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Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/141458> since 2016-10-08T15:54:24Z

Published version:

DOI:10.1002/chem.201303156

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This is an author version of the contribution published on:

Questa è la versione dell'autore dell'opera:

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Chem. Euro J., **19** (2013) 17277-17282

DOI: 10.1002/chem.201303156

The definitive version is available at:

La versione definitiva è disponibile alla URL:

<http://onlinelibrary.wiley.com/doi/10.1002/chem.201303156/abstract>

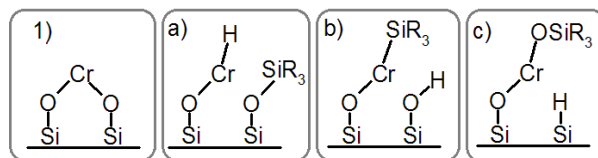
The effect of hydrosilanes on the active sites of the Phillips catalyst: the secret for in situ α -olefin generation

Caterina Barzan,^[a] Diego Gianolio,^[b] Elena Groppo,^{*,[a]} Carlo Lamberti,^[a] Vincent Monteil,^[c] Elsje Alessandra Quadrelli^{*,[c]} and Silvia Bordiga^[a]

Polyolefins are among the most widespread plastics in use today; in 2010 their world production amounted to more than 120 Mt, 30% of which was constituted by polyethylene.^[1] A dominant share of polyethylene market is based on the silica-supported chromium-based Phillips catalyst (Cr/SiO_2),^[2] whose largest industrial application is high-density polyethylene (HDPE) production (about 40–50% of the total HDPE market).^[1] Modified versions of the Phillips catalyst account for the production of some linear-low-density polyethylene (LLDPE), either by ethylene/ α -olefins co-polymerization or directly from neat ethylene polymerization.^[1] This latter co-monomer-free industrial process presents several commercial advantages with respect to the co-polymerization route,^[1,3,4] such as: i) lower feedstock cost (ethylene is cheaper than the typical co-monomers), ii) feasibility on production sites where the co-monomer is not available, and iii) reduced cost of loading, purification, storage, feeding or downstream recycling in absence of co-monomer. Consequently, modified Phillips catalysts capable of yielding LLDPE without the use of external α -olefins as co-monomers have become the basis for some unique low-density commercial polymer grades introduced during the early 1990's.^[1,5]

In 1991 Martin et al.^[6] patented the use of hydrosilanes as modification agents for the Cr/SiO_2 catalyst to produce LLDPE by co-

monomer free ethylene polymerization. Among many co-catalysts (such as AlR_3 , BR_3 , MgR_2 and ZnR_2),^[5d] hydrosilanes remain the most effective ones for specific LLDPE production.^[1] So far, mechanistic insight into such hydrosilane-induced modification has been gathered essentially from the analysis of the resulting reaction products. The presence of large quantities of α -olefins along with LLDPE was traced back to the ability of the hydrosilane-modified catalyst in oligomerizing ethylene to short α -olefins, which are then incorporated in the growing polymer chain through an “*in situ* branching” mechanism.^[1] More recently, the α -olefins produced in situ were detected by means of temperature- and pressure-resolved FT-IR spectroscopy before their incorporation in the polymeric chain.^[7] All the hydrosilane compounds presenting at least one Si-H bond have been claimed to act as efficient modifiers of both the oxidized and reduced Phillips catalyst, whereas tetra-alkylsilanes have no effect.^[1] This observation, combined with the analysis of the resulting polymer, led to the proposal of a chromium hydride as the catalytically active modified site (structure a) in Scheme 1), originated by the cleavage of a Cr-O bond from the starting Cr species (structure 1) in Scheme 1).^[1] However, other possible structures can be hypothesized for the chromium modified sites, such as those shown in Scheme 1b) and c).



Scheme 1. Schematic representation of the local structure of starting Cr sites in $\text{Cr}(\text{II})/\text{SiO}_2$ (part 1) and possible structures for the hydrosilane-modified Cr sites (parts a, b and c). Note that in part 1) the active Cr sites are considered to be in +2 oxidation state, as accepted by the majority of authors, although some works are in favour of +3 oxidation state.^[1]

Despite the commercial and fundamental interest in the hydrosilane-modified Phillips catalysts presented above, no direct observation of the modified catalytic sites has been reported so far.

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Hereafter, we present the first molecular-level spectroscopic study of a hydrosilane-modified Cr(II)/SiO₂ catalyst active in LLDPE production. The data shown are related to triethylsilane (TES) as modifying agent, but other hydrosilane compounds have shown similar modifications, both in terms of polyethylene product and of the chromium sites.

The polyethylenes obtained with TES-modified Cr(II)/SiO₂ catalyst (hereafter **Cr_{TES}**) and SiH₄-modified Cr(II)/SiO₂ catalyst^[7] show similar physical properties (see Table 1, Figure 1 and S2), in agreement with literature data.^[1] In particular broad bimodal molecular weights distributions, reported in Figure 1 are observed, composed of an heavier component in the same molecular weight range to that obtained with the Cr(II)/SiO₂ (hereafter **Cr_{PHL}**) catalyst ($M_p \sim 10^5$ g mol⁻¹) and a very low molecular weight fraction ($M_p < 10^3$ g mol⁻¹). These polymers exhibit low T_m values (123°C) characteristic of a branched polyethylene, corresponding to LLDPE. The results are in agreement with in situ FT-IR studies during ethylene polymerization (Figure S1), evidencing a higher level of CH₃ moieties (characteristic of higher branching) with respect to the polymer obtained with **Cr_{PHL}**.^[7]

Table 1. Melting temperature (T_m) and molecular weight distribution (M_p or dispersity $D = M_w/M_n$) of the polyethylenes obtained with Cr(II)/SiO₂ catalyst without modifiers and after modification with SiH₄ and TES.

Modifying agent	T_m (°C)	molecular weight distribution (g mol ⁻¹)
-	134	$M_p = 320000$ ($D = 7.0$)
SiH ₄ ^[a]	123	bimodal: $M_{p1} \sim 500$ / $M_{p2} \sim 100000$
TES	123	bimodal: $M_{p1} \sim 320$ / $M_{p2} \sim 100000$

^[a] Data from Ref. ^[7]

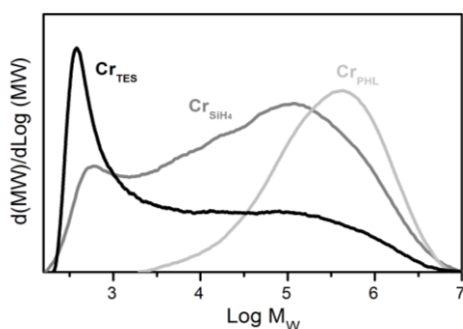


Figure 1. Molecular weight distributions obtained from size exclusion chromatography (SEC) of the polyethylenes obtained on **Cr_{PHL}** (in light grey), **Cr_{SiH4}** (in dark grey) and **Cr_{TES}** (in black).

The reactivity of TES with Cr(II)/SiO₂ at room temperature *before* ethylene polymerization was studied *in situ* by FT-IR spectroscopy. Figure 2a shows the IR spectrum of *i*) the initial **Cr_{PHL}** catalyst (black), *ii*) after exposure to an excess of TES from the gas phase (light grey), and *iii*) after prolonged degassing at room temperature (dark grey). The absorption band at 2100 cm⁻¹ due to $\nu(\text{Si-H})$, present after exposure to an excess of TES and assigned to physisorbed un-reacted TES (light grey), disappears after prolonged degassing (dark grey spectrum), providing an evidence that no physisorbed TES remains on the surface of **Cr_{TES}**. On the contrary, the IR absorption bands due to the alkyl groups (in the 3000-2700 cm⁻¹ and 1500-1350 cm⁻¹ regions) remain observable, although less intense, showing that some chemisorption of TES involving a loss of the Si-H bond has occurred. These IR absorption bands are not observed when the same experiment is performed on pure SiO₂ treated at the same temperature; hence, the Cr(II) sites are involved in the reaction with TES.

In situ FT-IR spectroscopy of CO adsorbed on **Cr_{TES}** at room temperature was used to probe the coordinative unsaturation of the chromium sites in the catalyst. This method is largely employed in the characterization of surface sites^[8,9] and in particular of Cr(II) sites in **Cr_{PHL}**.^[10,11] The IR spectrum of **Cr_{PHL}** in interaction with CO at room temperature (black in Figure 2b) shows a characteristic triplet of bands in the $\nu(\text{CO})$ region (absorption bands at 2191, 2184 and 2179 cm⁻¹) due to “non-classical” mono- and di-carbonyls formed on a variety of Cr(II) species, grafted on the silica surface through two siloxy [$\equiv\text{SiO}^-$] monoanionic ligands and in interaction with a different number of adjacent siloxane bridges (vide infra Scheme2, structure b).^[11-13]

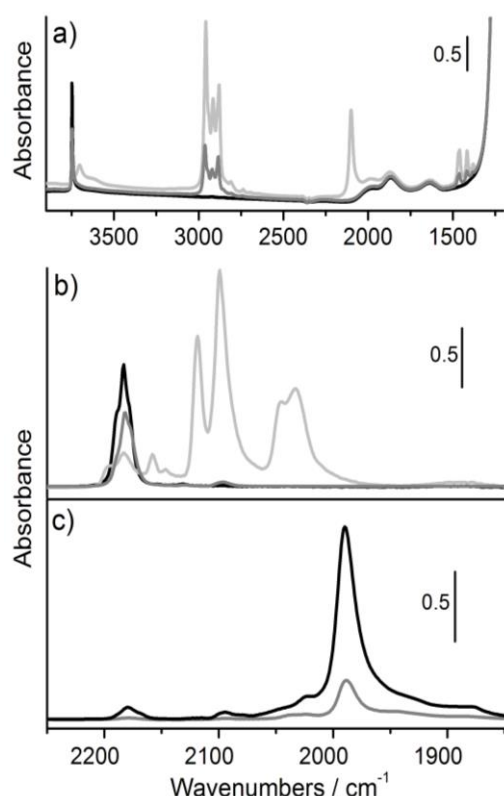


Figure 2. Part a): FT-IR spectra of **CrPHL** before (black) and after (light grey) interaction with TES from the vapour phase, and after prolonged degassing (dark grey). Part b): FT-IR spectra in the $\nu(\text{CO})$ stretching region of CO adsorbed at room temperature (equilibrium pressure = 100 Torr) on **CrPHL** before (black), and after 1 minute of ethylene polymerization (dark grey). The spectrum of CO adsorbed on **CrPHL** at 100 K is also shown (light grey curve). Part c): the same as part b) for CO adsorbed on **CrTES**.

The non-classical nature of the formed carbonyl complexes, due to the fact that charge and σ effects of the M-CO system outweigh any π -backdonation effects, revealed also that silica plays an active role in stabilizing Cr(II) sites in geometries which are unlikely for homogeneous complexes. The IR spectrum of CO adsorbed at room temperature on **CrTES** catalyst (black in Figure 2c) displays only traces of such “non-classical” triplet characteristic of unmodified **CrPHL**-species, demonstrating that a substantial fraction (over 85%) of the Cr(II) sites was modified by TES. Instead, the IR spectrum is dominated by a strong and sharp absorption band at 1990 cm^{-1} (accompanied by a weaker absorption band at 2024 cm^{-1}), which indicates the formation of “classical” chromium carbonyl species (*i.e.* characterized by a strong Cr \rightarrow CO π -backdonation contribution, which overcomes the Cr \leftarrow CO σ -donation and leads to the weakening of the C-O bond),^[14] as typically observed in

homogeneous organometallic carbonyl complexes, including chromium complexes.^[15-18] In order to quantify the number of CO molecules that adsorb on **CrTES**, the same IR experiment was repeated with ^{13}CO and with a mixture of ^{12}CO and ^{13}CO isotopes in 1:1 ratio. The results (shown in section S4) indicate that di-carbonyl species are prevalently formed.

By lowering the temperature of the sample in presence of CO (*i.e.* increasing the CO pressure on **CrTES**) no substantial changes in the IR spectrum are observed. This behaviour is markedly different from that shown by **CrPHL** for which, upon lowering the temperature, a multitude of “classical” IR absorption bands in the $2100\text{--}1950\text{ cm}^{-1}$ region appear to the expenses of the starting “non classical” triplet (light grey line in Figure 2b).^[11,12b,17b] This phenomenon on **CrPHL** was attributed to a ligand displacement of the aforementioned adjacent siloxane bridges by a third incoming CO ligand,^[11,12b,19] and provided a further evidence that silica is not an inert support but behave as an active ligand in the definition of the Cr(II) properties. The lack of novel $\nu(\text{CO})$ absorption bands in the IR spectrum of **CrTES** upon decreasing temperature in presence of CO indicates that, if present in the coordination sphere of **CrTES**, siloxane ligands are strongly interacting and not easily displaceable. The formation of classical carbonyls at room temperature implies that the modified Cr sites are able to optimize the interaction with CO already at the lowest coverage.

Additional information on the properties of the modified Cr sites can be obtained by repeating the *in situ* FT-IR experiment of adsorbed CO on **CrTES** after ethylene polymerization (the results obtained during the polymerization being analogous to those already reported for SiH_4 -modified catalyst,^[7] see above and in Figure S1). As previously reported for **CrPHL** catalyst,^[13a] the difference between the IR spectrum of adsorbed CO before and after ethylene polymerization gives a direct estimation of the fraction of active Cr(II) sites (*i.e.* no longer available for CO adsorption because carrying the polymer chain).^[13b] The IR spectra of CO adsorbed on both **CrPHL** and **CrTES** after one minute of ethylene polymerization at room temperature are shown in Figure 2b and c, respectively (dark grey). For **CrPHL** catalyst 90% of the original

$\nu(\text{CO})$ triplet is observed after polymerization, which means that only 10% of the Cr(II) sites are active, in agreement with literature reports.^[13,20,21] On the contrary, the IR spectrum of CO adsorbed on **Cr_{TES}** after ethylene polymerization shows a drastic decrease of all the IR absorption bands, accounting for a total of 80% of sites. Note that all the residual unmodified sites react with ethylene (no residual triplet around 2180 cm^{-1}). The much higher fraction of active Cr sites explains the faster ethylene polymerization rate observed for **Cr_{TES}** with respect to **Cr_{PHL}**.^[1,7]

In conclusion, FT-IR spectroscopy of adsorbed CO on **Cr_{TES}** *before* and *after* ethylene polymerization highlights the concurrent presence of two types of Cr sites: i) a predominant fraction of highly active modified Cr sites, able to oligomerize ethylene to higher α -olefins; and ii) a small fraction of unmodified Cr(II) centers (less than 15%), very similar to those observed for unmodified **Cr_{PHL}**, known to yield linear polyethylene chains (HDPE synthesis), as well as to co-polymerize ethylene with α -olefins (HDPE and LLDPE synthesis depending on the α -olefin content).^[1] Such a dual catalytic system is compatible with the bimodal mass weight distribution observed in the resulting products (see Table 1). According to the FT-IR results, the modified Cr sites have a homogeneous behaviour, and show up to two coordination vacancies available at room temperature. It must be underlined that the term “homogeneous” has a double meaning here: i) ability to form carbonyl complexes having a strong metal π -back-donation contribution, and ii) all the sites have relatively uniform structure. It is also important to note that the fraction of unmodified Cr(II) centers in **Cr_{TES}** keeps its “heterogeneous” character (meaning here exhibiting a non uniform structure usually referred as a multi-site character) as attested by the diversity of CO adsorptions.

The electronic properties of the most abundant sites in **Cr_{TES}** catalyst were successively investigated by DR UV-Vis and XANES techniques (Figure 3a and b, respectively). Both DR UV-Vis and XANES spectra of **Cr_{TES}** (grey) are very similar to those of **Cr_{PHL}** catalyst (black). In particular, both the intense band at 30000 cm^{-1} in the UV-Vis spectrum (assigned to $\text{O} \rightarrow \text{Cr(II)}$ charge transfer transition)^[10,11,22] and

the edge position in the XANES spectrum, remain almost unaffected. Both features are very sensitive to the chromium oxidation state and type of ligands;^[10] as a consequence, their invariance upon modification of **Cr_{PHL}** by TES provides evidence that no substantial changes in the chromium oxidation state, nor in the type of ligands (*viz.* siloxy [$\equiv\text{SiO}-$] monoanionic ligands and adjacent siloxanes [$\equiv\text{SiOSi}\equiv$] neutral ligands) occur in the chromium coordination sphere. Some changes between the spectra of **Cr_{PHL}** and **Cr_{TES}** samples take place in the d-d region of the UV-Vis spectrum and in the pre-edge region of the XANES spectrum, suggesting a modest increase of the ligand field around chromium sites upon reaction with TES, but no substantial modification of the coordination sphere. When **Cr_{TES}** is contacted with CO (Figure S4) UV-Vis and XANES spectra greatly change, consistently with the formation of “classical” carbonyls, in agreement with FT-IR results (see discussion in Section S5). In summary, the electronic spectroscopies point out the presence of siloxy and siloxane bridges in the coordination sphere of the modified chromium sites in **Cr_{TES}**.

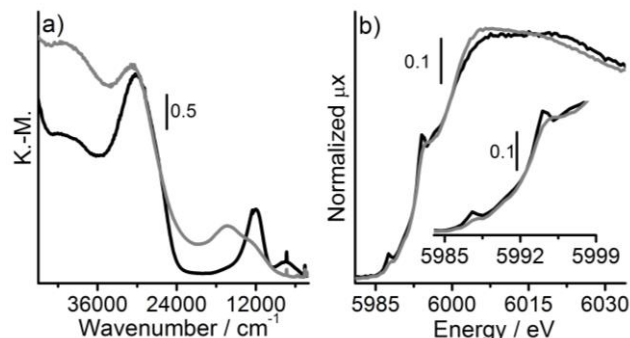


Figure 3. DR UV-Vis (part a) and XANES (part b) spectra of Cr(II)/SiO₂ before (black) and after (dark grey) interaction with TES from the vapour phase. Inset in part b) shows a magnification of the pre-edge region.

To gain further structural insight on the nature of the most abundant sites in **Cr_{TES}**, we turned our attention to EXAFS spectroscopy, which is a powerful technique in the structural investigation of amorphous materials, although only rarely applied to Cr/SiO₂ catalysts.^[10,11,19,23-25] We adopted the same experimental set-up successfully employed to characterize the **Cr_{PHL}** catalyst.^[10,19] Figure 4 shows the k^3 -weighted $\chi(k)$ functions of both **Cr_{PHL}** and **Cr_{TES}** catalysts (black and dark grey in the inset) and the corresponding FT, in both modulus and imaginary parts. The FT spectrum of **Cr_{PHL}** is

dominated by a first shell signal at 1.47 Å (not corrected in phase), due to two oxygen neighbors.^[19] The first shell signal is clearly shifted at longer distance for **Cr_{TES}**. Although the above discussed results demonstrated the co-presence of two types of Cr sites in **Cr_{TES}**, EXAFS data are dominated by the signal coming from the modified Cr sites, since it is well known that its sensitivity is limited to phases present in a percentage higher than ca. 10%. Therefore, in the EXAFS data analysis (details are given in section S7) we used as input models the three schematic [O-Cr^{II}-X] structures shown in Scheme 1 (where X = H, Si or O). Only structure c) [O-Cr^{II}-O] was able to reproduce the experimental spectrum, whereas the fit performed starting from structures a) and b) gave non-physical results. In average, the modified chromium sites appear surrounded by two oxygen atoms in the first (covalent) coordination shell, as in unmodified **Cr_{PHL}**, but at a longer distance (1.95 Å in **Cr_{TES}** vs. 1.86 Å in **Cr_{PHL}**); their “homogeneous” nature is testified by the small σ^2 value (0.004 Å² vs. 0.015 Å²). The local structure around chromium sites greatly changes in presence of CO (Figure S8); the analysis of the corresponding EXAFS spectrum provides a direct evidence that di-carbonyl species are formed, in agreement with FT-IR results.

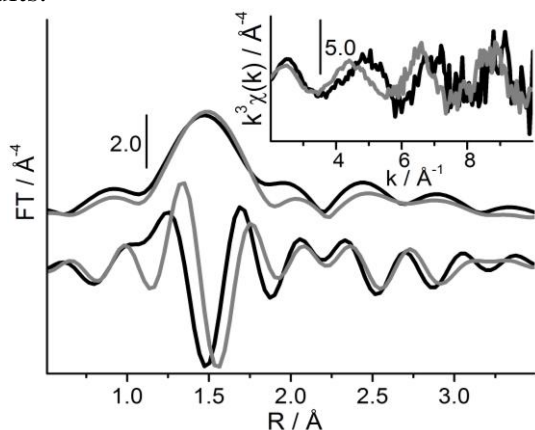


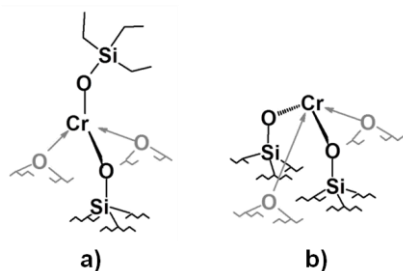
Figure 4. k^3 -weighted $\chi(k)$ functions (inset) and corresponding FT (in both modulus and imaginary parts, vertically translated for clarity), calculated in the $\Delta k = 2.0$ - 10.0 Å⁻¹ range for Cr(II)/SiO₂ catalyst before (black) and after (dark grey) interaction with TES.

The whole set of spectroscopic tools employed herein allows to unravel the role of hydrosilanes in modifying the chromium active sites at the surface of the Phillips catalyst. It was demonstrated that the hydrosilane modification affects a large proportion of the Cr sites present

in the original catalyst, leaving a fraction of Cr(II) unmodified sites (about 15%) catalytically active keeping their multi-site character. Such observed coexistence of two significantly different families of active sites in **Cr_{TES}** (see Scheme 2) is thus to be connected with the in-situ branching co-polymerization mechanism, leading to the observed bimodal distribution of products. Modified Cr sites (structure a in Scheme 2) oligomerises ethylene to higher α -olefins. At the same time unmodified ones (structure b) co-polymerizes ethylene and a part of the α -olefins produced on site a). The fraction of non-copolymerized \square -olefins constitutes the low molecular weight component of the bimodal molecular weight distribution of polyethylenes (Table 1, Figure 1 and S2). The incorporation of \square -olefins into the polyethylene backbone results in the formation of LLDPE rather than HDPE exhibiting an higher branching degree and therefore lower melting temperatures as “classical” LLDPE^[1] (meaning here obtained by copolymerization of ethylene and \square -olefins). This corresponds to the heavier fraction of the bimodal distribution. The molecular weight of this fraction is slightly lower than HDPE produced with **Cr_{PHL}** due to more frequent transfer reactions after \square -olefin insertion, in agreement with literature data.^[1] The broadness of the molecular weight distribution of this fraction is similar to that of HDPE (Figure 1) or “classical” LLDPE^[1] produced with **Cr_{PHL}** and reflects once again the multi-site character of these unmodified Cr(II) species. It has been reported that the co-monomer incorporation efficiency increases of two to four times for in-situ produced α -olefins, thus explaining the enhanced activity of **Cr_{TES}** with respect to **Cr_{PHL}**. To the best of our knowledge, this report contains the first direct spectroscopic observation and molecular assignment of the dual-type of active sites in hydrosilanes-modified Phillips catalysts for industrially relevant LLDPE production.

The spectroscopic data discussed above demonstrate that the modified Cr sites retain the +2 formal oxidation state and the same type of ligands of the original **Cr_{PHL}** (two oxygen atoms in the first shell, [O-Cr(II)-O]). However, they benefit of a much larger flexibility due to the substitution of one of the two rigid surface siloxy bonds with the more flexible -OSiEt₃ ligand, which resembles the ancillary ligands

characteristic of the homogeneous chromium-based complexes highly active (and selective) in ethylene oligomerization.^[3,26,27] This flexible ligand allows a more efficient interaction of the chromium sites with adjacent surface siloxanes (Scheme 2), which in turn explains the increased back-donating ability of the Cr(II) centers in **CrTES** with respect to **CrPHL** (as experimentally observed above). The “homogeneous” nature of the newly formed sites seems to be the key to explain their tendency to oligomerize ethylene, rather than polymerize it. It is worth noticing that modified Cr(II) sites supported on silica by only one Si-O-Cr bond and having a flexible electron-rich ligand were previously suggested for the Cr[N(SiMe₃)₂]₃/isobutylalumoxane/silica catalyst highly active and selective for 1-hexene production by ethylene trimerization.^[28] In this respect, the results shown herein could be of help for the understanding of chromium-based catalysts active in selective oligomerization of ethylene.



Scheme 2. Schematic structures (only two of the several possible second-shell siloxane interactions are shown) of two representative types of active sites responsible for ethylene oligomerization in **CrTES** (a) and ethylene polymerization in **CrPHL** (b). The variability in number of adjacent siloxane bridges and their possible distances around the Cr(II) centres are omitted for clarity but clearly affect the multi-site character of Cr(II) centers especially for (b).

Experimental Section

Cr/SiO₂ samples were prepared by impregnating SiO₂ (aerosil, surface area ca. 360 m²g⁻¹) with aqueous solutions of CrO₃ having the right concentration to give a Cr/SiO₂ ratio of 1.0 and 0.5 wt.%, respectively. The former was used for FT-IR measurements, and the latter for DR UV-Vis, XANES and EXAFS experiments. In all cases the Cr/SiO₂ ratio was low enough to avoid segregation of a Cr(III) oxide phase during the subsequent thermal treatments.^[11] From these parent materials, the corresponding reduced form of the Phillips catalyst, Cr(II)/SiO₂, was prepared (inside the cell used for spectroscopic

measurements) by heating at 923 K under a dynamic vacuum followed by heating in oxygen at 923 K and reduction in CO at 623 K. Further details concerning this procedure can be found elsewhere.^[11] The standard Cr(II)/SiO₂ catalyst, **CrPHL**, was modified by dosing triethylsilane from the vapor phase at room temperature, resulting in **CrTES**.

Transmission FT-IR spectra were collected at 2 cm⁻¹ resolution on a Bruker Vertex70 instrument, on samples in the form of thin self-supported wafers (surface density ca. 10 mg cm⁻²). Reflectance UV-Vis spectra were recorded on a Varian Cary5000 instrument on a sample in the form of a thick self-supported pellet (surface density ca. 60 mg cm⁻²). XAS measurements at the Cr K-edge were performed at the BM01 beamline at ESRF (Grenoble, F), in fluorescence mode; the samples were closed inside sealed capillaries in controlled atmosphere, to prevent contamination, as successfully done in previous experiments.^[19] Differential scanning calorimetry (DSC) was performed with a Mettler Toledo DSC1 Star System; size exclusion chromatography (SEC) measurements were performed with a Waters Alliance GPCV 2000 instrument.

Acknowledgements

Prof. A. Zecchina (UniTO) is kindly acknowledged for his constant guide and for sharing with us his large experience in the field of Phillips catalyst. The authors are grateful to Dr. A. Damini (UniTO) for useful discussion; Olivier Boyron in UMR C2P2 is kindly acknowledged for assistance in polymer characterization.

Keywords: Heterogeneous catalysis • Ethylene oligomerization • Chromium • Phillips catalyst • LLDPE

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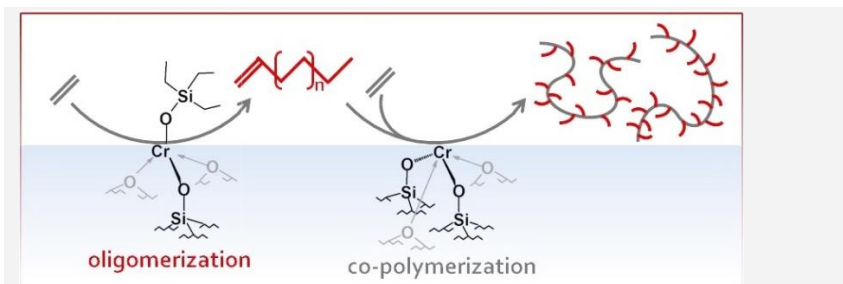
Entry for the Table of Contents

When silane makes the difference

Caterina Barzan, Diego Gianolio, Elena Groppo, Carlo Lamberti, Vincent Monteil, Alessandra E. Quadrelli* and Silvia Bordiga*

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The effect of hydrosilanes on the active sites of the Phillips catalyst: the secret for in situ α -olefin generation



Heterogeneous Phillips catalyst modified with hydrosilanes reveals the concomitant presence of two chromium catalytic sites: a modified site with an homogeneous behaviour

able to oligomerize ethylene and a classical heterogeneous one which co-polymerizes ethylene and the olefins produced from the former.