. XPS spectra were recorded by a Perkin-Elmer PHI 5600 ci spectrometer with a monochromatic Al K α source operating at 350 W. The base pressure in the XPS chamber was typically about 10^{-6} Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f_{7/2} line at 84.0 eV with respect to the Fermi level. Extended spectra (survey) were collected between 0 and 1350 eV (187.85 eV pass energy, 0.4 eV per step, 0.05 s per step). Detailed spectra were recorded for the following regions: C 1s, O 1s, Mg 2s, Mg 2p, Cl 2p, Ti 2p, Al 2p (23.5 eV pass energy, 0.1 eV per step, 0.1 s per step). The standard deviation in the BE values of the XPS lines is 0.1 eV. The atomic composition, after a Shirley type background subtraction [16], was evaluated by using the PHI sensitivity factors [17]. To take into consideration charging problems the C 1s peak at 285 eV was considered and the BE differences between the different peaks were evaluated. The composition of the catalyst surface and the atomic ratios reported throughout the text and in the tables are always expressed as atomic percentage and calculated by dividing the peak area by the corresponding sensitivity factor. The sensitivity factors are obtained from calculated photo-ionisation cross-sections [17].

A special steel-transfer tube equipped with a gate valve allowed transferring the sample from the dry-box to the reaction chamber and vice versa under strictly inert atmosphere or vacuum.

The polymerisation tests were carried out in a 1 l steel reactor charged with propene or ethene.

The FT-IR spectra were recorded by a Bruker IFS66 spectrometer on CsI pellets ($3500\text{--}400\text{ cm}^{-1}$, resolution 2 cm^{-1}).

2.2. Procedure

The sample of $\delta\text{-MgCl}_2$ (200 mg), was prepared in dry-box by pressing the powder at 2.5×10^8 Pa for 2 min and fixing the obtained pellet to the sample holder. The transfer to the UHV system was carried out by mean of the stainless steel transfer-tube kept in inert atmosphere and equipped with a gate valve. Ion-sputtering with argon (3 keV) activated at room temperature the sample, whereas the elemental

surface composition was monitored by XPS. The activated $\delta\text{-MgCl}_2$ was exposed to TiCl_4 vapours in the preparation chamber ($P = 1 \times 10^{-2}$ Pa, $T = 303$ K) and the surface composition was monitored (XPS) as a function of the exposure time. The obtained precatalyst was activated for a long time, typically at least 40 h, by exposure to TEA vapours at 333 K. The vapours composition was always monitored by means of QMS-High Vacuum. The catalyst obtained in the UHV system was transferred to the reactor by means of the transfer-tube kept at 10^{-5} Pa. Polymerisation of either ethene or propene was carried out in a steel reactor charged at 6×10^5 Pa of monomer at 30°C . The polymerisation lasted from 60 to 80 h. After the reaction (after each polymerisation test) the sample was transferred with the transfer-tube to the UHV system and analysed by means of XPS. In order to study the influence of the presence of TEA in high concentration on the precatalyst surface composition, we treated in dry-box at room temperature a sample of $\text{MgCl}_2/\text{TiCl}_4$, obtained in the UHV system, with a solution of TEA in hexane (0.7859 M). The surface composition was determined by means of XPS. Propene and ethene polymerisation tests were then performed as above reported and the surface was analysed (XPS, FT-IR) in order to detect the polymer presence.

3. Results and discussion

3.1. Synthesis and activation of the MgCl_2 surface and exposure to TiCl_4

In Table 1, the position and the FWHMs (only for Cl 2p) of the XPS peaks (Mg 2s, Mg 2p, and Cl 2p) are reported as a function of the sputtering time. They well agree with the expected values for MgCl_2 as well as Mg/Cl atomic ratios (Table 2).

Table 1
BE and FWHM values relative to Cl 2p, Mg 2s, Mg 2p and O 1s XPS peaks during the argon-sputtering activation

Argon-sputtering (min)	Cl 2p BE (FWHM)	Mg 2s BE	Mg 2p BE
0	199.3 (3.8)	90.1	51.3
10	199.5 (3.2)	90.2	51.3
25	199.6 (3.5)	90.2	51.3
35	199.2 (3.4)	90.2	51.2
55	199.2 (3.5)	90.1	51.1

Table 2
Evolution of Mg/Cl atomic ratio as sputtering time function on δ -MgCl₂

Sputtering time (min)	Mg/Cl
0	32/68
5	36/64
10	39/61
15	42/58
35	44/56

Preliminary experiments have shown that TiCl₄ does not fix on the δ -MgCl₂ surface as prepared. While Somorjai and co-workers [6] activated the MgCl₂ surface by means of a strongly reductive electron beam, we devised to “activate” the MgCl₂ surface by Argon-sputtering. In Table 2, the Mg/Cl atomic ratio values (determined by means of XPS), are shown as function of the sputtering time. It can be observed that the chlorine content decreases on increasing the sputtering time. This behaviour suggests that the argon-ion sputtering, in our conditions, activates the MgCl₂ surface by creation of chlorine

vacancies, so that the surface reactivity is greatly increased.

It is important to report that the BE of Mg 2s (90.1 eV) and Mg 2p (51.3 eV) change very slightly in the course of this treatment. Moreover, we want to underline that, unlike the case of activation by means of electron beam [7], we did not detect the formation of metallic magnesium (Mg 2p BE = 49.4 eV).

The activated support was then exposed to TiCl₄ vapours. The titanium content fixed on the surface is shown in Tables 3 and 4, as a function of the exposure time for the δ -MgCl₂ samples sputtered for 35 and 55 min, respectively. A careful inspection of these data shows that prolonged sputtering times allow to prepare procatalysts (δ -MgCl₂/TiCl₄) with higher titanium content and that the titanium atomic percentage increases with the exposure time reaching a plateau value after more than 3 h (Tables 3 and 4).

The plateau composition is Mg₄₁Cl₅₅Ti₄ if the support is sputtered for 35 min and Mg₅₃Cl₄₀Ti₇ when the support is sputtered for 55 min. These results indicate that the Mg coordinative unsaturations are responsible for the chemisorption of TiCl₄.

Table 3
Evolution of XPS atomic composition of the MgCl₂/TiCl₄ system as function of TiCl₄ exposure time^a

TiCl ₄ exposure (min)	Cl (%)	Mg (%)	Ti (%)	Cl/Mg	Cl/(Ti + Mg)	Ti/Mg	Ti/Cl
0	56.0	44.0	0	1.27	1.27	0	0
2	55.0	44.6	0.4	1.23	1.22	0.009	0.007
7	55.0	44.0	1.0	1.25	1.22	0.023	0.018
30	55.0	43.5	1.5	1.26	1.22	0.034	0.027
60	54.5	43.5	2.0	1.25	1.20	0.046	0.037
90	54.8	42.5	2.7	1.29	1.21	0.063	0.049
120	53.8	42.8	3.4	1.26	1.16	0.079	0.063
150	54.9	41.4	3.7	1.33	1.22	0.089	0.067
180	55.0	41.4	3.6	1.33	1.22	0.087	0.065

^a δ -MgCl₂ sputtered for 35 min.

Table 4
Evolution of XPS atomic composition of the MgCl₂/TiCl₄ system as function of TiCl₄ exposure time^a

TiCl ₄ exposure (min)	Cl (%)	Mg (%)	Ti (%)	Cl/Mg	Cl/(Ti + Mg)	Ti/Mg	Ti/Cl
0	49.0	51.0	0	0.96	0.96	0	0
90	39.9	55.5	4.6	0.72	0.66	0.083	0.115
120	41.0	53.4	5.9	0.78	0.69	0.110	0.164
300	40.2	52.9	6.9	0.76	0.67	0.130	0.172
420	40.9	53.1	6.4	0.77	0.69	0.120	0.156
540	42.3	50.7	6.9	0.83	0.73	0.136	0.163

^a δ -MgCl₂ sputtered for 55 min.

It is important to observe that the same treatment was carried out on a sample of α - MgCl_2 , the ordered cubic form modifications of MgCl_2 . In order to show the large difference in the structural order between the α - and δ - MgCl_2 support, the corresponding XRD spectra are reported in Fig. 1. The broad bands typical of δ - MgCl_2 are due to its structural disorder [1].

In fact, even though the α - MgCl_2 was argon-sputtered until the Mg/Cl atomic was 45/55, the sputtered support was unable to fix titanium tetrachloride, even after a prolonged (3 h) exposure.

These results allow us to conclude that (1) the support for procatalyst preparation must be structurally disordered, as δ - MgCl_2 and (2) the surface needs to be activated in order to fix TiCl_4 . The activation mainly consists in the creation of coordinatively unsaturated magnesium atoms.

The Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks positions (Figs. 2 and 3) observed after exposure to TiCl_4 (458.9 and 464.5 eV, respectively), are in agreement with the literature values for Ti in TiCl_4 supported on activated MgCl_2 [10]. Contributions due to reduced species (TiCl_3 at 457.8 eV [10] or TiCl_2 at 456.2 eV [9]) have not been detected. The Mg 2s, Mg 2p, and Cl 2p peaks positions and shape do not change after exposure to TiCl_4 . As expected, the Ti/Cl and Ti/Mg atomic ratios increase (Table 3) with the exposure time. A more careful analysis of the XPS atomic ratios evidences that the chlorine content is not enough to satisfy the Mg and Ti co-ordination and the Cl/(Ti + Mg) atomic ratio does not increase as expected. This chlorine impoverishment is particularly evident in the system sputtered for 55 min (Table 4). The intensity of the O 1s peak increase (Fig. 4) after exposure to TiCl_4 vapours. This results as well as the chlorine shortage suggests the formation of oxygenated species, such as $\text{MgCl}(\text{O})_x$ or $\text{MgCl}(\text{OH})_x$.

3.2. $\text{MgCl}_2/\text{TiCl}_4$ procatalyst activation and exposure to the monomers

The $\text{MgCl}_2/\text{TiCl}_4$ procatalyst was activated by exposure to TEA vapours. The Cl 2p XPS position and shape do not change after exposure to TEA vapours as well as the surface composition. As a matter of fact, the XPS analysis shows only the presence of traces of Al even after prolonged exposure (Fig. 4). The very low Al 2p signal can be ascribed to the high

volatility of Al-containing compounds that causes the lack of Al on the surface, as previously described [7].

The treatment with TEA caused a shift towards higher BE values (458.9 \rightarrow 459.4 eV) of the Ti 2p peaks for the catalyst supported on δ - MgCl_2 sputtered for 35 min (see Fig. 2) and moreover, the peaks of both samples with the support activated by sputtering 35 and 55 min (see Fig. 3) appear narrowed after the TEA treatment. These results are unexpected, especially considering the strong capability of TEA to reduce the MgCl_2 -supported TiCl_4 [2].

Nevertheless, a different behaviour has been observed by Gasmann and Callstrom [5] and Atiqullah et al. [18], respectively for unbonded metallocene and for heterogenised metallocene both activated by methylalumoxane (MAO). MAO is the most employed and effective co-catalyst in metallocenic catalysis [19]. In particular, the treatment of zirconocene with MAO causes a shift toward higher BE values of the metal XPS peaks. According to Gasmann and Callstrom [5] and Atiqullah et al. [18] this shift indicates that the catalytic species in the mixture is electron-deficient compared to the corresponding metallocene before the MAO-activation. This phenomenon has also been observed by other authors by means of different techniques [20]. Moreover, Gasmann and Callstrom [5] and Atiqullah et al. [18] also observed that the alkylation of titanium chloride by MAO did not affect the BE of the metallic peak centre (the alkylated species are usually characterised by lower BE than the full-chlorinated, or oxygenated species). Atiqullah et al. postulates the formation of species in which the metal centre is trapped in a multi-coordinated crown of MAO. Therefore, these electron-deficient catalytic species are suggested to be responsible of the BE increase. Finally, they observed that the BE decreased slightly when the catalytic system was exposed to ethene. This means that the catalyst surface changed in the course of the polymerisation [12]. In particular the Ti 2p peak position shifted towards lower BE when the catalyst was treated with the olefins (459.4 \rightarrow 458.9 eV).

On the bases of these results we propose an interpretation for the mechanism of activation, in our experimental conditions. In order to explain the shift of the Ti 2p peaks towards higher BE, observed in our case, the traces of H_2O present in the chamber must be considered. A reaction between AlEt_3 and small

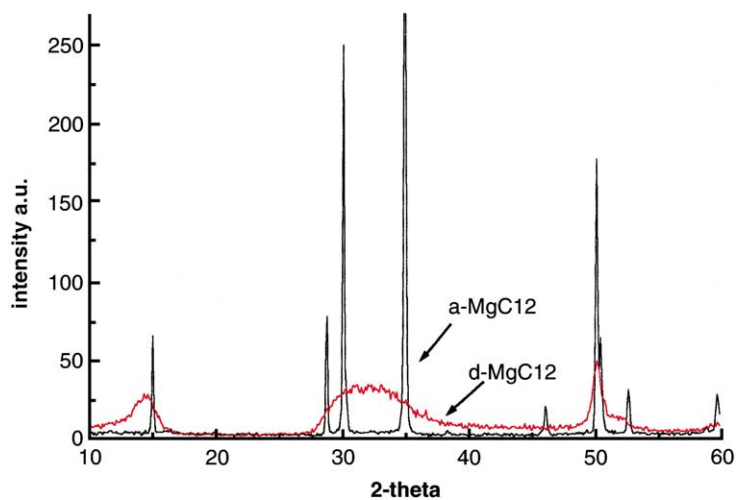


Fig. 1. XRD spectra of α -MgCl₂ and δ -MgCl₂.

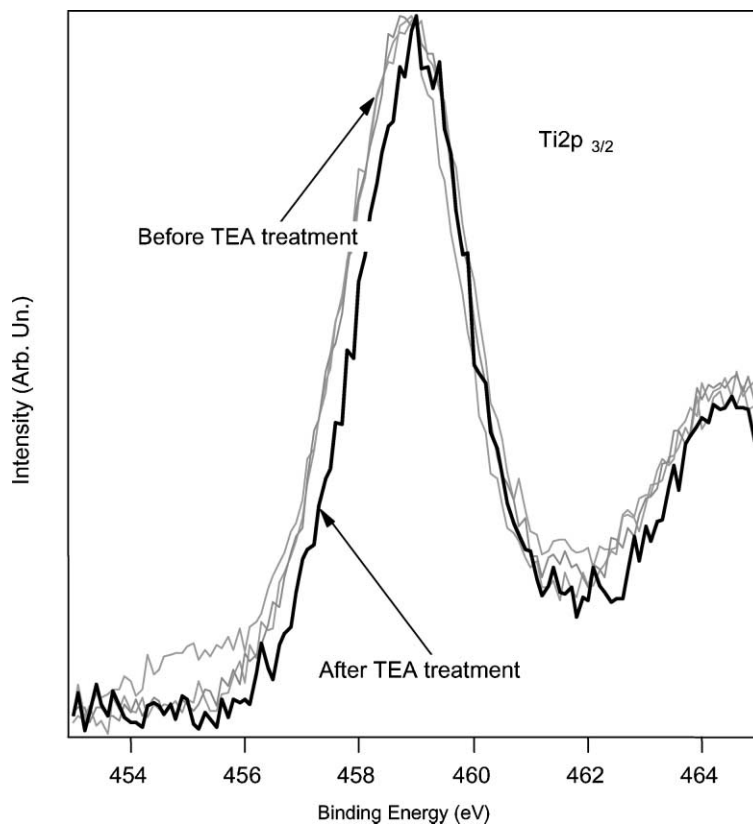


Fig. 2. Ti 2p XPS spectra of TiCl₄ on δ -MgCl₂ support (activated with 35 min of sputtering) obtained after the TEA treatments. The reported curves are the average of several peaks XPS acquisitions.

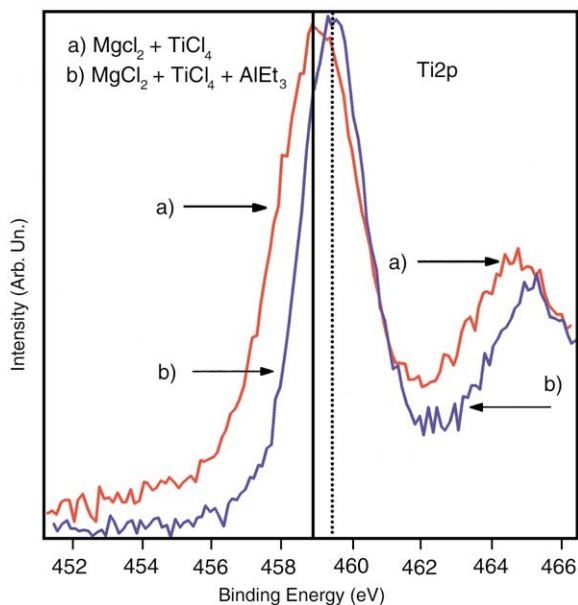


Fig. 3. Ti 2p XPS spectra of the δ -MgCl₂ support (activated with 55 min of sputtering) obtained after the treatments described in Section 2 (activation by exposure to TEA vapours at 333 K for 40 h).

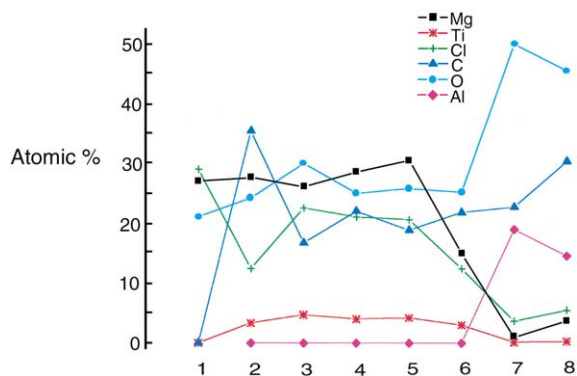


Fig. 4. Surface atomic composition observed (XPS) as a function of the following treatment. (1) δ -MgCl₂ activated with 55 min of argon-sputtering; (2) MgCl₂/TiCl₄ (activated δ -MgCl₂ + 5.5 h exposure to TiCl₄ vapours); (3) MgCl₂/TiCl₄ (activated δ -MgCl₂ + 9 h exposure to TiCl₄ vapours); (4) MgCl₂/TiCl₄/TEA (δ -MgCl₂/TiCl₄ + 50 h exposure to TEA vapours); (5) MgCl₂/TiCl₄/TEA (δ -MgCl₂/TiCl₄ + 96 h exposure to TEA vapours); (6) MgCl₂/TiCl₄/TEA/ethene (δ -MgCl₂/TiCl₄/TEA + 84 h exposure to ethene); (7) MgCl₂/TiCl₄/TEA/ethene/TEA solution (δ -MgCl₂/TiCl₄/TEA₃/ethene + 1 h exposure to TEA solution); (8) MgCl₂/TiCl₄/TEA/ethene/TEA solution/ethene (δ -MgCl₂/TiCl₄/TEA/ethene/TEA solution + 90 h exposure to ethene).

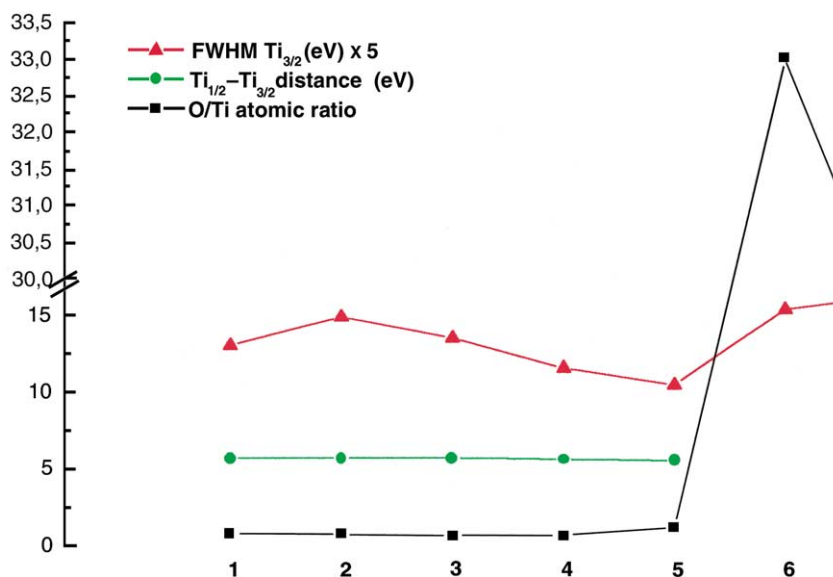


Fig. 5. O/Ti atomic ratio, FWHM of Ti 2p_{3/2} and Ti 2p_{1/2}-Ti 2p_{3/2} distance calculated as a function of described treatment on sample with support, δ -MgCl₂ activated 55 min by argon-sputtering. (1) δ -MgCl₂ activated with 55 min of argon-sputtering; (2) MgCl₂/TiCl₄ (activated δ -MgCl₂ + 5.5 h exposure to TiCl₄ vapours); (3) MgCl₂/TiCl₄ (activated δ -MgCl₂ + 9 h exposure to TiCl₄ vapours); (4) MgCl₂/TiCl₄/TEA (δ -MgCl₂/TiCl₄ + 50 h exposure to TEA vapours); (5) MgCl₂/TiCl₄/TEA (δ -MgCl₂/TiCl₄ + 96 h exposure to TEA vapours); (6) MgCl₂/TiCl₄/TEA/ethene (δ -MgCl₂/TiCl₄/TEA + 84 h exposure to ethene).

amounts of H₂O may lead, in controlled conditions, to the formation of Al alkoxy-species similar to those obtained by reaction of AlMe₃ and H₂O leading to species which can mime the behaviour of MAO [21], namely able to form cage structures which encapsulate the titanium species. In this situation the Ti species are characterised by higher BE values.

In Fig. 5, the data relative to the FWHM of Ti 2p_{3/2} are also reported.

The Mg and Cl XPS peak positions do not change after exposure to the monomer. The C 1s XPS peak position (285 eV) and FWHM (≈ 2 eV) are compatible with the presence of hydrocarbons and suggest the existence on the catalyst surface of the polymerisation reaction products. In Fig. 4, the surface composition is reported after each treatment. As one can observe the carbon content increases after exposure to the monomers (ethene and propene). The massive presence of carbon on the catalyst surface causes the attenuation of the other signals (Al, Mg, Ti, Cl; see Fig. 4).

The FWHM of the Ti 2p_{3/2} (shown in Fig. 5) and that of the C 1s peaks strongly decrease (from 2.6 to 1.8 eV and from 2.4 to 2.0 eV, respectively), suggesting a different chemical environment.

To investigate the effect of the catalyst activation with TEA in high concentration, we treated the procatalyst MgCl₂/TiCl₄ with a solution of TEA (0.8759 M in hexane, ageing time 1 h) and then, after evacuation to 10⁻⁸ Pa for 24 h, the XPS analysis was performed. The exposure to liquid TEA causes the increase of C, O and Al surface concentration (Fig. 4). This is probably due to the presence of oxygenated contaminants in the reaction chamber causing the formation of Al oxygenated compounds. This hypothesis is compatible with the Al 2p peak position (75.5 eV) that is characteristic of the Al–O bonds. The exposure method causes the formation of a thick contaminant layer on the sample and the Mg, Cl and Ti XPS signals are strongly attenuated. Nevertheless, no evidence of reduced titanium species was found.

The exposure to the monomers (propene or ethene) causes a further increase in the carbon content on the surface (Fig. 4). Although the conditions used for the polymerisation process are far from those normally used in the polyethene and polypropene production, we attempted to detect the presence of polymers on the surface using a more diagnostic technique (IR) for

carbonaceous species than XPS. The IR-spectra of the catalyst after exposure to the monomers show typical bands due to polypropene and polyethene. In particular, the sample exposed to propene presents bands centred at: 2950 cm⁻¹ (CH₂ asymmetric stretch); 2865 cm⁻¹ (CH₂ symmetric stretch); 1440 cm⁻¹ (CH₂ scissoring); 720 cm⁻¹ (CH₂ rock). Whereas the sample exposed to ethene shows the following bands: 2960 cm⁻¹ (CH₂ asymmetric stretch); 2860 cm⁻¹ (CH₂ symmetric stretch); 1440 cm⁻¹ (CH₂ scissoring); 1365 cm⁻¹; 1112 cm⁻¹, 835 cm⁻¹ (CH₂ bending/rock) [22]. The IR data thus indicate that the obtained catalyst may have some catalytic activity in ethene and propene polymerisation. It is important to point out that the amount of polymer detected was very small, because the active catalyst was confined on the surface of the MgCl₂ pellet and because the polymerisation conditions used were very far from those required to have a good catalytic activity.

We want to outline that we never detected the presence of titanium reduced species after TEA vapours treatment, but only changes in the Ti(IV) FWHM. The question concerning which oxidation state is active in the polymerisation process is still actual even though it interested the researches since 1950s [23–28]. The hypothesis that the Ti(IV) species are the active sites in the polymerisation process is not in disagreement with literature data. Indeed, recently reported X-ray absorption fine structure (EXAFS) experiments [29] as well as indications from industry [30,31] identify Ti(IV) as the dominant catalytic species.

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