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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/141783> since 2016-10-03T12:34:35Z

Published version:

DOI:10.1039/c2cy20559a

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UNIVERSITÀ DEGLI STUDI DI TORINO

This is an author version of the contribution published on:

Questa è la versione dell'autore dell'opera:

[Groppo et al., 3, Catalysis Science Technology, 2013, pagg 858--878]

The definitive version is available at:

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The potential of spectroscopic methods applied to heterogeneous catalysts for olefin polymerization

Elena Groppo,^{*a} Kalaivani Seenivasan^a and Caterina Barzan^a

Heterogeneous Ziegler-Natta and Phillips-type olefin polymerization catalysts have the monopoly of isotactic polypropylene production and a large share in the market of high density polyethylene, respectively. Their high industrial impact and the relatively mild conditions at which they work explain why both catalysts have been the subject of an intense research. The industrially adopted strategy to improve catalyst's formulation is still based on a trial-and-error procedure; however, a rational design of new and more efficient catalysts (which is the key to produce polyolefins having a specific architecture) necessarily implies to achieve a detailed understanding of the structure of the active sites at a molecular level. Herein, it is shown that spectroscopic methods have this potential, especially when several complementary techniques are adopted and coupled with theoretical calculations. This is valid for both Phillips-type and Ziegler-Natta catalysts, because most of the problems encountered in their characterization and understanding are common, although for decades they were not considered to be closely related. The main advantages and disadvantages of several spectroscopies in the investigation of both categories of catalysts are critically analyzed, by discussing many examples taken from the recent literature.

1. Introduction

Polyolefins are among the most common and versatile plastic materials, because they find application in many diverse fields, replacing more expensive natural and synthetic materials, as well as materials or processes that are associated with health and environmental risks. To mention only a few examples, High-density-Polyethylene (HDPE) has the unique portfolio in pipes production, about 20% of the materials used in the cars are polyolefins (which reduce the weight and, therefore, CO₂ emission), Polypropylene (PP) is the most used materials in the medical sector because it is clean, transparent, and does not contain impurities and finally, being light and cheap, polyolefins have become ubiquitous for packaging applications.

With the exception of Low-Density-Polyethylene (LDPE), which is obtained following a radical process, the majority of polyolefins are produced in a catalytic way. The last decades witnessed a remarkable growth of interest towards homogeneous (metallocene-based) catalysts, which allows a fine control of the polymer properties through a rational design of the active sites. However, at present their industrial applications are still focusing on niche markets. Most of the industrial catalysts for olefin polymerization are heterogeneous: besides the much lower cost, heterogeneous catalysts allow control of the morphology of the polymeric products as a replica of the catalyst morphology. Generally speaking, two main categories of heterogeneous catalysts for olefin polymerization can be identified: (a) the Phillips-type catalysts, where the active metal is chromium grafted on the surface of an amorphous support (porous silica);¹⁻³ and (b) the Ziegler-Natta catalysts, where the active metal is titanium (usually coming from a simple precursor of the type TiCl_x(OR)_{4-x}) supported on a crystalline, high surface area, anhydrous MgCl₂ support.⁴ For decades, these two types of catalysts were not considered to be closely related, mainly

because they find widely different applications. The Phillips-type catalysts are specific for the production of HDPE, a homopolymer with a nearly perfect linear structure. The Phillips HDPE presents a very broad molecular weight distribution ($M_w/M_n > 15 - 20$) that confers characteristic rheologic properties useful for specific application.² However, the Phillips catalysts (unless modified)³ show a very poor reactivity towards alpha-olefins, and therefore are not able to co-polymerize the ethylene monomer with higher 1-alkenes (e.g. 1-butene, 1-hexene, 1-octene) to give Linear-Low-Density-Poly(Ethylene) (LLDPE), a segment of polymeric material which is currently in rapid expansion. On the other side, the Ziegler-Natta catalysts have the monopoly of the production of isotactic polypropylene (iPP), and they also show a fairly good ability to insert 1-alkenes inside growing polyethylene chains.⁵

The high industrial impact of heterogeneous catalysts for olefin polymerization and the promise of an improved control of the polymer properties, easily explain why these catalysts have been the subject of an intense research. As a matter of fact, the micro-structure and the physical properties of polyolefins depend greatly on the polymerization catalyst used for their production. This is the reason why one of the traditional methods employed to get information on the catalyst structure is the investigation not of the catalyst itself, but of the polymer it produces and of its response to catalyst variables. Unfortunately, this approach is not sensitive enough to obtain a comprehensive description of the catalyst structure at a molecular level and, therefore, any attempt to tune the catalyst properties is necessarily based on a trial-and-error approach. This is especially true for Ziegler-Natta catalysts. Since the 1970s, four successive generations of Ziegler-Natta catalysts for the industrial production of iPP have evolved, differing mainly in the nature of the Lewis bases (such as esters, ethers, alkoxysilanes, and others) added as the third component to modify the catalytic activity of the binary TiCl₄/MgCl₂ mixtures. The exact role of the Lewis basis in constructing the active sites

was debated since the beginning and up to now there are no unequivocal models broadly accepted that can explain the details of the interaction between Lewis bases and the $\text{TiCl}_4/\text{MgCl}_2$ components.

Nonetheless, the detailed understanding of the structure of the active sites and of how they work is mandatory to rationally design new and more efficient catalysts, in order to get polyolefins having a specific architecture. The aim of this perspective review is to show that, although not easy, this goal is at least feasible. The herein proposed strategy involves the combination of several, highly sensitive, *spectroscopic techniques*. To the best of our knowledge, this contribution is the first one that tries to address both classes of catalysts using a unified approach. This methodology, which is mature for the Cr-based catalysts and still at the beginning for the Ziegler-Natta ones, could be potentially extended to other heterogeneous olefin polymerization and oligomerization catalysts. The achievement of a basic knowledge on the nature of the active sites, which is still absent notwithstanding several decades of scientific research, is of industrial and economic significance, because the active species dictate the behaviour of the catalyst in the olefin polymerization process.

2. Two different catalysts, but common questions, common problems, and a single methodology

2.1. Brief overview on the Phillips and Ziegler-Natta catalysts

2.1.1. The Phillips-type catalysts

The origin of the Phillips catalyst dates back to 1951, when J. P. Hogan and R. L. Banks at the Phillips Petroleum Company accidentally discovered that chromium oxide supported on silica can polymerize α -olefins.¹ The same catalyst is still used today, although modified and evolved, and it accounts for a large share of the world's HDPE supply, as well as some low-density polymers. The synthesis procedure of the standard Cr/SiO_2 catalyst is fairly simple.^{2,3,6} Initially, hydroxyl groups at the surface of amorphous silica react with a chromium precursor; this step, which is conducted at high temperature under oxidizing conditions, leads to chromate formation, and also to extensive dehydroxylation of the silica surface. The grafted Cr^{VI} species are then reduced by ethylene (industrial process)² or by CO (model laboratory process), yielding anchored Cr^{II} species,⁷ which are the species active in ethylene polymerization.

The chemical composition of Cr/SiO_2 is apparently very simple, and for this reason the Phillips catalyst has served for many years as model system for basic spectroscopic investigations.⁶ However, the structure of the active sites at the molecular level is far from being understood and for this reason the Phillips catalyst continues to be one of the most studied and controversial system. Spectroscopic methods have played the major role in defining the structure of the active Cr sites, as it will be summarized in the following chapters. Currently, there is broad agreement that the active sites are isolated Cr^{II} species, having a quite heterogeneous structure (as schematically shown in Fig. 1), as a consequence of the high heterogeneity of the amorphous silica support. This heterogeneity was claimed to be the origin of the Phillips's ability to make a HDPE with a very broad molecular weight (MW) distribution. It was shown that the

relative abundance of each category of Cr^{II} sites can be tuned as a function of the activation conditions, which control the hydroxylation degree of the silica surface.⁸ Moreover, recent spectroscopic results suggest that the key for understanding the high catalytic activity of Cr^{II} sites in absence of any activator relies on their high structural flexibility in presence of adsorbates (above all ethylene).⁹

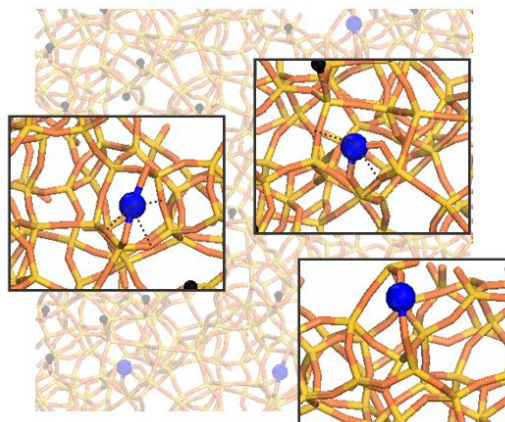


Fig. 1 Representation of the Cr/SiO_2 surface obtained by grafting Cr^{II} ions on a partially dehydroxylated silica surface (red, yellow, black and blue represent O, Si, H and Cr atoms, respectively). Three different Cr^{II} ions characterized by a different coordinative unsaturation are shown.

2.1.2. Classical Ziegler-Natta catalysts

The discovery of the Ziegler-Natta catalysts is almost contemporaneous with that of the Phillips catalyst. At the end of 1953 K. Ziegler (at the Max Planck Institute in Mulheim, Germany) was able to polymerize ethylene gas in mild conditions, obtaining a high molecular weight plastic. The catalyst employed in the first experiments was a mixture of aluminum triethyl and TiCl_4 , and the first patent was confined to ethylene polymerization.^{10,11} A few months later, the group of G. Natta at the Milan polytechnique succeeded to polymerize propene using Ziegler's catalyst, and soon realized that the obtained polypropylene was composed by several stereoisomers having different physical properties.¹² These first generation catalysts suffered, however, of a low activity and of a poor selectivity in propene polymerization. A great evolution took place in the mid of 1970's after the discovery of crystalline MgCl_2 as a support for TiCl_4 .^{4,13} The MgCl_2 -supported catalysts brought about a remarkable simplification of polymerization processes, and led to revolutionary developments for the commercial production of linear PE and isotactic PP. The discovery that addition of a Lewis base (or electron donor, e.g. an organic ester, ether, alcohol, or amine) to the $\text{TiCl}_4/\text{MgCl}_2$ binary mixture increased the isotactic content of polypropylene by greatly diminishing the yield of the atactic one was the second major breakthrough in this field.⁴ Nowadays, the majority of heterogeneous Ziegler-Natta catalysts for olefin polymerization are $\text{TiCl}_4/\text{MgCl}_2$ /Lewis base ternary mixtures, which become active after addition of the aluminum-alkyl co-catalyst.

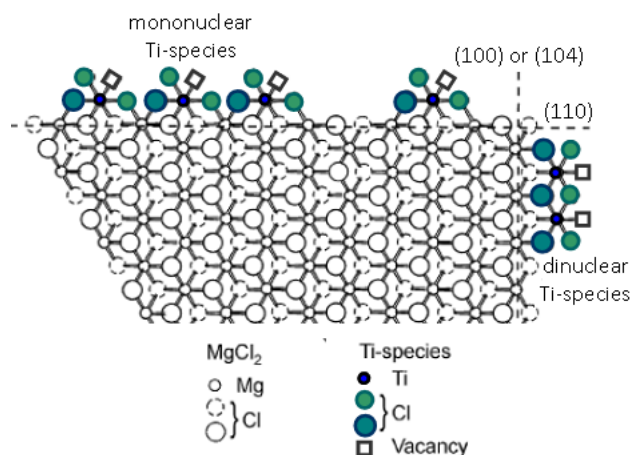


Fig. 2 Model showing different possible Ti(III)-chloride species (having different steric environment) on the two favourite MgCl_2 lateral cuts, according to the first molecular mechanics calculations. Adapted from Ref. ¹⁴

Opposite to the Phillips catalyst, spectroscopic methods played up to now only a marginal role in the direct characterization of Ziegler-Natta catalysts. The reason is mainly due to the fact that two alternative methods, which are precluded for the Phillips-type catalysts, have been traditionally used for the characterization of the active sites of Ziegler-Natta catalysts. The first one is the determination of the fingerprint of the active sites from the analysis of the microstructure of the polymer product by ^{13}C NMR.⁵ This is an indirect method that has the advantage of picking selectively the information on the active sites on which the polymer is formed. However, even the most advanced NMR instruments and techniques have not the sufficient sensitivity to obtain a description of the active sites at a molecular level.

The second characterization tool traditionally used to investigate the structure of heterogeneous Ziegler-Natta catalysts is the application of computational methods based on crystal models.¹⁵⁻¹⁸ Since the early 1970s, molecular mechanics calculations suggested models where TiCl_4 interacts directly with well defined MgCl_2 surfaces. According to the pioneering work of Corradini et al.,¹⁹ MgCl_2 shows two favourite exposed faces coordinatively unsaturated, namely (104) (called (100) in the old literature) and (110). The Mg sites at the exposed (110) face are 4-coordinated, and hence they are more acidic (in Lewis terms) than 5-coordinated Mg sites at the (104) face, and 6-coordinated sites in the bulk (see Fig. 2). When TiCl_4 interacts with the (104) faces of MgCl_2 the formed dinuclear Ti_2Cl_8 precursor species would be stereo-selective in propene polymerization; whereas non stereo-selective mononuclear precursor species would be formed on the (110) faces (see Fig. 2). According to this hypothesis, the Lewis bases can have, at most, an influence in the distribution of TiCl_4 on the support. In particular, the Lewis base could shield the (110) termination of MgCl_2 , thus precluding formation of non stereo-selective catalytic sites.¹⁹ However, this interpretation, accepted for a long time, does not survive to the calculations performed with modern quantum-mechanical methods. In particular, periodic DFT calculations suggested that TiCl_4 is not chemisorbed at all (or only very weakly coordinated) to the previously discussed MgCl_2 faces.^{15,16,20-22} Therefore, the question on the role of the electron donors and on the structure of

the active sites is still open.

2.2. Common problems

Although traditionally the Phillips-type and Ziegler-Natta catalysts have been considered by many scientists and technologists as belonging in two separate fields, most of the problems encountered in their characterization and understanding are common to both of them. Among the main problems that have to be overcome when trying to define the structure of these catalysts at a molecular level, we mention: i) the heterogeneity of sites; ii) the high dilution of the really active centres; iii) the high air sensitivity; and iv) the high speed of the polymerization reaction.

Heterogeneity of sites is a common problem in the characterization of heterogeneous catalysts and also the main difference with respect to the homogeneous counterparts that, containing only a single active site for which the ligand sphere can be properly tailored, provide a much finer control over the final polymer product. The first source of heterogeneity is the support. Heterogeneous catalysts for olefin polymerization intrinsically have a multi-site nature because of the heterogeneity of the support. They consist of many types of surface sites, difficult to be characterized at a molecular level, which would be responsible of the production of polymers having different properties (e.g. different distribution of molecular weight). This is the situation of the Phillips-type catalysts that, although apparently simple in chemical composition, contain a multitude of chromium sites having a slightly different structure and producing PE chains having different molecular weights.³ Ziegler-Natta catalysts are even more complex because, beside the multi-site nature conferred by the support, they are constituted by many components, each one responsible of a specific function, and often interacting together. Nevertheless, even starting from an intrinsic heterogeneity, a very good stereo-selectivity was obtained by a continuous controlled increase of the complexity of the active sites, following a design which renders the difference with homogeneous polymerization catalysts smaller than would have been anticipated.

On top of the heterogeneity of the metal sites, these catalysts are usually highly diluted (Cr loading around 0.5-1.0 wt% in the Phillips catalyst, and Ti loading around 1.0-2.0 wt% in the Ziegler-Natta catalysts), and very often only a small fraction of the sites (a few percent of the total) are *really* active in olefin polymerization. In addition, both Phillips and Ziegler-Natta catalysts are extremely air sensitive. Taken together, these two problems constitute a great challenge for characterization methods because, whatever are the techniques used for the definition of the active sites, they should be very sensitive, able to discriminate between active and spectator species and adaptable to work in controlled atmosphere. In the following sections it will be shown that the overall set of experimental tools available has progressed enormously in the last years, allowing the investigation of very diluted systems in controlled conditions. For this reason, the achievement of a comprehensive picture on the properties of the active sites seems realistic.

Finally, another problem commonly encountered when investigating heterogeneous catalysts for olefin polymerization is the high rate of the polymerization reaction that makes difficult any spectroscopic investigation of the initial steps. This is

particularly crucial for the Phillips catalysts, as it will be discussed in the following; but it could be of high interest for Ziegler-Natta catalysts as well, whenever the question of olefin insertion in the active site is raised and stereo-selectivity issues are addressed. Nevertheless, the experimental work is facilitated by the fact that olefin polymerization reaction is usually conducted in mild conditions, hence allowing the investigation of the catalyst surface in conditions close to that of the industrial process.

2.3. A common strategy to address common questions

2.3.1. Which is the structure of the active sites?

The first, fundamental, question common to both categories of the catalysts investigated herein is the structure of the active sites. Even when the catalyst composition is very simple, the local structure of the active sites at a molecular level is difficult to be determined in details, as a consequence of the problems discussed above (heterogeneity, high dilution and air sensitivity). Understanding the relationship existing between structure of the active sites and their activity and selectivity is the first step towards a rational tuning of the catalyst properties in view of the production of polymers having specific properties.

It will be shown in the following that the synergic use of many spectroscopic techniques allowed to improve enormously the knowledge on the structure of the active sites for the Phillips catalysts, although a few open questions are still unanswered. In contrast, the level of knowledge of the active sites for traditional Ziegler-Natta catalysts is still quite low. Very recently, a few papers reported on the application of complementary spectroscopic techniques to the characterization of Ziegler-Natta catalysts prepared following a "direct titaniation" method,²³⁻²⁶ that is starting from different MgCl_2 adducts, after reaction with the active Ti phase without first removing the donor ligand. This synthesis method allows the systematic characterization of the precursors (i.e. complexes of TiCl_4 and MgCl_2 with donor ligands), of the pro-catalysts (obtained by reacting together the Ti and Mg precursors) and, in very few cases, of the final catalysts obtained after interaction with the aluminum alkyl activator. In our opinion this is the most promising approach to get insights into the structure of the active sites in Ziegler-Natta catalysts.

2.3.2. Which is the polymerization mechanism?

An opposite situation is observed for what concerns the understanding of the polymerization mechanism, which is the second major question to face when dealing with polymerization catalysts. The polymerization mechanism (both initiation and propagation steps) on Ziegler-Natta catalysts is well known, whereas many doubts remain on the Phillips catalysts.

For Ziegler-Natta catalysts, the accepted mechanism for the polymer chain growth reaction (propagation step) is based on that proposed by Cossee and Arlman in 1964 for the heterogeneous TiCl_3 based catalytic systems.²⁷ This mechanism is monometallic and the active centre is a transition metal-carbon bond. In the seminal work of Arlman,²⁸ it was claimed that the active catalytic centre (the first Ti-C bond) is formed through interaction of the surface Ti sites with the aluminum-alkyl activator. The chain growth mechanism basically occurs in two steps: i) olefin coordination to a vacant site; ii) olefin insertion into the metal-

growing chain bond through a *cis*-opening of the olefin double bond. Green, Rooney and Brookhart slightly modified this mechanism, introducing an α -agostic interaction which would facilitate the insertion reaction.^{29,30} At the end of the chain growth step the growing chain migrates to the coordination position previously occupied by the monomer (chain migratory mechanism).

The main open question remains the origin of stereo-selectivity. For well-defined homogeneous catalysts having an octahedral geometry around the active metal atom theoretical calculations showed that the stereo-selectivity is connected to the chiral orientation of the growing chain, which is dictated in turn by the chirality of the active site.¹⁴ However, extension of the models valid for homogeneous catalysts to the traditional heterogeneous Ziegler-Natta catalysts is only hypothetical, due to the limited experimental characterization of the active species in the latter case.

In contrast, no activators are used for the Phillips catalyst, and therefore the question on the initiation step of the polymerization reaction arises. It will be shown in the following (see Section 4.2.1) that recent progress in discerning the initiation mechanism of ethylene polymerization on the Phillips catalyst have been achieved through application of time- and temperature-resolved spectroscopic techniques, which allowed the detection of reaction intermediates having a metallacyclic nature.³¹ Nevertheless, many questions remain on the chain growth mechanism, although very recently McGuinness et al.³² provided strong support for a Cossee-Arlmann mechanism.

3. Surface science methods applied to planar model catalysts

Ultrahigh vacuum (UHV) spectroscopic techniques are potentially powerful tools for a microscopic characterization of catalysts in general, because they provide direct information on the atoms and molecules on the surface. However, application of UHV techniques to industrial catalysts are limited by the fact that the active phase is usually hidden inside a porous high surface area support (e.g., silica), and cannot be reached by surface spectroscopies (e.g., for XPS the surface sensitivity is restricted by the typical mean photoelectron escape depth to about 20 Å). Moreover, the catalyst supports are in general non-conductive, and hence the sample will charge when applying electron or ion-releasing techniques such as XPS, SIMS, or ion scattering. This is the reason why surface science studies on polymerization catalysts are rather scarce if compared with other catalytic systems. Only a few studies have been performed on model Ziegler-Natta catalysts, and even less on model Phillips catalysts.

3.1. Planar models for Ziegler-Natta catalysts

The pioneering works in the field of model Ziegler-Natta catalysts belong to the group of Somorjai and co-workers³³⁻⁴¹ who established an experimental route to prepare model Ziegler-Natta catalysts, consisting of an epitaxially grown MgCl_2 film onto which TiCl_4 was anchored as the active component. These model catalysts allowed to overcome the charging problem characterizing the real catalysts and thus to apply the modern surface science techniques (such as XPS, TPD, AES and ISS) to investigate each step of the preparation and activation procedure,

up to the polymerization reaction. More recently, Hajo Freund and co-workers successfully applied also EPR technique to characterize similar model systems.⁴²⁻⁴⁴

Epitaxial MgCl_2 films were grown on a large variety of clean metal surfaces, such as polycrystalline Au, Pd(111), Pd(100), and others (step i) in Fig. 3a), through thermal evaporation of molecular MgCl_2 under UHV conditions. Since the beginning, it was shown that surface defects in the MgCl_2 film are crucial to bind the TiCl_4 precursor (step ii) in Fig. 3a).^{33,42,45,46} It was also found that chlorine ions have a high mobility in the MgCl_2 structure and can rapidly diffuse to the surface to correct any defect, such as uncoordinated Mg surface atom. This observation is important to understand, at a molecular level, the role of MgCl_2 as a support for TiCl_4 . Indeed, the dynamic nature of the chemistry at the MgCl_2 surface is fundamental in determining the delicate equilibrium between the chemisorption of TiCl_4 and different electron donors used for the synthesis of the real catalysts. TiCl_4 was successively anchored to the defective MgCl_2 surfaces (step iii) in Fig. 3a) by following different methods, among which the vapour deposition under electron bombardment was the most employed. The amount of grafted TiCl_4 was estimated as corresponding roughly to 1-2 wt% of Ti, which is close to that found in actual ball-milled catalysts. Somorjai and co-workers^{33,37,47-49} showed by XPS measurements that Ti exists on the surface mainly as Ti^{2+} and Ti^{4+} , whereas Ti^{3+} species were detectable in lower amount, depending on the preparation conditions. On the other hand, Freund and co-workers,^{42,44} were able to detect the presence of Ti^{3+} species, although they did not found any correlation between Ti^{3+} concentration and polymerization activity. In this regard, it should be noticed that Ti^{2+} and Ti^{4+} ions are not EPR active because they are not paramagnetic and that the large majority of Ti^{3+} species could be EPR silent because of interaction with other adjacent Ti^{3+} species. Successively, the catalysts were activated by exposure to AlR_3 co-catalysts (step iv) in Fig. 3a). According to XPS investigations, interaction of triethylaluminum with Ti sites grafted on MgCl_2 leads to a reduction of Ti^{4+} to Ti^{2+} , whereas no indication of Ti^{3+} centres was found. Therefore, Ti^{2+} species were claimed to be the active species for polymerization, contrarily to the common belief. EPR measurements were in agreement with XPS results, since did not reveal an increase in the amount of detectable Ti^{3+} centres after alkylation. In addition, EPR technique was able to prove for the first time the formation of alkyl radicals during the alkylation process.^{43,44} Finally, ethylene polymerization was successfully performed on the model catalysts (step v) in Fig. 3a), demonstrating that, although much simpler, the surface science models well represent the real systems.

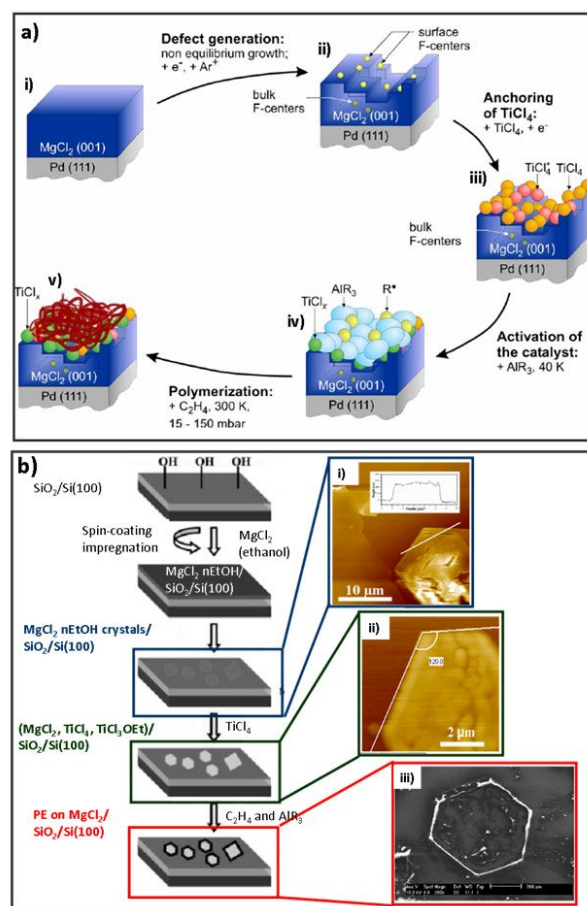


Fig. 3 Part a): Schematic representation of the preparation of model Ziegler-Natta catalyst, according to the following steps: i) preparation of a well ordered defect-free MgCl_2 film; ii) Defect creation by different techniques (colour centres are symbolized by yellow spheres); iii) anchoring of TiCl_4 ; TiCl_4^* (red) denotes TiCl_4 moieties adsorbed to colour centres of the substrate. iv) adsorption of AlR_3 on the surface at 40 K (alkyl radicals are symbolized by yellow spheres); v) catalyst after polymerization of ethylene (TiCl_4^* species in green). Adapted from Ref. 44. Part b): Schematic representation of sample preparation for Ziegler-Natta catalyst on flat silica surface. i): AFM image of MgCl_2 diethyl nEtOH crystallites on silicon wafer. ii): the same as part i) after treatment with TiCl_4 . iii): SEM image of polypropylene obtained after 16 h of polymerization on sample shown in part ii). Adapted from Refs. 50,51.

Beside the possibility to apply a large variety of surface science techniques, planar models of Ziegler-Natta catalysts offer the advantage, when compared to the real catalytic systems, to be suitable for morphological observation by electron microscopy. The main contributions in this field come from the group of P. C. Thüne and co-workers, who developed a realistic flat model system for Ziegler-Natta catalysts.⁵⁰⁻⁵³ The synthesis method involves the spin-coating of a MgCl_2 solution (with or without donor) in ethanol on a flat silicon wafer (Fig. 3b).^{50,52} Successive treatment with TiCl_4 and AlEt_3 resulted in an active catalyst for ethylene and propylene polymerization. This model allowed to investigate the surface chemistry and to perform a morphologic study of the catalyst and of the nascent polymer at the nanometer scale at each stage of catalyst preparation and polymerization, using not only surface science techniques (such as XPS), but also electron and scanning probe microscopy.⁵³ The same authors further demonstrated that the spin-coated MgCl_2 support

precursor could be converted by controlled crystal growth into well-formed crystallites.⁵⁰ Incorporation of different internal donors, such as a diether and esters, in the crystal growth process generated large crystallites and provided strong evidence that the distribution of the active species in Ziegler-Natta catalysts depends on the nature of the internal donor, as a consequence of the ability of the donor to steer the formation of a particular MgCl_2 crystallite face during catalyst preparation.⁵¹ AFM and SEM measurements indicate that the presence of an electron donor could promote the formation of the (110) surface, even though this surface has substantially higher energy than the (104) one.¹⁷ These results are in agreement with the previous findings that chemisorptions of a donor on different surfaces may lower surface energies to different extents, thus changing their relative stabilities.¹⁷ Finally, a variant of the spin-coating method discussed above has been optimized for the in situ investigation of planar Ziegler-Natta model catalysts by means of ATR-IR spectroscopy. Following this method, interaction of electron donor with both MgCl_2 and $\text{TiCl}_4/\text{MgCl}_2$ was investigated, as well as in situ ethylene and propylene polymerization.^{54,55}

3.2. Planar models for Phillips catalysts

A surface science model for the Phillips catalyst was prepared by Thune et al.,^{53,56-62} following an approach similar to that already described for planar Ziegler-Natta systems. A silicon single crystal covered with a thin (about 90 nm) overlayer of amorphous silica, was impregnated by spin coating with an aqueous solution of chromic acid. Using a combination of X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and Rutherford backscattering spectrometry, authors studied the effect of the activation procedure on the state of the supported oxidized chromium sites.^{59,61,62} The reversible red-ox reactivity of the surface Cr species was followed by using Refl-EXAFS technique.⁶³ All of the above-mentioned UHV techniques, however, failed in the investigation of reduced Cr^{II} sites, mainly because of the high sensitivity of the samples to moisture, enhanced by the very low Cr concentration (far below the monolayer coverage).

Nevertheless, the planar model of the Phillips catalyst displayed representative polymerization activity and offered the opportunity for visualizing growing polyethylene by atomic force microscopy (AFM) in the early stages of reaction.^{53,62} It was found that the catalytically active Cr centres were not homogeneously distributed over the silica surface on a sub-micrometer scale, but formed islands, with shape and size dependent on the exact catalyst pre-treatment.

3.3. Final remarks on the role of surface science methods

Investigation of planar models of both, Ziegler-Natta and Phillips catalysts constitutes undoubtedly a small, but very interesting, piece of the complex puzzle that is the understanding of these catalysts at a molecular level. Apparently, the most was already done in this direction and there is a few space for progress. However, some of the experimental results obtained on surface science models of both catalysts are still controversial. In particular, the questions on the oxidation state of the active Ti sites in Ziegler-Natta catalysts remain still unanswered and further progress in this direction are possible.

One of the major issue is how far the model systems are from

the real catalysts. Catalysts prepared under UHV conditions are surely different from the real ones, even though they show a remarkable polymerization activity. Active sites on planar MgCl_2 are likely formed on the basal planes (only if defects are intentionally created), rather than on the more coordinatively unsaturated (110) and (104) faces. Therefore, any spectroscopic detail is only partially connected with the properties of the active sites in real catalysts. Slightly different, and maybe more promising, is the method developed by P. Thune and co-workers, in which the catalyst is prepared from solution, following several steps that resemble those employed to prepare the real catalysts. This method allows to perform simultaneously XPS and ATR spectroscopy for in situ studies on all the steps of catalyst preparation, including olefin polymerization.^{54,55} Moreover, this method is versatile because it allows to change several variables (such as temperature, electron donors, and others) during the catalyst preparation. As a consequence, a systematic study following this approach would allow to improve the knowledge on the structure-activity relationship.

4. Spectroscopic methods applied to real catalysts

4.1. Structural techniques (XRPD and EXAFS)

4.1.1. The role of X-ray Powder Diffraction

Although it is not a spectroscopic technique (and therefore it should not be discussed here), we start this section by summarizing the role of X-ray powder diffraction (XRPD) in the structural characterization of polymerization catalysts. As a matter of fact, XRPD is the best technique to structurally characterize crystalline materials and to identify the crystalline phases present in the investigated sample. However, it fails when the crystalline phase is highly dispersed, or when the material of interest is amorphous (i.e. in absence of a long-range order). Unfortunately, this is the situation for heterogeneous catalysts in general, and of catalysts for olefin polymerization in particular. Therefore, XRPD technique is of scarce utility to determine the structure of the active phase in such catalysts.

In particular, XRPD is not useful at all to determine the structure of the Phillips catalysts, because the active sites are highly diluted centres grafted on the surface of amorphous silica. In most of the cases, XRPD is not able to shed light also on the structure of the active phase in Ziegler-Natta catalysts, however it can provide information on the MgCl_2 supporting phase. As a matter of fact, although both MgCl_2 and TiCl_3 in the bulk form are crystalline materials, the catalytically active phases are usually highly dispersed and defective; hence, the resulting diffraction patterns are generally very broad or even featureless. Even when Ziegler-Natta catalysts are obtained by direct titaniation of well defined MgCl_2 adducts, the structure of the MgCl_2 precursors is usually completely destroyed. Examples can be found in the recent literature for different $\text{MgCl}_2 \cdot n\text{ROH}$ adducts.^{24,26} After treatment with TiCl_4 , the diffraction peaks characteristic of the molecular adducts disappeared and only very broad features corresponding to structurally disordered $\delta\text{-MgCl}_2$ were observed. On the contrary, direct titaniation of a Mg chloride tetrahydrofuranate precursor (grey in Fig. 4) lead to the formation of a bimetallic Ti-Mg salt, showing a characteristic diffraction pattern (green in Fig. 4).²⁵ However, addition of aluminum alkyl

(trioctyl aluminum) to this bimetallic salt caused the rupture of the original crystalline phase and the appearance in the XRPD pattern of diffraction peaks that, although slightly broader, were easily associable to the Mg parent precursor (orange in Fig. 4). In all the cases discussed above, whichever is the nature of the Ti phase, it is dispersed enough to escape XRPD detection; therefore, XRPD alone is not sufficient and other techniques are necessary to get information on the Ti active species present in the final catalyst.

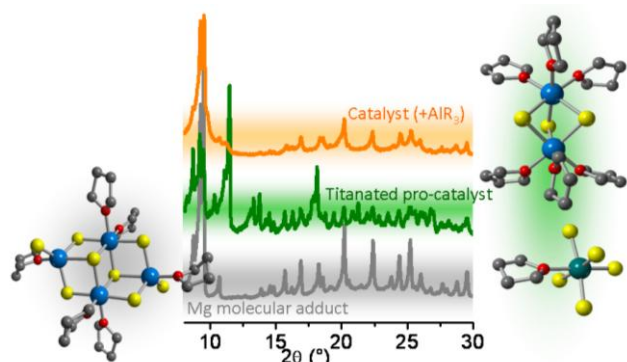


Fig. 4 XRPD patterns of the Mg chloride tetrahydrofuranate precursor, of the Ti-Mg bimetallic salt obtained upon direct titration of the Mg precursor, and of the final catalyst after interaction with the AIR_3 activator. Data taken from Ref. ²⁵.

4.1.2. The role of Extended X-Ray Fine Structure Spectroscopy

Because of its atomic selectivity, EXAFS spectroscopy represents the technique of choice in the characterization of highly diluted species. Moreover, the short mean free path of the photoelectron limits the sensibility of the technique to a few Å around the absorbing atom; therefore, opposite to XRPD, no long-range order is required and structural information can be obtained from amorphous systems also.

For the reasons outlined above, EXAFS spectroscopy is, in principle, a powerful technique to understand the local structure of grafted Cr species on the Phillips catalyst. Nevertheless, in contrast to the large amount of XAS studies on various chromium compounds reported in the past,⁶⁴⁻⁶⁹ only a few works appeared about XAS applied on the Phillips catalyst or on related systems.^{9,70-76} This is mainly due to the low Cr loading (in the 0.5-1.0 wt% range) and to its high reactivity toward oxygen and moisture. As a matter of fact, highly diluted systems need to be measured in fluorescence mode, a demand that increases the acquisition times, making the contamination problems more severe. Moreover, the absence of a structural model for the grafted Cr sites and the difficulty in treating open shell systems (Cr^{II} are d^4 species) make the computational approach necessary for data analysis not straightforward (vide infra Section 5.2). Notwithstanding these problems, remarkable structural data were obtained by several research groups on the oxidized form of the Phillips catalyst (see orange spectrum and step i) in Fig. 5),^{70,72,73,75,76} as well as on the catalyst after in situ ethylene polymerization.⁷² The latter data, coupled with FT-IR spectroscopy, allowed to evaluate the fraction of Cr sites active in ethylene polymerization as a function of the activation procedure.⁷⁷

Much more challenging was the investigation by EXAFS of

the reduced form of the Phillips catalyst, $\text{Cr}^{\text{II}}/\text{SiO}_2$. A few preliminary attempts were done in the past,^{70,72} but only very recently Gianolio et al.⁹ were able to overcome the experimental problems cited above by adopting an advanced experimental set-up (Fig. 5). The samples were measured inside sealed capillaries, in order to avoid any contamination even during the long acquisition times required by the fluorescence set-up; the use of capillaries for EXAFS measurements is not straightforward, because the X-ray beam must be vertically focused in the same point along the whole energy scan. The authors succeeded in determining the structural properties of the reduced $\text{Cr}^{\text{II}}/\text{SiO}_2$ Phillips catalyst. In particular, the high quality of the data allowed the local structure of the grafted Cr^{II} sites to be determined up to the third coordination sphere. It was found that, besides two oxygen atoms at around 1.86 Å (step ii) in Fig. 5), other 2.8 oxygen ligands at longer distance (2.64 Å) are present in the Cr^{II} coordination sphere (not shown in the scheme for clarity), in agreement with the indirect results obtained by other spectroscopic measurements. Moreover, the EXAFS data demonstrated that the structure of the Cr^{II} sites is modified upon interaction with CO (pink spectrum and step iii) in Fig. 5), providing the first direct experimental evidence of an adsorption induced mobility of Cr^{II} sites. This structural flexibility was supposed to be the key for understanding the catalytic activity of Cr^{II} sites in presence of adsorbates, especially ethylene.

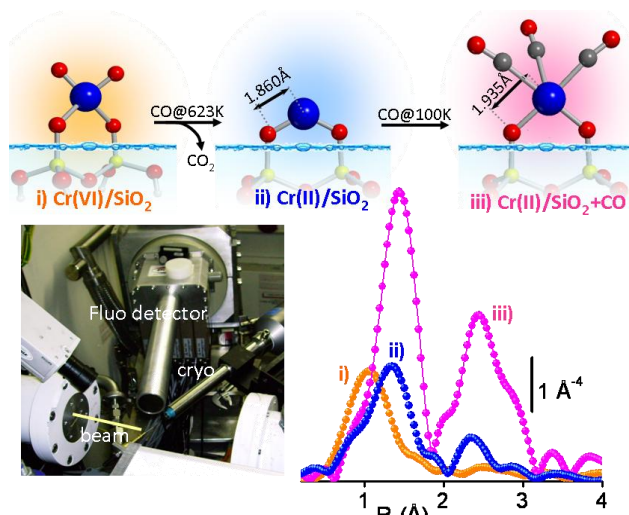


Fig. 5 Top: schematic representation of the structure of the oxidized (i) and reduced (ii) forms of Cr/SiO_2 catalyst, and Cr^{II} extraction from SiO_2 surface by CO adsorption (iii). Bottom: experimental set-up at ESRF BM26A used for fluorescence EXAFS measurements (left) and $|FT|$ of the EXAFS signals for $\text{Cr}^{\text{VI}}/\text{SiO}_2$ (orange), $\text{Cr}^{\text{II}}/\text{SiO}_2$ (blue) and $\text{Cr}^{\text{II}}/\text{SiO}_2+\text{CO}$ at 100 K (pink). Data taken from Ref. ⁹.

Also for Ziegler-Natta catalysts one of the major problems in applying EXAFS spectroscopy for a structural characterization is the sensitivity of the samples to moisture. In this case, the problem is even most severe than for the Phillips catalyst, because the Ti K-edge is at a lower energy, thus precluding the use of capillaries (because most of the X-ray beam would be absorbed by the glass). Nevertheless, a few studies dealt with the characterization of Ziegler-Natta catalysts by EXAFS. Potapov et al.⁷⁸ investigated a $\text{TiCl}_4/\text{MgCl}_2$ binary catalyst and suggested an asymmetric structure for Ti sites, which justifies the ease of the

Ti atoms' alkylation by alkyl-aluminum compounds. For $\text{TiCl}_3/\text{MgCl}_2$, Usami et al.⁷⁹ observed that the Ti-Cl distance was shorter in comparison to that found for $\alpha\text{-TiCl}_3$ and $\gamma\text{-TiCl}_3$. The same authors concluded that the number of first shell neighbours was reduced from 6.0 of $\alpha\text{-TiCl}_3$ to 2.42 of $\text{TiCl}_3/\text{MgCl}_2$; authors interpreted this result as an effect of the high dispersion of TiCl_3 . Similar results were reported by Vlaic et al.⁸⁰ and by Reed et al.⁸¹ It is well known that the first shell coordination number of an absorbing species decreases when the corresponding phase reaches nanometric dimension. Nevertheless, a coordination number lower than 4.0 seems unrealistic, even for highly dispersed TiCl_3 . Instead, this low coordination number might be the result of a "cancellation" effect by other lighter atoms (such as O belonging to some Ti-oxo-chloride species) to the expenses of the Cl ligands. Although not frequent, cases in which O and Cl contributions are out of phase and cancel each others were already reported in literature.⁸²⁻⁸⁴ Larger (and more realistic) coordination number values were reported by Da Silva Filho et al.⁸⁵, who analyzed the EXAFS data of a $\text{TiCl}_3/\text{MgCl}_2$ catalyst after addition of tri-ethyl aluminium. The authors found two Ti-Cl distances: a shorter one (1.92 Å, coordination number of 1.5) and a longer one (2.6 Å, coordination number of 2.5), accounting for a total of 4.0 Cl ligands in average. The shorter Ti-Cl distance suggests a close interaction between Ti and MgCl_2 , through bridged Cl species.

4.1.3. Some final considerations on the role of EXAFS spectroscopy

As summarized above, EXAFS spectroscopy was an useful technique to get relevant information on the local structure of the active Cr sites for both oxidized and reduced forms of the Phillips catalysts. However, it is worth mentioning that EXAFS data provide only average structural information and do not account for the structural heterogeneity of the Cr sites. Even more important, the achievement of these results was possible only because of the presence of a large amount of complementary

spectroscopic data, which constituted the starting point for a careful analysis of the EXAFS data. Now that the technical aspects have been optimized, further progress can be foreseen in the characterization of modified versions of the catalyst, with the final aim to trace a relationship between catalyst structure and activity.

On the contrary, a clear determination of the local structure of the Ti sites in classical Ziegler-Natta catalysts by EXAFS is still absent. The few data summarized above are quite scattered (especially in terms of coordination numbers) and are related only to simple binary systems. In our opinion, the path towards a deep understanding of the structure of the active Ti sites by EXAFS is still long, and it should proceed in a systematic way, starting from the investigation of the largest possible number of Ti model systems, and gradually increasing the sample complexity. Moreover, following the lesson of the Phillips catalyst, experimental results from other spectroscopic techniques would be required in order to interpret the EXAFS data that, otherwise, might risk to be over-analyzed.

4.2. Vibrational spectroscopies (Raman and Infrared)

4.2.1. Direct spectroscopic methods

Role of Raman and Infrared spectroscopy in the direct characterization of both Phillips and Ziegler-Natta catalysts

It is well known that vibrational spectroscopies are powerful techniques to provide information at the molecular level. Vibrational spectra (both infrared and Raman) are sensitive to the molecular properties of the investigated samples, such as type of atoms, chemical bonding, geometry, and intra/intermolecular interactions; moreover, they successfully provide surface structural information, because of their ability to discriminate between different species that may simultaneously be present in the investigated system. In addition, both techniques are highly sensitive, and therefore ideal to investigate diluted samples.^{86,87}

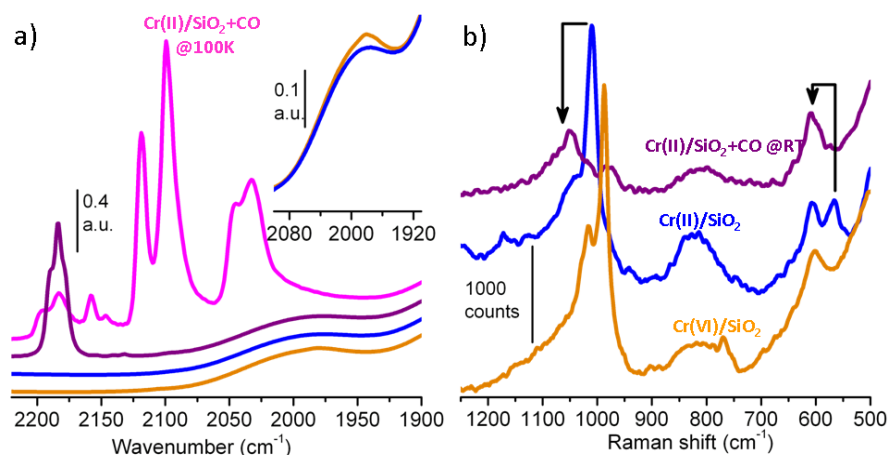


Fig. 6 FT-IR (part a) and Raman (part b) spectra of the oxidized (orange) and reduced (blue) form of the Phillips catalyst, and of $\text{Cr}^{\text{II}}/\text{SiO}_2$ in interaction with CO at room temperature (violet) and at 100 K (pink). The inset in part a) shows a magnification of the frequency region where the vibrational manifestations of Cr=O species occur. The arrows in part b) put in evidence the perturbation of the vibrational modes associated to Cr^{II} upon CO adsorption. Data taken from Refs. ⁸⁸ and ⁸⁹.

Both IR and Raman techniques played an important role in the characterization of the Phillips catalyst. IR spectroscopy was traditionally used to study the reduced $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst in an

indirect way (through the adsorption of probe molecules, vide infra Section 4.2.2, Fig. 6a), whereas it was scarcely useful in the characterization of the oxidized form of the catalyst. In fact, the

vibrational manifestations of Cr=O species fall in a region obscured by the intense modes of the silica support, and only very weak IR absorption bands assigned to the first overtones of $\nu_{\text{sym}}(\text{CrO}_2)$ and $\nu_{\text{asym}}(\text{CrO}_2)$ can be observed in the IR spectrum (inset in Fig. 6a).⁷⁵ On the contrary, Raman spectroscopy was applied essentially to characterize the $\text{Cr}^{\text{VI}}/\text{SiO}_2$ catalyst. The pioneering works belong to Wachs et al.,^{70,90-92} who investigated the $\text{Cr}^{\text{VI}}/\text{SiO}_2$ catalyst as a function of chromium loading and calcination temperature. Further progress in the characterization of surface chromate species were done by exploiting the resonance effect,^{88,93,94} by adopting silica supports characterized by exceptionally good light scattering properties,^{73,88} and by performing isotopic labelling and polarization studies.^{73,95} At low Cr loadings, only monochromates are present, characterized by intense and sharp absorption bands around 1000 cm^{-1} (orange spectrum in Fig. 6b).

Opposite to the abundant Raman literature on the $\text{Cr}^{\text{VI}}/\text{SiO}_2$ catalyst, to the best of our knowledge, only one work reported Raman characterization of the reduced $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst. Beside the already cited problems of the small fraction of Cr sites and of their air sensitivity, direct characterization of the $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst by Raman spectroscopy is a challenging task because the Cr-O-support bond has a partly ionic character, which results in a very low Raman intensity because of the decrease of polarizability. Nevertheless, Damin et al.⁸⁹ demonstrated that resonant Raman spectroscopy can provide direct vibrational information also on the grafted Cr^{II} sites (blue spectrum in Fig. 6b). The vibrational modes of surface Cr^{II} species (absorption bands at 1009 and 568 cm^{-1}) are strongly mixed to the support modes, and are perturbed by the adsorption of probe molecules, such as CO (violet spectrum in Fig. 6b).

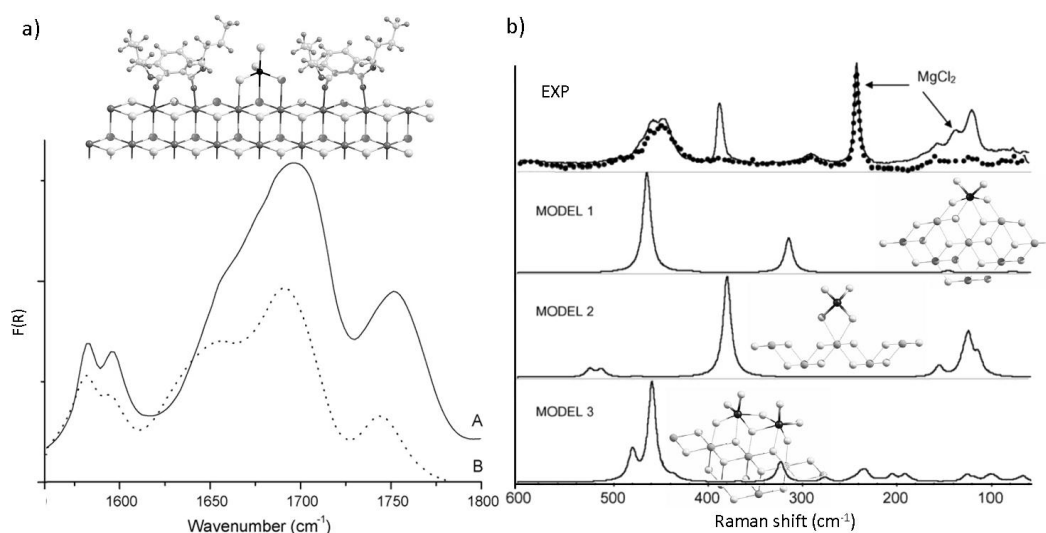


Fig. 7 Part a): DRIFT spectra of $\text{TiCl}_4/\text{DBP}/\text{MgCl}_2$ before (A) and after (B) interaction with AlEt_3 and possible scheme of DBP and TiCl_4 coadsorption on the (104) MgCl_2 surface (DBP = di-iso-butyl phthalate). Adapted from Refs.^{96,97} Part b): Comparison between experimental Raman spectra of $\text{MgCl}_2/\text{TiCl}_4$ sample ($\text{Mg}/\text{Ti} = 10/1$ mol/mol) before and after washing in n-hexane (solid and dotted spectra, respectively) and calculated Raman spectra of models shown on the right. Model 1 is the one that better reproduce the experimental datum. Adapted from Ref.⁹⁸

Vibrational spectroscopies (both IR and Raman) were extensively used also to characterize Ziegler-Natta catalysts.⁹⁶⁻¹⁰⁴ The majority of the IR works are devoted to the characterization of the complexes formed between the catalyst precursors and the electron-donor molecules added to improve the stereospecificity in 1-olefin polymerization. Intense IR absorption bands characteristic of the chemical group directly interacting with Mg or Ti centres (e.g., C-O stretching vibrations in ethyl benzoate, dialkyl phthalate, or dieters donors) were used as markers of complexation. Very often, in absence of other experimental results obtained by complementary techniques, the vibrational spectra were interpreted by means of quantum chemical calculations performed on selected molecular models.

Among the cited literature, we mention in particular the series of works of Potapov et al.,^{96,97,104} who performed a systematic DRIFT study to investigate the surface complexes formed between different internal donors (such as ethyl benzoate and di-iso-butyl phthalate) and the $\text{TiCl}_4/\text{MgCl}_2$ binary system, and the successive interaction of $\text{TiCl}_4/\text{MgCl}_2/\text{donor}$ with AlEt_3 co-

catalyst. An example is shown in Fig. 7a, which shows the DRIFT spectra in the $1500\text{--}1800\text{ cm}^{-1}$ region for the $\text{TiCl}_4/\text{DBP}/\text{MgCl}_2$, before (full spectrum and scheme at the top) and after interaction with AlEt_3 (dotted spectrum). The DRIFT spectrum of the pre-catalyst (spectrum A) is quite complex and reflects the multiplicity of species present in the sample: the main IR absorption bands were assigned to $\nu(\text{C}=\text{O})$ ($1650\text{--}1700\text{ cm}^{-1}$) and phenyl rings modes ($1500\text{--}1600\text{ cm}^{-1}$) of adsorbed DBP, and to $\nu(\text{C}=\text{O})$ of phthaloyl chlorides (around 1750 cm^{-1}). Marked changes occur in the DRIFT spectrum upon interaction of the pre-catalyst with AlEt_3 (spectrum B in Fig. 7a), revealing that most of the phthaloyl chlorides are removed (decrease of the IR absorption band around 1750 cm^{-1}), and that different DBP adducts are formed (decrease in intensity and shift in frequency of the absorption bands around 1700 cm^{-1}).

Finally, the geometries of 9,9-bis(methoxymethyl)-fluorene as internal electron donor were investigated by Brambilla et al.,¹⁰² combining data from experiment (infrared absorption) and theory (quantum chemical calculations), with the aim to find information

on the structure of the catalytic sites in mechanically activated Ziegler-Natta catalyst precursor. Authors gained convincing evidence to propose the conformations of the pure donor, of the donor complexed with MgCl_2 , and of the donor in the pro-catalyst (i.e. in presence of both TiCl_4 and MgCl_2).

Raman spectroscopy offers the additional possibility to investigate the frequency region where $\nu(\text{M-Cl})$ vibrations can be observed (below 500 cm^{-1}). However, Raman spectroscopy suffers of two main drawbacks that limit its applicability: i) highly coloured samples may absorb the incoming light and therefore can be difficult to be measured; ii) in many cases, investigated samples show a strong fluorescence, especially when organic species are present. Ziegler-Natta catalysts (and their precursors) are usually highly coloured, and very often contain organic moieties in the chemical composition (e.g. Lewis bases). This is the reason why very few works are present in literature on a direct characterization of Ziegler-Natta catalysts in the highly informative $\nu(\text{M-Cl})$ region. Brambilla et al.^{98,101} reported a very detailed Raman investigation of a series of mechanically prepared $\text{TiCl}_4/\text{MgCl}_2$ samples with increasing content of TiCl_4 . The Raman spectra revealed that, during the grinding process, at least two types of TiCl_4 molecules complexed on the lateral cuts of activated MgCl_2 crystals are formed, whose relative concentration depend on the initial TiCl_4 loading. One of them is unstable and is easily removed when the samples are washed with n-hexane. The corresponding Raman bands at 386 , 137 and 120 cm^{-1} (solid spectrum in Fig. 7b) are assigned to TiCl_4 molecules that are physisorbed or weakly bounded to the MgCl_2 crystal keeping the tetrahedral structure (model 2). The remaining complex is stable and it is found in every sample also after washing. This stable complex shows a characteristic Raman spectrum having bands at 450 and 290 cm^{-1} (dotted spectrum in Fig. 7b), which has been interpreted as due to the complexed TiCl_4 molecules with the Ti atoms in an octahedral coordination. Calculated Raman spectra, molecular energy considerations and Raman lines intensity ratios strongly supported the fact that the stable complexes are the monomeric TiCl_4 species complexed along the (110) MgCl_2 faces (model 1 in Fig. 7b).

To the best of our knowledge, there are very few examples of combination of IR and Raman spectroscopy adopted to investigate Ziegler-Natta catalysts.^{24,25} A very recent example is the work of Seenivasan et al.,²⁵ who reported a combined IR and Raman study on different Ti and Mg chloride tetrahydrofuranate precursors, and on the catalyst obtained after interaction of the precursors with the aluminum alkyl activator. IR spectra in the $4000\text{--}500\text{ cm}^{-1}$ range contained information on the vibrational modes of tetrahydrofuran (i.e. the electron donor), which are affected by complexation to the metal site (both Ti and Mg). Complementary information in the same wavenumber region was obtained by Raman spectroscopy that, in addition, allowed the observation of the $\nu(\text{M-Cl})$ vibrations. In particular, comparison of the Raman spectrum of the final catalyst with those of the precursors demonstrated that the Ti phase in the catalyst is in the form of highly dispersed violet TiCl_3 , not visible by XRPD (see Fig. 4).

In conclusion of this section, it is worth recalling that information in the $\nu(\text{M-Cl})$ vibrational region can be obtained also by Far-IR spectroscopy, which has the advantage to

overcome the two above-mentioned problems affecting Raman spectroscopy. However, collection of Far-IR spectra requires a dedicate instrument and a complex experimental set-up, especially when dealing with air-sensitive samples. Moreover, Far-IR spectra are characterized usually by broader absorption bands than the Raman ones and, consequently, their interpretation is more difficult. For all these reasons, works reporting Far-IR spectra of Ziegler-Natta samples, or related compounds, are very rare.¹⁰⁰

Role of FT-IR spectroscopy in the investigation of the olefin polymerization mechanism

As briefly mentioned in Section 2.3.2, the Phillips catalyst works without the need of any activator; this makes it peculiar, but also one of the rare catalytic systems in which investigation of the reaction mechanism directly involves the real active sites (or their precursors) and not only the pro-catalyst. Since the precursors of the active sites are naked Cr^{II} species, several additional and yet ill-defined steps must precede the polymerization itself, in order to transform the Cr^{II} precursors into the active sites.⁶ Investigation of these first reaction steps is not an easy task because of the low concentration of the active sites, and the high turnover frequency (as summarized in Section 2.2). In order to identify the intermediate species in the polymerization reaction using a spectroscopic technique, the time needed to perform the measure must be shorter than the short lifetime of the intermediates.⁸⁶

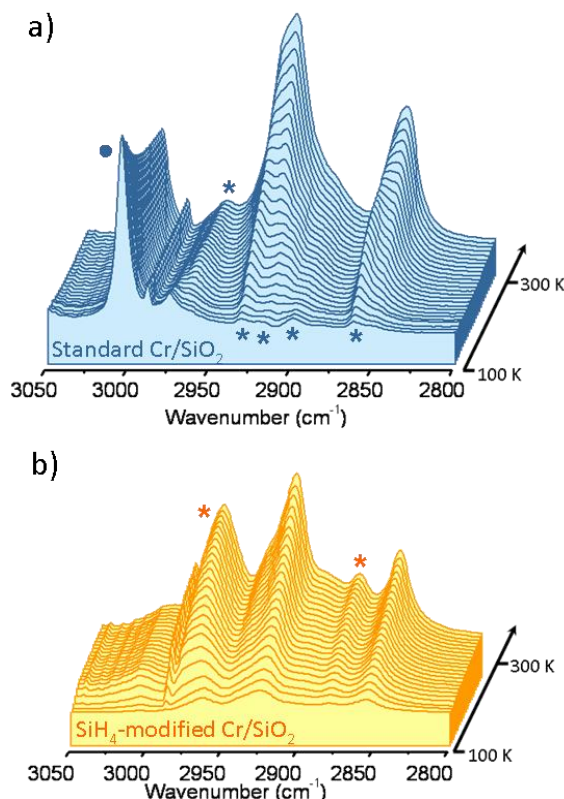


Fig. 8 Temperature and pressure-resolved FT-IR spectra collected during ethylene polymerization on the standard $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst and on a silane-modified Cr/SiO_2 catalyst (parts a and b, respectively). Data taken from Refs. ³¹ and ¹⁰⁵.

Progress in this direction can be achieved either by improving the time response of the instrument or by finding the way to slow the reaction speed, or both. Furthermore, the spectroscopies adopted must be very sensitive. Among all of the spectroscopic techniques, in situ FT-IR spectroscopy was the most widely used to identify the intermediate species present during the initial steps of ethylene polymerization on the Phillips catalyst, being able to directly discern between the vibrational manifestations of different species even under operando conditions.^{86,87} The first attempts in this direction date back to 1988, when Ghiotti et al.¹⁰⁶ followed by in situ FT-IR spectroscopy the ethylene polymerization on the $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst, at room temperature and at low ethylene pressure. The idea was that short contact times and low ethylene pressures should result in a slow polymerization, thus allowing the study of the initial steps of polymerization reaction. However, only the IR absorption bands characteristic of the CH_2 groups of the growing polyethylene chains were detected at that time. The same results were obtained ten years later by Zecchina et al.,¹⁰⁷ although FT-IR spectra were collected at a time-resolution lower than 0.25 seconds. Only recently it was possible to gain some more insights in the very first steps of ethylene polymerization by decreasing significantly the ethylene polymerization rate (Fig. 8a). This was possible at first by lowering the reaction temperature, and secondly by poisoning the catalyst with CO. In these conditions, in situ FT-IR spectroscopy revealed the formation of $\text{Cr}^{\text{II}}\text{-C}_2\text{H}_4$ π -bonded complexes, having characteristic IR absorption bands that remain visible until the onset of the polymerization reaction (blue circle in Fig. 8a).^{108,109} Moreover, a complex series of IR absorption bands were observed in the initial steps of the polymerization reaction (blue stars in Fig. 8a), before the appearance of the intense $\nu(\text{CH}_2)$ absorption bands due to the growing PE chains. These “anomalous” IR absorption bands were associated to small and strained metallacycle intermediate species,³¹ leading to the conclusion that the initiation of ethylene polymerization on the Phillips catalyst follows a metallacycle route. It is worth mentioning that the metallacycle mechanism was shown to occur for several Cr-based ethylene trimerization and tetramerization catalysts¹¹⁰⁻¹¹⁵ and for Cr-based homogeneous olefin polymerization catalysts.^{116,117} For these systems, both the oxidative coupling of the first two ethylene molecules to form the metallacyclopentane intermediate¹¹³ and the insertion of an additional ethylene into the metallacyclopentane species^{118,119} have been claimed to constitute the rate-determining step.

Very recently, FT-IR spectroscopy applied under operando conditions was used to investigate ethylene polymerization on two modified Phillips catalysts, in comparison with the standard one. In one case, the modification of the Phillips catalyst occurred through controlled oxidation of the reduced Phillips catalyst with N_2O , resulting in the formation of surface $\text{Cr}^{\text{IV}}=\text{O}$ oxo species.¹²⁰ The kinetic of ethylene polymerisation was studied on both standard and modified catalysts by recording the ethylene pressure inside a closed IR cell while simultaneously collecting IR absorption spectra at a 1 s time resolution. These data provided an evidence that ethylene polymerisation readily proceeds at room temperature about 15 times faster with the modified catalyst than with the standard one, which could be highly relevant to the production of some varieties of

polyethylene. In the second case, modification of the Phillips catalyst was carried out by interacting it with silane.¹⁰⁵ Time-resolved in situ FT-IR spectra collected at room temperature revealed that the ethylene polymerization rate is 7 times higher on the SiH_4 -modified catalyst than on the standard one. The produced PE is a LLDPE, in good agreement with the literature results.³ Application of temperature- and pressure-resolved FT-IR spectroscopy (following the same strategy discussed above to detect the metallacycle intermediates) allowed the detection of in situ produced α -olefins (orange stars in Fig. 8b), before their incorporation in the polymer chains. These results gave a direct spectroscopic insight into the in situ branching process,³ which is at the basis of the LLDPE production with a hydrosilane modified Phillips catalyst.

The much more complex chemical composition of Ziegler-Natta catalysts didn't allow, up to now, to exploit IR spectroscopy to follow in situ olefin polymerization on these catalysts. To the best of our knowledge, the only work showing FT-IR spectra of the in situ growing polyolefin chains on Ziegler-Natta catalysts is that of Andoni et al.;⁵⁴ the spectra were collected in ATR mode on a planar model of Ziegler-Natta catalysts (Section 3.1). The major difficulty in applying in situ FT-IR spectroscopy to real Ziegler-Natta catalysts consists in the fact that the activator should be put in contact with the pro-catalyst in presence of the olefin monomer and of the solvent. Beside the experimental difficulties (e.g. the presence of the solvent prevents the adoption of standard transmission set-ups) the presence of aluminum alkyl activator and of the solvent limits the region of transparency of the FT-IR spectrum and makes difficult the detection of the IR bands characteristic of the growing polymer. In these conditions, no mechanistic hypothesis can be formulated.

4.2.2. Indirect spectroscopic methods

Vibrational spectroscopy of adsorbed probe molecules is a powerful technique for characterizing surface metal sites.^{86,87,121-126} The method has the advantage to be very sensitive, even for highly diluted species, and allows to distinguish among surface sites characterized by similar properties. Among the molecules employed to probe the structure of surface sites, carbon monoxide is one of the most used, because its interaction is normally rather strong. Generally speaking, interaction of CO with a transition metal ion can be separated into electrostatic, covalent σ -donative, and π -back donation contributions. The first two cause a blue shift of the $\nu(\text{CO})$ (with respect to that of the molecule in the gas phase, 2143 cm^{-1}), whereas the latter causes a red shift. Therefore, measurement of $\nu(\text{CO})$ for a given metal-carbonyl complex gives information on the nature of the metal-CO bond.⁸⁷

Vibrational spectroscopy of adsorbed probe molecules was largely used in the characterization of the active sites in the reduced $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst.^{6,108,127-130} Various diatomic and triatomic gases (NO , CO , CO_2 , and N_2O) have been used as adsorbates, but CO played by far the major role. Interaction of $\text{Cr}^{\text{II}}/\text{SiO}_2$ with CO at room temperature results in the formation of non classical mono- and di-carbonyls (prevailing σ -donation) on a heterogeneity of Cr^{II} sites (violet spectrum in Fig. 6a). The nature of the carbonyls changes to a classical one (prevailing π -back donation) upon lowering the temperature (increasing the coverage), as monitored by a spectacular evolution of the IR

spectra (pink spectrum in Fig. 6a). This phenomenon has been interpreted in terms of formation of multi-carbonyls through the displacement of weaker siloxane ligands. More recently, in situ Raman experiments highlighted that the vibrational modes characteristic of supported Cr^{II} sites are significantly perturbed upon CO adsorption (see Fig. 6b).⁸⁹ The behaviour of $\text{Cr}^{\text{II}}/\text{SiO}_2$ observed in presence of CO provides an evidence of the unique role of the silica surface in the optimization of the Cr–CO interaction and gives a clear, although indirect, proof that an important rearrangement of the local environment of the Cr^{II} site at the silica surface occurs upon CO adsorption (as demonstrated in direct way by EXAFS spectroscopy, see above Section 4.1.2 and Fig. 5).⁹

The method of adsorption of probe molecules was much less employed for characterizing heterogeneous Ziegler-Natta catalysts. When pre-catalysts are considered, most of the Ti active sites are 6-fold coordinated, and therefore there are no coordination vacancies available for insertion of the probe. Instead, activation of the pre-catalyst with the aluminum-alkyl is usually performed in presence of the monomer, in order to avoid fast deactivation. To the best of our knowledge, only very few works are related to the adsorption of CO on activated MgCl_2 ,¹³¹⁻¹³³ whereas no data are available on the use of probe-molecules to characterize ZN catalysts. However, the electron donor molecules present in the chemical composition of the traditional Ziegler-Natta catalysts might be considered as indirect probes for the metal site to which they are coordinated. In this sense, the vibrational characterization of a traditional Ziegler-Natta catalyst can offer both, direct and indirect information on the structure of the investigated catalyst.

In conclusion of this session it is important to notice that FT-IR spectroscopy of adsorbed probe molecules has also some disadvantage. In particular: i) it is not an absolute method, because the probing process is necessarily associated to a perturbation of the surface; ii) different probe molecules might give different answers (according to the interaction strength); and iii) the probe molecule may bind not only at the real active sites, but also on spectator species, leading to misleading information. To account (at least in part) to these problems, it is always preferable to use more than one molecule. In this respect, it should be noticed that the olefin monomer itself is the best probe for the active sites, provided that the polymerization reaction is switched off (or slowed down). As an example, IR spectroscopy at low temperature allowed to monitor the formation of π -bonded ethylene complexes on $\text{Cr}(\text{II})$ sites on the Phillips catalyst.¹⁰⁸ Another interesting approach consists in dosing the probe molecule on the catalyst of interest before and after the olefin polymerization reaction. Comparison of the two vibrational spectra should allow to obtain information on the types and the fraction of the active sites.⁷⁷

4.2.3. Final remarks on the role of vibrational spectroscopies

Up to now, vibrational spectroscopies played the major role in the investigation of the properties of heterogeneous catalysts for olefin polymerization. Several reasons can account for their success: i) the ability to provide information at the molecular level; ii) the high sensitivity towards extremely diluted surface species; iii) the high versatility, which implies the possibility to perform measurements in situ, in presence of reagents or probe

molecules, at different temperature, and different pressure; iv) the large availability of standard FT-IR and Raman instruments; v) the availability of a large set of experimental and theoretical data to which compare the experimental results. On the other side, application of both IR and Raman techniques to the study of Phillips and Ziegler-Natta catalysts is not straightforward: i) the air sensitivity of the samples requires the adoption of many precaution in their manipulation; ii) not always it is possible to distinguish between active species and spectators; iii) identification of reaction intermediates can be limited by the time-resolution of the techniques.

The abundant literature present in the field demonstrate that direct IR and Raman spectroscopy are invaluable techniques to obtain information at the molecular level on the active sites of both Phillips and Ziegler-Natta catalysts, and on their modified versions. Further progress in this field could be achieved by developing experimental tools that could allow to monitor in situ all the steps of the preparation of Ziegler-Natta catalysts, up to the in situ olefin polymerization, in a similar way to what is already possible for the Phillips catalyst.

4.3. Electronic spectroscopies (UV-Vis and XANES)

Diluted transition metal ions in heterogeneous catalysts are characterized by peculiar electronic properties, which can provide direct information on the oxidation state and coordination geometry of the metal, as well as on the number and type of ligands. UV-Vis (in diffuse reflectance mode, DR) and XANES spectroscopy are the electronic spectroscopies mostly employed for characterizing heterogeneous catalysts, although also XPS, EPR and others can be very useful. Generally speaking, the occurrence of an absorption band in the visible region of a UV-Vis spectrum is usually associated to d-d transitions; the position and intensity of a d-d band is a function of both, oxidation state and symmetry of the metal species (according to the ligand field theory). Complementary information are contained in the pre-edge part of the metal K-edge XANES spectrum, which monitors transitions of an 1s electron to molecular orbitals having mainly a d character; the number and intensity of these bands are a function of the local symmetry of the metal (according to the dipole selection rule). Moreover, the edge-position of the XANES spectrum depends on the oxidation state of the metal, although care must be taken to avoid misinterpretations.¹³⁴

In addition, both UV-Vis and XANES spectroscopy are informative on the type of bonding between the metal and the ligands. Intense bands at wavenumber higher than about 20000 cm^{-1} in a UV-Vis spectrum are usually due to charge-transfer (CT) transitions (i.e. transfer of an electron from molecular orbitals mainly centred on the ligand to molecular orbitals mainly centred on the metal). Similar information are contained in the first resonance after the edge (white-line) of a XANES spectrum, which is due to the promotion of the excited electron to molecular orbitals strongly associated with the ligands. For diluted metal species a pretty good assignment of the electronic transitions can be performed by applying the molecular orbital approach, i.e. by considering the active metal site as a molecular complex where only the first ligands contribute to define the metal coordination sphere. Although simple, in many cases this method allowed the assignment of most of the bands observed in a UV-Vis and in a XANES spectrum, without performing ab initio calculations,

which are more rigorous but also much more demanding.

4.3.1. Electronic spectroscopies applied to the Phillips catalyst

The above mentioned approach was revealed successful in the definition of the oxidation state and local symmetry of grafted Cr sites in the Phillips catalyst. In particular, UV-Vis spectroscopy was largely used to solve the debate on the nuclearity of chromate species in the SiO₂ surface (mono-, di-, or polychromates) as a function of the Cr loading.^{6,70,135-139} It was reported that the UV-Vis spectrum of highly diluted mono-chromate species (orange spectrum in Fig. 9a) shows a characteristic CT band at an unusually low frequency value (around 20000 cm⁻¹), which was assigned to the transfer of an electron from O to Cr in the Cr(VI)=O₂ moiety. The corresponding XANES spectrum (orange spectrum in Fig. 9b) is characterized by a strong pre-edge peak, due to the transition of the excited 1s electron to hybrid p-d orbitals for Cr species in a nearly perfect tetrahedral symmetry.^{9,70,72,75,76} The colour of Cr/SiO₂ changes from light yellow to light blue upon reduction in CO; correspondingly, both UV-Vis and XANES spectra are modified and provide an

evidence that isolated Cr(II) sites (d⁴ electronic configuration) are formed.⁶ In particular, the UV-Vis spectrum (blue in Fig. 9a) is characterized by a strong CT band at about 30000 cm⁻¹ and by two d-d bands at 12000 and 7500 cm⁻¹, whose intensity is strongly influenced by the activation procedure; these bands are the fingerprints of Cr(II) centres having a highly distorted structure and preferentially sensing the crystal field caused by two strong SiO- ligands.⁶ The corresponding XANES spectrum (blue in Fig. 9b) shows a strong pre-edge peak at 5994.4 eV, mainly due to Cr_{1s}→Cr_{4p} transition, and by two weak bands at 5987.7 and 5990.0 eV, due to Cr_{1s}→(Cr_{3d} + O_{2p}) dipole-forbidden transitions;⁹ the edge is downward shifted with respect to that of the oxidized catalyst. As already observed with other spectroscopic techniques, the fingerprints of grafted Cr(II) species in both UV-Vis and XANES spectra are highly perturbed upon interaction with probe molecules such as CO, as a consequence of the increased crystal field (violet and pink spectra in Fig. 9a and b, respectively).⁹

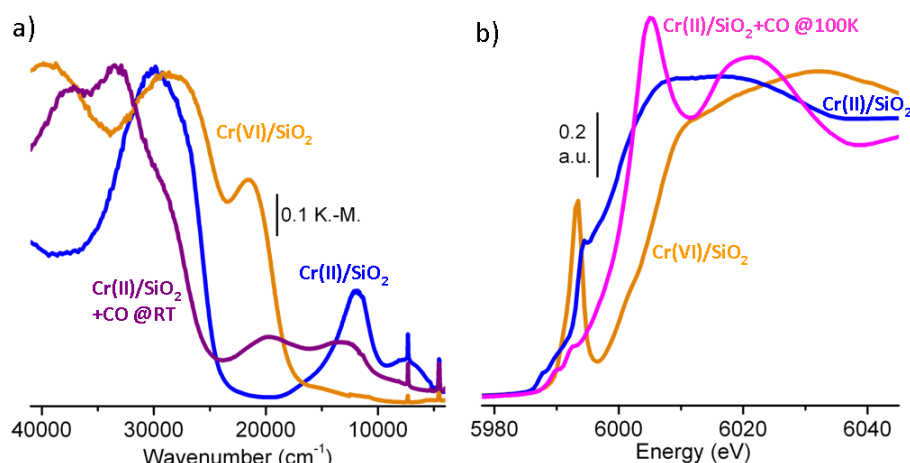


Fig. 9 DR UV-Vis (part a) and XANES (part b) spectra of the oxidized (orange) and reduced (blue) form of the Phillips catalyst, and of Cr^{II}/SiO₂ in interaction with CO at room temperature (violet) and at 100 K (pink). Data taken from Refs.⁶ and ⁹.

Finally, it is worth noticing that both UV-Vis and XANES spectroscopy are highly sensitive to the presence of a small fraction of clustered Cr₂O₃ phase,^{63,72} which is an undesired phase inactive in ethylene polymerization; Cr₂O₃ is easily formed when the catalyst is not properly activated, especially at Cr loadings higher than 1 wt% and in presence of moisture. In particular, the presence of a fraction of clustered Cr₂O₃ in the CO-reduced Cr(II)/SiO₂ catalyst is revealed, in the UV-Vis spectrum, by two d-d transitions at around 21500 and 16500 cm⁻¹, which occur in a wavenumber range where the spectrum of Cr(II) sites do not give any contribution. In the XANES spectrum of a not properly activated Cr(II)/SiO₂ catalyst, clustered Cr₂O₃ is responsible of a broad and weak absorption in the white line region (around 5989-5995 eV), where crystalline Cr₂O₃ shows two well defined bands.

4.3.2. Electronic spectroscopies applied to Ziegler-Natta catalysts

The use of UV-Vis and XANES spectroscopy for characterizing Ziegler-Natta catalysts is much less widespread than for the

Phillips catalyst. Very recently, Kalaivani et al.²⁵ reported a comprehensive UV-Vis characterization of different Ti and Mg chloride tetrahydrofuranate precursors, and of the catalyst obtained after interaction of the precursors with the aluminum alkyl activator. The work demonstrates that UV-Vis spectroscopy is a valuable method to determine the Ti oxidation state, as well as its coordination geometry in terms of number and type of ligands. As an example, the UV-Vis spectrum of the TiCl₄(thf)₂ precursor (black in Fig. 10a) is characterized by a very intense CT transition around 25000 cm⁻¹, which is assigned to a Cl(π) → Ti(d) charge transfer transition for a Ti⁴⁺ in a distorted octahedral coordination. A similar spectrum is obtained for the bimetallic salt originated from interaction of TiCl₄(thf)₂ with MgCl₂(thf)_{1.5} (green in Fig. 10a), where Ti shows a similar coordination (Fig. 4). However, the UV-Vis spectrum drastically changes after interaction of pro-catalyst with the aluminum activator (orange in Fig. 10a). In particular, an intense and complex absorption appears in the visible region, which is typical of d-d transition and intersite transfer transitions of the type 2(3d¹) → 3d⁰+3d² for Ti³⁺ species.¹⁴⁰ Moreover, the absorption

edge ($\text{Cl}(\pi) \rightarrow \text{Ti}(\text{d})$ CT transition) shifts upward with respect to that of the pro-catalyst, up to coincide with that of $\gamma\text{-TiCl}_3$, which was assigned to a CT transition from π orbitals of bridged Cl ligands to d orbitals of Ti^{III} .^{25,140} The corresponding Ti K-edge XANES spectra are shown in Fig. 10b. The XANES spectrum of the Ti^{IV} precursor (black in Fig. 10b) is characterized by an evident pre-edge feature (main peak at 4970.6 eV, shoulder at 4968.3 eV), which demonstrates that the Ti sites are in a distorted octahedral coordination; a similar spectrum is observed for the pro-catalyst (green in Fig. 10a), in agreement with the UV-Vis data. The slightly higher intensity of the pre-edge peak testifies

that the Ti octahedral symmetry is further distorted with respect to that of Ti in the precursor. Upon interaction with the activator (orange spectrum in Fig. 10b), the absorption edge shifts at lower energy, demonstrating that Ti^{IV} are reduced to Ti^{III} species. More interesting, the pre-edge region, which is very sensitive to the local environment around the Ti atoms, is very similar to that of $\gamma\text{-TiCl}_3$ (inset in Fig. 10b). Both UV-Vis and XANES spectra shown in Fig. 10 provide an evidence that after interaction with the AlR_3 co-catalyst the Ti^{4+} species are reduced to Ti^{3+} , having a coordination sphere very close to that shown by Ti^{3+} sites in $\gamma\text{-TiCl}_3$.

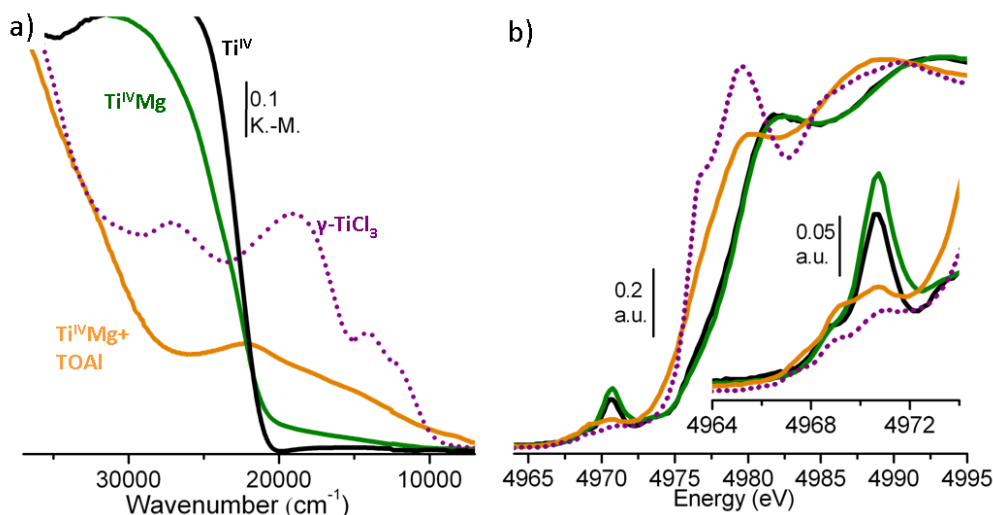


Fig. 10 DR UV-Vis (part a) and XANES (part b) spectra of $\text{TiCl}_4(\text{thf})_2$ precursor (Ti^{IV} , black), of the pro-catalyst obtained interaction of the Ti precursor with $\text{MgCl}_2(\text{thf})_{1.5}$ ($\text{Ti}^{\text{IV}}\text{Mg}$, green) and of the final catalyst after interaction with the AlR_3 activator ($\text{Ti}^{\text{IV}}\text{Mg}+\text{TOAl}$, orange). Also the spectra of $\gamma\text{-TiCl}_3$ are shown for comparison (dotted violet spectra) UV-Vis spectra from Ref. ²⁵; XANES spectra unpublished.

4.3.3. Final remarks on the role of electronic spectroscopies

The examples discussed above demonstrate that electronic spectra (both UV-Vis and XANES) contain a great number of information (at the molecular level) of heterogeneous catalysts for olefin polymerization. Nevertheless, their application is still limited with respect to other techniques, especially the vibrational ones. A first reason is that the interpretation of electronic spectra is much more challenging than the assignment of vibrational spectra. As a matter of fact, experimental data are usually quite scarce in literature, and theoretical simulations are much less widespread and validated than calculations of the vibrational frequencies. In addition, there are also experimental difficulties; for example, the intensity of most of the band in the UV region (having a charge transfer nature) is usually too high and therefore quantitative information can be obtained only upon dilution of the samples, which is not always straightforward. A step forward in the interpretation of the electronic properties of the investigated catalysts requires, in our opinion, the collection of a great number of experimental spectra of reference compounds and simple related systems in a systematic way; the spectra database resulting from this procedure would allow a better understanding of more complex systems, such as the real catalysts.

5. The role of theoretical calculations

5.1. Computational methods applied to Ziegler-Natta catalysts

Theoretical calculations have been traditionally used to investigate Ziegler-Natta catalysts, since the early works of Corradini et al.,¹⁹ as discussed in the Section 2.1.2. Recently, more reliable approaches have been applied, which go beyond the purely mechanics calculations (computationally inexpensive), ranging from semi-empirical approaches,¹⁴¹ quantum molecular mechanical approaches (such as embedded QM/MM method),^{15,16} full quantum mechanical calculations¹⁴² and periodic density functional calculations.^{17,22,132,133,142-144} The number of papers dealing with theoretical investigation of heterogeneous Ziegler-Natta catalysts is increasing exponentially in the last decades. In particular, the following main problems have been addressed: (i) the stability of different MgCl_2 lateral cuts either in absence or in presence of electron donors; (ii) the coordination of the Ti species on different active MgCl_2 surfaces, and the role of different electron donors in modulating the stereo-selectivity of the Ti sites; and (iii) the role of aluminum alkyls in defining the structure of the active sites.

Starting from point (i), in approaching the modeling of MgCl_2 most of the times the MgCl_2 surfaces were not allowed to relax. Un-relaxed cluster models were studied by Barino and Scordamaglia,¹⁴⁵ by Monaco et al.¹⁶ and by Seth et al.,¹⁵ who,

however, did not provide information on the relative stability of the surface models. More recently, Busico and co-workers^{17,144} carried out a periodic DFT study on the bulk and surface structure of MgCl_2 . They found that various surfaces exposing 5-coordinated Mg sites are very similar in energy and are the lowest non-trivial species. Surfaces exposing 4-coordinated Mg sites are significantly less stable, and they should normally not be formed to a significant extent. In a successive work, Credendino et al.¹³³ modelled with the same approach several MgCl_2 crystallites, investigating the effect of size, shape and number of Mg atoms exposed on the edges, arriving to define a unique rule that rationalizes their relative stability, both in presence and in absence of an electron donor. It was found that the important parameter in determining the formation energy of uncovered crystallites is the density of vacancies (measured as the ratio between the number of Mg vacancies and the number of MgCl_2 units in the crystallite). The interactions occurring between

several electron donors and the MgCl_2 support was investigated in details also by Correa et al.¹⁴³ (see Fig. 11). They found that electron donors can be separated into two main classes, depending on their coordination mode: those having a shorter spacer between the coordinating O atoms coordinate preferentially to the same Mg atom of the (110) lateral cut (chelate coordination mode); whereas electron donors having a larger spacer between the coordinating O atoms can adopt a variety of coordination modes including the “bridge” coordination mode (both oxygens of the donor are attached to two Mg atoms of the same layer) and the “zip” coordination mode (both oxygens of the donor are coordinated to two Mg atoms on different adjacent MgCl_2 layers). According to the preferential coordination mode, each electron donor may play an important role in stabilizing specific lateral cuts of MgCl_2 , thus explaining some recent experimental observation.

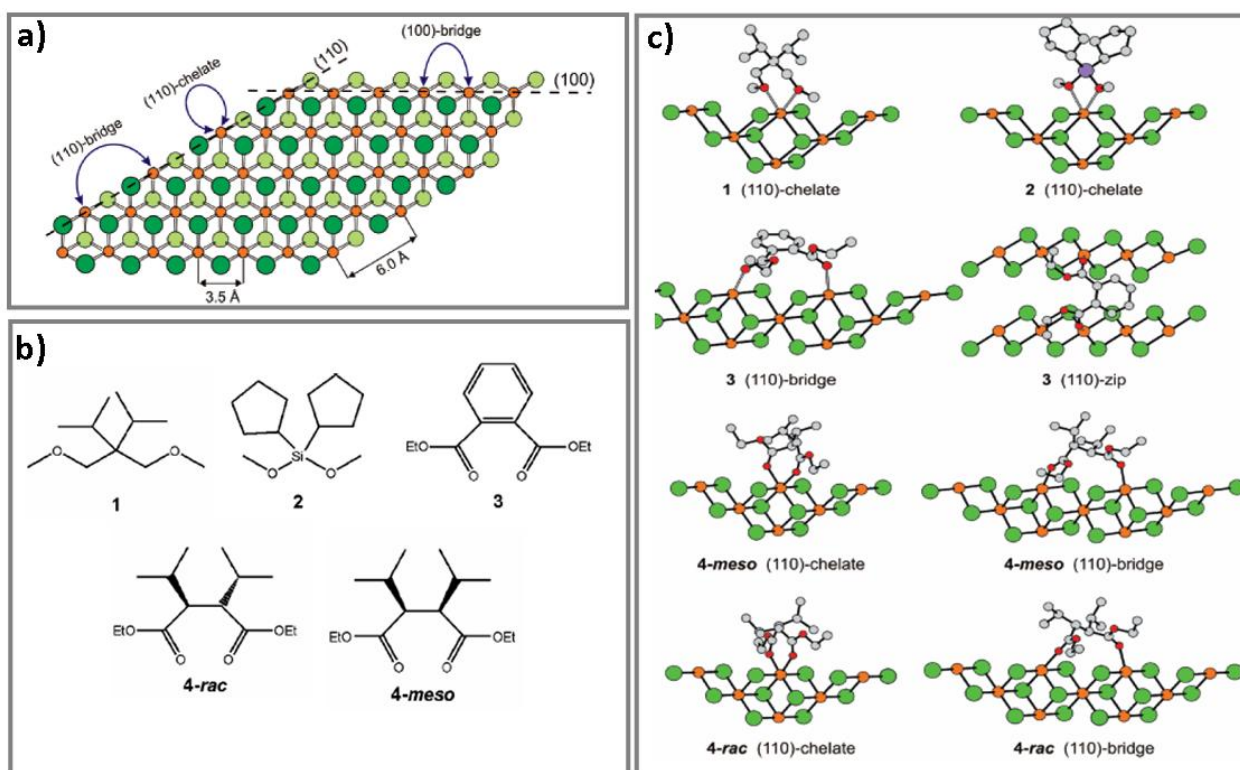


Fig. 11 Part a): Schematic representation of a MgCl_2 monolayer (Mg, Cl above the Mg plane, and Cl below the Mg plane are shown in orange, dark green and light green, respectively). The double arrow curves represent possible coordination modes of the electron donors. Part b): Example of commonly used Lewis bases. Part c): representative geometries of the Lewis bases shown in part b) coordinated to the (110) lateral cuts of MgCl_2 . Adapted from Ref. ¹⁴³.

Many efforts have been devoted to investigate the coordination of TiCl_4 on MgCl_2 surfaces (point (ii) of the list above), and controversial results were obtained by different research groups. However, most of the results concluded that TiCl_4 coordination to the (104) plane is rather weak or even unstable, whereas TiCl_4 coordination to the (110) plane is energetically favoured.^{15,16,20-22} Further models have been proposed to explain in a simple way the stereo-selective induction promoted by Lewis bases when coordinated nearby a TiCl_4 molecule adsorbed on the less stable (110) surface.¹⁴³ For this reason, an octahedral (mononuclear) Ti atom adsorbed on the (110) plane has become a good model of the real active species

and has been used often to rationalize many experimental results (see Fig. 7b, where model 1 explains the Raman spectra). In the context of stereo-selectivity, it should be mentioned that a partial mobility of the Lewis basis could explain at a certain extent the micro-structure of the produced polypropylene, and therefore should be taken in account in the near future.

Much less has been done from a theoretical point of view to understand the role of aluminum alkyls in the active sites formation (point (iii) of the list above). Only very recently, DFT calculations were undertaken in the attempt to shed light on possible pathways for reduction of Ti^{IV} to Ti^{III} and for the formation of the first Ti-C bond, which actually corresponds to

the Ti activation.¹⁴⁶⁻¹⁴⁸ However, the possible role of the aluminum alkyl in influencing the Ti sites in terms of stereoselectivity has still to be investigated. This would explain the ability of Ziegler-Natta catalysts to produce a small amount of isotactic PP even in absence of the Lewis basis.

5.2. Computational methods applied to the Phillips catalyst

In contrast to the huge amount of theoretical work devoted to the description of the Ziegler-Natta catalysts, the number of papers based on computational methods applied to the Cr/SiO₂ catalyst is still quite limited.^{76,149-155} The amorphous nature of the silica support prevented in this case the direct use of periodic codes and required the adoption of cluster models. However, a cluster approach has many limitations and introduces a high degree of subjectivity in the choice of both, the cluster (in terms of type, size, and termination) and the basis set.¹⁵⁶

A series of systematic ab initio density functional theory studies on the structure and stability of the Cr^{II} sites at the surface of silica was conducted by Espelid and Børve,^{149,150} who adopted three small silica-chromate clusters as representative of the multitude of sites present on Cr^{II}/SiO₂, as shown in Fig. 12a. Although the whole series of works merit to be cited for the pioneering character, these models have some limitations in the assumptions made in their construction, such as the neglect of the extended silica structure, as well as the accuracy with which the electronic structure is described. In particular, one of the weakest and more debated aspects is the choice to saturate the silicon dangling bonds with the very electronegative fluorine atoms. The structure, stability, and vibrational properties of the carbonyls formed on each cluster model was also investigated.¹⁵⁰ Notwithstanding the presence of fluorine, none of the models was able to reproduce the experimentally observed $\Delta\nu(\text{CO})$ values, which were strongly underestimated. Authors themselves recognized that the adopted B3LYP hybrid functional overestimated the back-donation from the Cr centres to the π^* orbitals of the CO molecule. The failure of the B3LYP hybrid functional (containing 20% of Hartree-Fock exchange) in reproducing with reasonable accuracy the experimental observables was confirmed recently by Damin et al.,¹⁵⁴ who obtained a much better agreement by increasing the percentage of Hartree-Fock exchange (up to 35-40%).

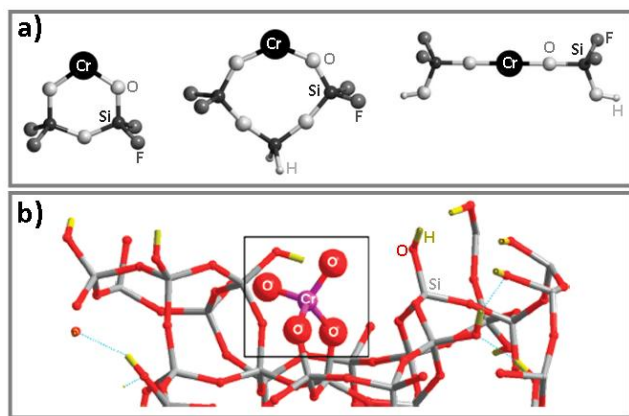


Fig. 12 Part a): Graphical representation of the three simple cluster models proposed in Refs. ^{149,150} to simulate the Cr(II) species of the Phillips catalyst. Adapted from Ref. ¹⁵⁴. Part b): Magnification of a small fraction of the surface of amorphous silica having a dioxo di-grafted

chromium species, as optimized by periodic DFT calculations. Adapted from Ref. ¹⁵⁵

Very recently, periodic DFT calculations were applied to calculate the oxidized Cr(VI)/SiO₂ catalysts at different degrees of hydration.¹⁵⁵ An amorphous silica surface slab was adopted and enabled reproduction of many experimental results. The main result is that the simple model cluster shown in Fig. 12b used to represent the dehydrated Cr(VI)/SiO₂ system is a valuable molecular representation of the oxidized catalyst. The step forward will be the simulation of the reduced form of the catalyst, for which several molecular models are possible, characterized by different Cr-O distances and O-Cr-O/Si-O-Cr angles.

Simple cluster models of the type shown in Fig. 12a were adopted by Espelid and Børve to shed light on the second major question related to the Phillips catalyst, i. e. the initiation mechanism of ethylene polymerization.¹⁵¹⁻¹⁵³ They proposed different reaction pathways characterized by different reaction energy barriers. The best model cluster found for interpreting the polymerization of ethylene by the Cr/SiO₂ system was a Cr dinuclear site, due to a low insertion barrier. More in general, the authors proposed that the energy barriers involved in the polymerization reaction via metallacycle mechanism may be lowered by the proximity of two chromium sites, even when they do not constitute a formal dinuclear site. Beside the general problem of the reliability of these simple cluster models and of the adopted functional, this observation is quite interesting from a mechanistic point of view. Very recently, it was proposed that couples of Cr sites in close proximity (or even dinuclear chromium species) would play an important role in formation of methyl branching in Phillips polyethylene through an olefin metathesis mechanism.^{157,158}

Very recently, B. Liu and co-workers¹⁵⁹ adopted DFT calculations over cluster models to achieve a basic understanding of the effect of formaldehyde coordination and desorption on the active site transformation during the induction period of the Phillips catalyst. It was found that the first reaction over cluster models on which either one or no formaldehyde molecule is adsorbed follows the metallacyclic mechanism into chromacyclopentane. Subsequent dimerization to 1-butene and metathesis to propylene and ethylene are more favourable when one formaldehyde molecule is adsorbed. Only after a complete desorption of formaldehyde does further ring expansion to chromacycloheptane, followed by 1-hexene formation, become preferential. Moreover, a spin state crossing from quintet di-ethylene-Cr(II) complex to triplet chromacyclopentane with a spin acceleration effect was revealed.

5.3. Final remarks on the role of theoretical methods

The use of computational methods to study metal-catalysed olefin polymerisation is increasing fast and very often publications in the field rely entirely on theoretical results, especially for Ziegler-Natta catalysts. This is a consequence of the fast improvement of the computational methods in terms of speed and reliability from one side, and of the difficulty in performing experiments to characterize the active sites from the other side.

Periodic DFT calculations were able to answer many questions on the Ziegler-Natta catalysts, although many others that could be potentially addressed by theoretical methods are

still open, such as are the role of defect sites, the role of different Lewis basis in determining the catalyst activity, and in changing the morphology of MgCl_2 crystals during the catalyst synthesis. It should be remarked that dispersion contributions play a fundamental role in the evaluation of the adsorption energies, as demonstrated recently in the elegant work of D'Amore et al.,²² where it is shown that the binding of TiCl_4 onto MgCl_2 is dominated by such long-range interactions. Although the electronic interactions between different MgCl_2 layers are expected to be small, steric hindrance on one layer by the next could be potentially an important factor in determining binding strengths of bulky donors or in tuning the selectivity of different active sites. Therefore, any future computational method aiming to describe these aspects of Ziegler-Natta catalysis must include a reasonable description of interlayer binding. On the contrary, cluster models were adopted up to now to simulate the properties of Cr sites in the Phillips catalyst. The calculations performed so far demonstrate that care must be taken in the choice of both, models and functionals adopted; but simple cluster models seem able to reproduce most of the experimental results. Further progress in this field would be the ability to simulate the electronic properties of the grafted chromium sites as a function of the structural parameters; and the systematic investigation of ethylene coordination and polymerization over different Cr structures.

For both Ziegler-Natta and Phillips catalysts, the results of theoretical calculations need to be compared with experimental data. Therefore, the fast increase of works entirely based on theoretical methods must be followed by an increased effort in experimental characterization and a constant dialog between experimentalists and theoreticians is a fundamental pre-requisite for further advances in the field.

Conclusions

Evolution of heterogeneous catalysts for olefin polymerization has been a subject of remarkable industrial importance over the last half a century, and at the same time, has fascinated scientists. Likely, this interest will remain high for some time to come, in view of the huge quantities in which polyolefins are produced and of their increasing number of applications. A rational catalyst design appears to be the logic alternative to the trial-and-error approach, which is still the most applied method to carry out catalyst's evolution. However, a rational design requires a deep understanding of the active sites and of how they work, and this goal can be achieved only thorough the direct experimental observation of the working centres, as well as of reaction intermediates. The need of suitable characterization techniques directly follows.

The results summarized in this review provide an evidence that spectroscopic methods do have enough sensitivity to highlight the structure and the properties of the active sites for both Ziegler-Natta and Phillips catalysts, which are the two classes of heterogeneous olefin polymerization catalysts accounting for most of the production of HDPE and i-PP. It was shown that both classes of catalysts have in common similar problems and open questions, and that the methods to solve the problems and to answer the questions can be the same. One of the main problem of any spectroscopic technique is that usually they give

information on the whole population of the metal sites, whereas in most of the cases only a small fraction is *really* active in olefin polymerization. The best approach to face this issue is to carefully combine the data obtained with different spectroscopic methods and compare them with results coming out from theoretical calculations; and this should be the strategy to be followed in the near future to get further advances in the field.

Finally, it comes out that an intense and constant discussion between scientists working on Ziegler-Natta catalysts and scientists working on Phillips catalysts would be beneficial for both parts; there should not be any limits between the two communities, rather we should speak about a single community.

Acknowledgments

We wish to thank all the colleagues (younger and less young) who shared with us the passion for spectroscopy and catalysis. This work was supported by Progetti di Ricerca di Ateneo-Compagnia di San Paolo-2011 - Linea 1A, progetto ORTO11RRT5.

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