Surface chromium single sites: open problems and recent advances

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The results of decades of studies on the Phillips chromium (Cr)/silica polymerization catalyst are briefly summarized. The application of several characterization methods has allowed a detailed knowledge of the structure and reactivity of Cr centres to be obtained. In particular, many aspects of this apparently simple single-site catalyst, including the heterogeneity, the modification of the ligand sphere upon interaction with many molecules and the initiation mechanism of the ethylene polymerization reaction, have been clarified. It is shown that based on the acquired knowledge, it is now possible to proceed further towards the intelligent modification of the ligand sphere with the scope to increase the reaction rate and selectivity. It is also illustrated that, besides polymerization/oligomerization reactions, it is possible to extend the study of CrII reactivity towards new reactions.

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1. Single-site heterogeneous catalysts: a definition

Following the usual definition, a single-site heterogeneous catalyst is constituted by metal atoms, ions or small clusters of atoms, held to a rigid framework through surface ligands; these sites are isolated inside the hosting structure (Thomas & Thomas 1996; Zecchina et al. 2011). In some cases, the hosting matrix has crystalline character, and the position of the hosted centres is (consequently) well known. This is the case of the popular titanium silicalite (TS-1) catalyst where isolated titanium (Ti) centres occupy tetrahedral positions in substitution of silicon atoms in the mordenite framework inverted (MFI) structure (Ricchiardi et al. 2001). In the presence of reactants, the Ti centres assume a more open structure, where the metal atoms display a full ability to bind substrates, and where bonds are broken and formed.

However, in numerous and industrially relevant catalysts, the supporting solid (or rigid framework) is amorphous or, when crystalline, it exposes several different faces. In such cases, several anchoring situations are possible, characterized

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by different surface ligand arrangements whose structure is usually not well known. Heterogeneity of sites differentiates the heterogeneous single-site catalysts from the homogeneous counterparts, whose ligand sphere is, in principle, more accurately engineered. As a consequence, heterogeneous catalysts are often considered less defined than homogeneous ones. Nevertheless, many reactions catalysed by homogeneous single-site catalysts are characterized by an induction period, which suggests that the employed monometallic complexes are simply precursor species, whereas the real catalyst is formed successively only through interaction of these precursors with reagents. In other words, as mentioned for TS-1, also in homogeneous single-site catalysts, only the structure of the precursor species is well known; on the contrary, the structure of the active species formed in the presence of reactants is usually more the result of reasonable hypotheses on the nature of the reactions occurring during the promotion/induction phase, than of direct determination by means of structural methods (Zecchina et al. 2007).

Elucidation of the structure of active centres in single-site catalysts (both heterogeneous and homogeneous) requires the application of accurate characterization methods, such as vibrational (IR and Raman), UV–vis near-IR, X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy, magnetic resonance (electron spin resonance and nuclear magnetic resonance) and electron (electron energy loss spectroscopy, X-ray photoelectron spectroscopy and others) spectroscopies. The characterization of the active sites could be complex because of the presence of many types of sites (instead of only one) and because the active centres can represent a small fraction of the total species present in solution (homogeneous catalysts) or on the surface (heterogeneous catalysts). The choice of the best physical methods to be used depends upon the type of catalyst and reaction under investigation. The only general rule which can be advanced is that the characterization method must be able to distinguish between spectator and active species.

2. The chromium/silica Phillips catalyst for ethylene polymerization

(a) The structure of the active chromium sites

The Cr/SiO₂ Phillips catalyst for ethylene polymerization is by far one of the simplest single-site heterogeneous catalysts (McDaniel 1985; Groppo et al. 2005b; McDaniel 2010). The common synthesis receipt is very simple, as shown in figure 1. The surface hydroxyl groups of amorphous silica (figure 1a) react with a Cr precursor (such as chromic acid) forming surface chromate species (figure 1b). The Cr loading is very low, usually lower than 1.0 wt%. The activation procedure can be performed in two different ways. Industrially, the surface chromates are directly treated with ethylene at about 80–100°C; after an induction period, reduced Cr^{II} sites are formed that are able to polymerize ethylene with a high efficiency. Following the model route, the surface chromates are first reduced to Cr^{II} by CO with the attendant formation of CO₂, which is released without interference with the catalyst; a fraction of the so-formed Cr^{II} sites (figure 1c) are then able to polymerize ethylene at room temperature, without any induction period. In terms of productivity, the two activation routes are equivalent.
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Figure 1. (a–d) Schematic of the preparation and activation of Cr/SiO₂ Phillips catalyst for ethylene polymerization following either the industrial (path b–d) or the model (path c–d) route. The surface chromates (species 1; b) and the anchored Cr(II) sites (species 2; c) are both precursors of the same active species (d). The structure of the Cr active centre is hypothetical and is based on an analogy with the structure of active species in metallocenes and Ziegler–Natta catalysts; the active species contains a coordination vacancy available for ethylene coordination (coloured shadow). Hydrogen, oxygen and chromium atoms are represented as small, medium and large spheres, respectively. The silica surface is schematically shown in grey. (Online version in colour.)

(figure 1d). Surface chromate species (CrVI) or anchored CrII involve the totality of Cr present in the catalysts; therefore, this system can be properly considered as a model.

Owing to the amorphous character of the silica support, the environment of the anchored chromate species and the coordination sphere of reduced Cr ions is not well defined. For instance, for anchored CrII sites, besides the two SiO₂ groups linking CrII to the framework, a variable number of weaker ligands can be present, such as oxygen atoms of adjacent siloxane bridges. For this reason, it is better to speak of different types of single sites. In the past 50 years, the structure of the Cr ligand sphere was studied by means of many techniques (Weckhuysen et al. 1996; Groppo et al. 2005b; McDaniel 2010). Both indirect methods (mainly Fourier transform IR (FTIR) spectroscopy, using CO, NO and N₂ as probes of the number and reactivity of coordination vacancies; Zecchina et al. 1975a, b; Groppo et al. 2005c; Lamberti et al. 2010) and direct methods (such as UV–vis, XANES, resonant Raman spectroscopies and others; Weckhuysen et al. 1995; Groppo et al. 2005a; Damin et al. 2006; Moisii et al. 2006; Demmelmaier et al. 2009; Gianolio et al. 2010; Wachs & Roberts 2010) were able to give useful information on the CrII coordination sphere before and after interaction with reactants. It was found that the structure of reduced CrII sites is not as simple as it should appear at first consideration.
At least three types of different CrII species are present, differing in the number of available coordination vacancies. These species form with CO and NO different CrII(CO)_n and CrII(NO)_n complexes where, depending on the temperature, n can be as high as 3 or 4 (Zecchina et al. 1975a,b, 2010; Groppo et al. 2005b). It was proved that the position of the CrII sites on the silica surface can change under the influence of adsorbates (Gianolio et al. 2010), suggesting that the different types of CrII species protrude on the surface at different extents. When probed with O2, CO or NO, which strongly interact with the metal ions, the original heterogeneity of the CrII precursor centres is partially flattened. For instance, reaction of CrII with oxygen leads to instantaneous extraction of CrII from the anchoring surface and the formation of protruding chromates whose structure is no more substantially reminiscent of the underlying arrangements of surface siloxane ligands. Although most of the sites are able to form CrII(C2H4)_n complexes (with n = 1 or 2; Groppo et al. 2005c), only a fraction of them further evolve into the catalytically active species, and thus initiate ethylene polymerization at room temperature (Groppo et al. 2006b). A possible explanation is that only the most protruding CrII precursors are reactive enough to form the active sites by interaction with ethylene. The heterogeneity of CrII sites is thought to be the basis of the broad molecular weight distribution characteristic of Phillips polyethylene (McDaniel 2010).

(b) Mechanism of initiation of ethylene polymerization

The Phillips catalyst is peculiar among all the olefin polymerization catalysts because it is the only one for which the formation of the active centre does not involve the use of an activator, such as methylaluminoxane or aluminium alkyls (McDaniel 2010). The sole reactant (ethylene) is doing the job. As anticipated, two types of precursor species could be present according to the activation procedure: surface chromates (species 1 in figure 1b) or anchored CrII (species 2 in figure 1c). The active catalytic centre originated by both precursors is assumed to be the same (figure 1d) because the polyethylene obtained in the two cases is the same. By analogy with the Cossee–Arlman mechanism (Arlman & Cossee 1964; Cossee 1964), proposed for classical Ziegler–Natta catalysts (Ziegler et al. 1955; Natta 1956; Busico et al. 1999), as well as for metallocene catalysts (Resconi et al. 2000; Kaminsky & Laban 2001), it is arbitrarily assumed that the catalytic centre contains a coordination vacancy (coloured shadow in figure 1d), where the olefin molecule can insert, and a growing hydrocarbon chain. However, the initiation steps leading to the formation of the active centres constituted a matter of debate for many years, and were the subject of many investigations, also by means of surface science methods (Groppo et al. 2005b).

When the precursor structure is the chromate (industrial catalyst), the first step should imply the reduction of CrVI. Owing to the stability of the tetrahedral chromate structure, the reduction process proceeds only at a temperature higher than about 80°C. Many studies were devoted to investigate both the nature of the by-products obtained after reduction of chromates (mainly formaldehyde) and their possible influence on the formation of the active Cossee-type centres shown in figure 1 and, ultimately, on the polymerization mechanism. Some important mechanistic details were obtained by investigating the induction period before ethylene polymerization by means of temperature-programmed reduction coupled

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with mass spectrometry (Liu et al. 2003; Xia et al. 2009). Because the first and second hydrocarbon species found during the induction period were propylene and butene, an ethylene metathesis initiation mechanism was proposed. CrII species coordinated with formaldehyde, which is formed by the redox reaction between hexavalent chromate species and ethylene, act as the metathesis active precursors. Thus, the induction period corresponds to not only the reduction of surface chromate CrVI species to CrII species, but also to the initiation of bonding between Cr and carbon (C) through an ethylene metathesis mechanism.

Because of the complexity of reaction on the chromate precursors, our research group preferred to investigate the initiation steps of the ethylene polymerization mechanism on the reduced form of the Phillips catalyst, which contains only anchored CrII ions as precursor species. Indeed, in this case, the CrII precursors are transformed into the active species by interaction with ethylene, without the intervention of the by-products formed during the reduction of chromates. In particular, temperature- and pressure-resolved ethylene polymerization experiments allowed the detection of transient intermediates and clarification of the complexity of the initiation mechanism. The main conclusion of many studies on the topic was that the initiation mechanism involves cyclic intermediates (Bordiga et al. 2003; Groppo et al. 2005c, 2006a, 2007; Lamberti et al. 2007). A similar cyclic mechanism was also proposed for Cr-based homogeneous dimerization and trimerization catalysts (Ruddick et al. 1996; Dixon et al. 2004; McGuinness 2011).

Another fundamental question surrounding the Phillips catalyst is how each ethylene monomer is incorporated into a polymer chain, i.e. the chain growth mechanism. In contrast to the above-mentioned strong evidence of metallacycles during the initiation step, very recently, metallacycles have been ruled out as the main chain growth process in favour of the standard Cossee–Arlmann mechanism (McGuinness et al. 2010). According to this model, the active species during the propagation step should be a CrIII-alkyl (Theopold 1997, 1998) or a CrIV-dialkyl (Amor Nait Ajjou & Scott 2000), similar to the structure of the active sites in Ti-based heterogeneous Ziegler–Natta catalysts. The results obtained on the structure of the active sites during initiation and propagation are not inconsistent with each other because the metallacycle initiation mechanisms could lead to a CrIII-alkyl or CrIV-dialkyl growth centre (Groppo et al. 2005b). Finally, it is worth noticing that there is an important difference between Phillips and classical heterogeneous Ziegler–Natta catalysts, in that the Phillips catalyst cannot be used for stereo-specific polymerizations. This fact can be easily understood when the structural simplicity of the ligand sphere is considered. This does not mean that the Phillips catalyst does not show selectivity properties. In fact, the molecular weight of the polymeric chains can be modulated by changing the hydroxyl group’s population present on the silica surface, i.e. its surface strain (Groppo et al. 2005d).

(c) Engineering of the ligand sphere by means of activators

Attempts to modify the Phillips catalyst in order to obtain polyethylenes with different properties have been continuously made over past decades. In this respect, the above-mentioned annealing method (Groppo et al. 2005d) is a way to fine tune the relative populations of CrII sites, and thus the molecular
weight distribution of the polyethylene product. More recently, based on the addition of specific surface modifying agents, finer methods have been adopted (Nenu & Weckhuysen 2005; Nenu et al. 2006, 2007). In addition, the possibility of changing the catalytic activity of Cr/SiO₂ by altering the chemical composition of the support has been known since the 1970s. Ti, fluorine, boron or alkali metal ions have been investigated, but Ti is by far the most studied modifier (McDaniel 1985; Cheng et al. 2010). Depending on the choice of support, Cr catalysts can produce anything from liquid oligomers and low molecular weight wax to ultrahigh molecular weight grades. Polydispersity can vary from narrow (\(M_w/M_n < 4\) as in Ziegler polymers) to extremely broad (\(M_w/M_n > 100\)). Very recently, new attempts have been made to modify, in an intelligent way, the ligand sphere of CrII precursors through the intervention of promoters (Groppo et al. 2011; Barzan et al. 2012), similar to the approach adopted in enhancing the activity and stereo-selectivity of homogeneous metallocene catalysts, for which the ligand sphere is appropriately designed. A rational modification of the Cr sites on the Phillips catalyst was possible on the basis of the knowledge acquired in several years of research on the basic chemistry and on the structure of the CrII centres obtained after reduction in CO.

Two different paths have been considered experimentally, and are summarized herein. The first approach was based on the idea of increasing the fraction of protruding Cr centres able to initiate ethylene polymerization at room temperature. N₂O was chosen as a promoter because of its potential in releasing a single oxygen atom, following the path \(N₂O \rightarrow N₂ + O_{ads}\) (Panov et al. 1990; Li & Armor 1992; Yuzaki et al. 1998; Rivallan et al. 2009; Zecchina et al. 2010), with the formation of protruding mono-oxo CrIV species (species 3 in figure 2). This hypothesis was inspired by the well-known effect of dioxygen, which is able to extract the Cr ions from the original position through the formation of surface chromates (species 1 in figure 2). However, the main drawback in the use of dioxygen is that, although protruding, chromates are fully saturated, and therefore react with ethylene only at 80–100°C, forming redox by-products that can act as poisons of a fraction of sites. To circumvent the stability problem of chromates, we thought that the adsorption at a single CrII centre of a single oxygen atom through \(N₂O\) dissociation could have the ability to extract the CrII centre from the anchoring surface, without the formation of a fully saturated (and hence less-reactive) species. The validity of this approach was confirmed recently (Groppo et al. 2011). It was demonstrated that \(N₂O\) dissociates on all (or nearly all) CrII centres, with the attendant formation of coordinatively unsaturated mono-oxo CrIV=O species (species 3 in figure 2). The so-formed protruding mono-oxo CrIV=O species react readily at room temperature with ethylene, with generation of the catalytic centres; ethylene polymerization proceeds at room temperature and involves the majority of Cr centres. As a result, an increment in the initial reaction rate by approximately one order of magnitude was observed by in situ FTIR spectroscopy (sequence of spectra shown in the bottom part of figure 2).

As for the second approach, the potential ability of silane in modifying the coordination sphere of CrII centres, in positively influencing the reaction rate and, finally, in modifying the molecular weight distribution and the polymer branching, has been explored. The choice of this molecule as a modifying agent was stimulated by old observations documented recently by McDaniel.
Figure 2. (a) Schematic of silica-grafted chromate in the fully oxidized catalyst (species 1), corresponding CO-reduced Phillips catalyst precursor (species 2) and hypothesized mono-oxo CrIV=O surface species on the modified catalyst (species 3). (b) Ethylene polymerization kinetics on the standard CrII/SiO2 and modified catalyst obtained by collecting FTIR spectra within the first 2 min of reaction. FTIR spectra in the δ(CH2) region are shown; the intensity of the IR band at 1472 cm⁻¹ is reported versus time in the inset. (Online version in colour.)

(2010), who reported that the Cr/SiO2 Phillips catalyst is able not only to produce high-density polyethylene (HDPE) but also, when pre-treated with metal alkyl ‘cocatalysts’ such as AlR3, BR3 and ZnR2, linear low-density polyethylene (LLDPE) via in situ branching (figure 3a). The most effective cocatalysts are the hydrosilanes, provided that they contain at least an Si–H group. However, the effect of hydrosilanes in affecting the structure of the Cr sites was never investigated in detail, and only a few hypotheses were advanced in the specialized literature. In particular, the in situ production of α-olefins with a Phillips catalyst in the presence of hydrosilanes was claimed on the basis of the analysis of the final polymer product (amount of branching in the polymer, density, molecular weight distribution), but there was no direct experimental evidence of the processes occurring on the active sites at a molecular level. In a recent paper (Barzan et al. 2012), ethylene polymerization reactions on a CrII/SiO2 sample pre-treated with silane were investigated by FTIR spectroscopy. It was found that the reaction rate was increased by approximately an order of magnitude with respect to that shown by the parent CrII/SiO2 (as
found after pre-treatment of Cr$^{II}$/SiO$_2$ with the N$_2$O promoter). Moreover, the FTIR spectrum of the polymer obtained with the silane-modified catalyst was characterized by distinct absorption bands assigned to methyl groups, which indicate that the polymer growth is accompanied by branching. The FTIR results were further supported by complementary differential scanning calorimetry and size-exclusion chromatography measurements. In the same paper, it has been also demonstrated that by adopting temperature- and pressure-resolved FTIR spectroscopy under operando conditions, intermediate α-olefin species can be observed before their incorporation in the polymer chains (figure 3b). These results gave a direct spectroscopic insight into the in situ branching process at the basis of the LLDPE production by an SiH$_4$-modified Phillips catalyst.

3. Chromium/silica beyond polymerization

Cr sites grafted on amorphous silica or mesoporous silica or zeolitic materials have been recently investigated as catalysts in photocatalytic reactions such as CO oxidation in the presence of H$_2$, NO decomposition, partial oxidation of propane, oxidation of propene or other selective oxidation reactions, such as cyclohexane to cyclohexanone (Yamashita et al. 2001; Kamegawa et al. 2006; Anpo et al. 2009; Thomas et al. 2009). Usually, the starting point is Cr$^{VI}$ in the form of chromate, and a charge transfer excited state is claimed as intermediate species, sometimes as Cr$^V$ and others as Cr$^{IV}$. Often, the same reactivity is shown by Ti or Mo similarly grafted species. Other interesting reactions catalysed by Cr on siliceous materials are dehydrogenation reactions (of alkanes) and epoxidation (of styrene,
as an example. In all cases, a change in the Cr oxidation state is required, and usually the game is played between CrVI and CrIV. These observations suggest that the redox properties of anchored chromates (CrVI), chromyls (CrIV) and CrII species are far from being fully explored. Along this line, we anticipate that grafted CrII species are able to interact not only with the triatomic species N2O, but also with CO2 following the path CO2 + CrII → CO + (CrIV=O), which is similar to that depicted for N2O (E. Groppo, C. Barzan, J. G. Vitillo, A. Zecchina 2012, unpublished data).

4. Conclusions

During decades of studies on the Cr/SiO2 catalyst, a very detailed knowledge of the structure and reactivity of grafted Cr centres has been obtained. The application of several characterization methods has allowed clarification of many aspects of this apparently simple single-site system, including the heterogeneity, the modification of the ligand sphere upon interaction with many molecules and the initiation mechanism of the ethylene polymerization reaction. On the basis of the acquired knowledge, it is now possible to proceed further towards an intelligent modification of the ligand sphere, with the final aim to increase the reaction rate and selectivity. In addition to olefin polymerization and oligomerization reactions, it is also possible to extend the study of Cr reactivity towards new reactions.

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