The effect of Al-alkyls on the Phillips catalyst for ethylene polymerization: the case of diethylaluminum ethoxide (DEALE)

Giorgia A. Martino,[1] Alessandro Piovano,[1] Caterina Barzan,[1] Silvia Bordiga,[1] Elena Groppo[1,*]

[1]Department of Chemistry, NIS Centre and INSTM, University of Torino, via G. Quarello 15A, 10135 Torino, Italy
Corresponding author: elena.groppo@unito.it

Abstract

Al-alkyls are often used in the industrial practice for modifying the Phillips catalysts for polyethylene production: they are not necessary to develop the activity, but they have relevant effects on the catalysis, decreasing the induction time, promoting the in situ branching, and enhancing the H_2 sensitivity for the molecular weight regulation. Herein we investigate the effect of diethylaluminum ethoxide (DEALE) on $Cr(II)/SiO_2$ (in a stoichiometric amount of Al:Cr=2:1), focusing the attention on the modification of the Cr(II) sites at a molecular level. Diffuse reflectance UV-Vis and FT-IR spectroscopies, applied in the presence of CO and CD_3CN as molecular probes, unequivocally demonstrate that: 1) DEALE modifies only a fraction of the Cr(II) sites (ca. 30%) even if dosed in excess with respect to the Cr sites; 2) DEALE reacts with the silica surface, forming Al-grafted species which are at least partially in interaction with the Cr(II) sites and hence act as ancillary ligands; 3) the modified Cr(II) sites are more acidic and likely mono-grafted to the silica surface; the presence of Al-grafted species nearby is essential for their stabilization. Finally, kinetic experiments indicate that the modified Cr(II) sites are ca. 15 times faster in inserting ethylene than the unmodified Cr(II) sites. The intrinsic higher activity of the modified Cr(II) sites is a consequence not only of their molecular structure, but of the whole series of effects listed above.

1. Introduction

Polyolefins (POs) are ubiquitous materials in the modern economy, combining unrivalled functional properties with low cost, low weight and excellent barrier properties. In this market the Phillips catalyst produces hundreds of specialized PE grades, supplying almost 50% of the HDPE total world demand [1-3]. Since its discovery in 1951 [4], the Cr/SiO_2 Phillips catalyst was modified and evolved mainly following trial and error approaches or serendipitous discoveries. One of these discoveries was the possibility of introducing Al-alkyls in the catalytic process. Indeed, opposite to Ziegler-Natta catalysts, the Phillips catalysts do not require any co-catalysts (or activators) to develop an activity, while they are used to enhance it and to modify the produced polymer [5]. The idea of using Al-alkyls to change the performances of the Phillips catalyst originated from an accident occurred at an industrial plant running a Phillips catalyst, that was accidentally contaminated with the aluminium alkyls employed in a Ziegler-Natta polymerization line nearby. This "mistake" led to the unexpected production of a short-chain branched polyethylene with remarkable properties for technological applications [6]. Further investigations driven by the industrial curiosity revealed that many metal-alkyls bearing at least one M-R bond (hereafter referred to as MR) affect the Cr active sites distribution, promote in situ branching, and enhance the sensitivity to H_2 [5, 7]. This latter aspect is particularly interesting because the un-modified Phillips catalyst is not sensitive to the presence of hydrogen during the polymerization process, which is among the easiest methods for the regulation of the molecular weight. The modification of the Phillips catalysts by metal-alkyls can be carried out both on the oxidized form ($Cr(VI)SiO_2$) and on the CO-reduced form ($Cr(II)/SiO_2$). According to McDaniel [5], the $Cr(II)/SiO_2$ Phillips catalyst is more readily subject to attack by metal-alkyls, and by combining the catalyst activation with suitable reaction variables it is possible to increase enormously its H_2 sensitivity.

Metal-alkyls can potentially interact/react with both the silica support and the Cr sites. As far as the modification of the silica surface by MR is concerned, extensive studies can be found in the literature, since this is a really versatile approach for the surface functionalization [8-12]. MR can react with surface OH groups and/or with the strained siloxane bridges, whose relative amount is a function of the de-hydroxylation conditions [13, 14]. Several concomitant reaction pathways were identified [10-12], such as the M grafting by the protonolysis of one (Scheme 1a) or two silanols and the M grafting by the opening of a siloxane bridge through the nucleophilic attack of an alkyl group (Scheme 1b). Further rearrangements of the grafted M with other siloxane bridges nearby are also possible.
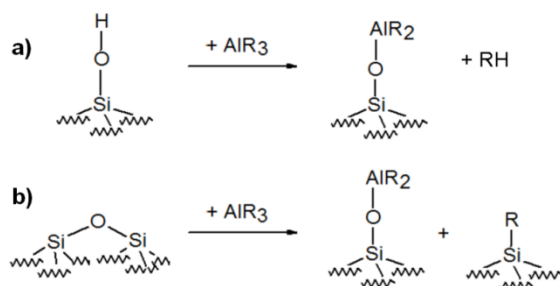
Scheme 1. Mechanisms proposed in the literature for the reaction of a metal alkyl (MR) with the surface of dehydroxylated silica [10-12]: grafting of M by protonolysis of one silanol group (part a); grafting of M by siloxane bridge opening through the nucleophilic attack of an alkyl group (part b).

In contrast, the reactivity of Al-alkyls with the Cr sites in Cr/SiO$_2$ was much less explored, and a wide range of possible products can be envisaged, depending on the reaction conditions, on the amount and type of co-catalyst, and on the pre-treatment of the catalyst [5]. The scientific literature in this field is very poor, with just a few articles and a few research groups working on this system [6, 15-22]. The few hypothesis that have been formulated are summarized in Scheme 2, considering the reaction of a generic MR with the Phillips catalysts either in the oxidized (parts a and b) or in the reduced (parts b and c) forms. Among the various possibilities, the MR can: a) reduce Cr(VI) to lower-valent active species, thus accelerating the development of the polymerization rate; b) alkylate the chromium, similarly to the role of the co-catalyst in Ziegler-Natta catalysis; c) react with the chromium site itself, or with neighbouring OH or siloxane groups, to modify the site or become part of its environment, thus influencing its behaviour; d) attack the Cr–support bonds, thus initially converting di-grafted chromium species into mono-grafted ones, and eventually destroying the sites and causing a loss of activity. Most of these hypotheses are not confirmed yet by direct experimental evidence on the structure of the active sites at molecular level.
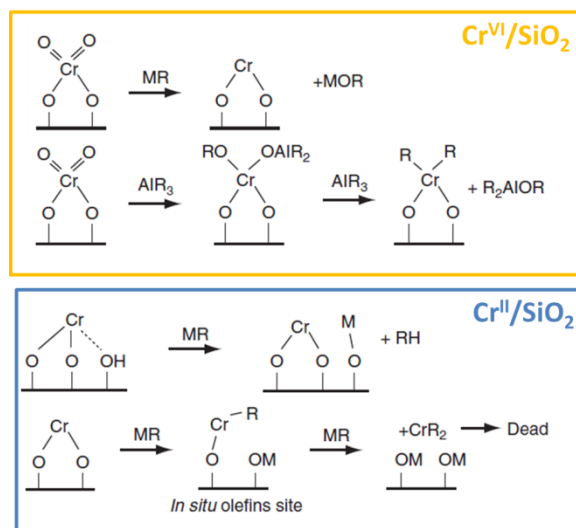
Scheme 2. Mechanisms proposed in the literature [5, 6, 15-22] for the reaction of AlR$_3$ with Cr(VI)/SiO$_2$ (parts a and b) and Cr(II)/SiO$_2$ (parts c and d).

In this work we propose for the first time an in-depth investigation on the effect of an Al-alkyl on the CO-reduced form of the Phillips catalyst, Cr(II)/SiO$_2$. We decided to focus our attention on Cr(II)/SiO$_2$ in order to limit the number of working hypothesis (formally only paths c and d in Scheme 2 are possible). Among all the possible Al-alkyls, we choose diethylaluminum ethoxide (DEALE = ROAlR$_2$, with R = ethyl), that is known to have a very pronounced influence on the H$_2$ sensitivity [5]. We adopted DR UV-Vis and FT-IR spectroscopies (the latter also in the presence of probe molecules), since these techniques have been demonstrated to be extremely sensitive and able to discriminate among several Cr sites differing in the coordination geometry, much more than other more sophisticated methods. Our spectroscopic investigation allowed us to get information on the fraction of the Cr sites modified by DEALE and on their structure at a molecular level.

2. Experimental Section

2.1 Catalyst activation and modification

The Phillips catalysts were prepared by wet-impregnation of a SiO_2 (Aerosil®380) with a solution of chromic acid (Sigma-Aldrich) as Cr precursor, according to the procedure widely adopted in the past [23]. Two Cr/SiO_2 samples differing in the Cr loading (1 wt% and 0.5 wt%) were prepared: the former was used for the FT-IR measurement and the latter for DR-UV-Vis-NIR. The choice was done to optimize the spectral quality. We have previously demonstrated that the properties of the Cr sites in the two catalysts are the same [23]. The catalysts were activated directly inside the measurement cells, to avoid any type of contamination. The activation procedure can be resumed in four main steps: i) degassing in dynamic vacuum at increasing temperature up to 650 °C to dehydroxylate the silica surface; ii) calcination at the same temperature, resulting in the grafting of the Cr species at the silica surface in the form of monochromates; iii) reduction in the presence of CO at 350 °C, followed by degassing at the same temperature; iv) cooling down at room temperature. The obtained material will be called hereafter $Cr(II)/SiO_2$.

The modification of $Cr(II)/SiO_2$ with DEALE was accomplished by impregnating $Cr(II)/SiO_2$ in the glove-box with a well-defined amount of DEALE in hexane, calculated considering a stoichiometric ratio Al/Cr of 2/1. In all the experiments, the DEALE/hexane mixture was left in contact with the catalyst for ca. 15-20 minutes, followed by removal of hexane immediately before the experiment. Hence, our procedure mimics the catalyst pre-treatment stage employed in commercial operations, where the catalyst is treated with the Al-alkyl for about 30 minutes directly in the polymerization reactor before the introduction of the monomer. This procedure is known to give a much more pronounced response than introducing the Al-Alkyl at the polymerization stage, i.e. in the presence of the monomer [5]. The Al/Cr stoichiometry is known to strongly influence the Cr speciation [24, 25], and the maximum activity is usually achieved at a ratio near 1/1 or 2/1. The resulting sample will be labelled as $Cr(II)/SiO_2$+DEALE in the following.

Finally, a series of blank experiments were performed on a bare SiO_2 activated with the same procedure as for $Cr(II)/SiO_2$ and successively reacted with DEALE in the same amount as for $Cr(II)/SiO_2$+DEALE. This sample will be labelled as SiO_2+DEALE.

2.2 Methods

Diffuse reflectance (DR) UV-Vis-NIR spectra were collected using a Varian Cary5000 spectrophotometer with a diffuse reflectance accessory. The samples were measured in the form of thick self-supported pellets (surface density ca. 200 mg/cm^2), placed inside a cell equipped with a quartz suprasil window, that allows performing thermal treatments and measurements in the presence of gases. The reflectance (R%) signal was later converted into Kubelka-Munk values F(R).

Transmission FT-IR spectra were collected at 2 cm^{-1} resolution with a Bruker Vertex70 instrument equipped with a MCT detector. The experiments were performed on samples in the form of thin self-supported pellets (surface density ca. 30 mg/cm^2), placed inside a quartz cell equipped with two KBr windows, which allows performing thermal treatments and measurements in the presence of gases. All the FT-IR spectra were normalized to the optical thickness of the pellet, in order to allow quantitative comparisons to be done.

The kinetics of ethylene polymerization was studied by sending 200 mbar of ethylene at room temperature over 0.2 g of catalyst inside a quartz reactor of known volume, and recording the ethylene pressure as a function of time, as already done in the past [26, 27]. A similar experiment was repeated for the catalyst inside the FT-IR cell, collecting the spectra as a function of time.

For probing the accessible Cr sites after modification with DEALE, FT-IR experiments of adsorbed carbon monoxide (CO) and d-acetonitrile (CD_3CN) were performed. CO was dosed in the gas phase (equilibrium pressure P_{CO} = 100 mbar) at room temperature. CD_3CN was dosed in the vapour phase (from the liquid vapour tension) at room temperature. A FT-IR spectrum was collected at the maximum CO (or CD_3CN) coverage, followed by step-by-step expansions to diminish the equilibrium pressure in a controlled way.

3. Results and discussion

3.1 Reactivity of DEALE with Cr(II)/SiO$_2$

Figure 1 displays the DR UV-Vis-NIR (part a) and the FT-IR spectra (part b) of the CO-reduced Cr(II)/SiO$_2$ catalyst before (black spectra) and after the reaction with DEALE in the stoichiometric ratio of Al/Cr = 2/1 (grey spectra). The spectra of Cr(II)/SiO$_2$ were deeply discussed in the past [23], and will be just commented briefly here. In the UV-Vis-NIR region, the two intense bands centred at ca. 41000 and 30000 cm^{-1} are attributed to O→Cr charge-transfer transitions, while the two bands at 12000 and 7500 cm^{-1} are assigned to the d-d transitions characteristic of 4-coordinated d^4 Cr(II) sites in a distorted tetrahedral environment. In the Mid-IR region, the spectrum is dominated by the fingerprints of a highly dehydroxylated silica, i.e. a very narrow absorption band centred at 3745 cm^{-1} due to the v(OH) of isolated silanol groups, the out-of-scale absorption below 1100 cm^{-1} due to the vibrations of the silica lattice and a triplet of bands in the 2100 − 1500 cm^{-1} region due to the overtones and combinations of the SiO$_2$ lattice vibrations.

After reaction with DEALE, both the DR UV-Vis and FT-IR spectra greatly change. In the UV-Vis region the bands characteristic of Cr(II) sites decrease in intensity, and at the same time also the v(OH) absorption band in the Mid-IR spectrum is consumed (inset in Figure 1b), indicating that DEALE reacts with both the Cr(II) sites and the silica surface. Simultaneously, new absorption bands appear in the 3000 − 2700 cm^{-1} and 1500 − 1350 cm^{-1} regions, which are straightforwardly assigned to v(CH$_x$) and δ(CH$_x$) vibrations. The corresponding overtones and combinations are observed in the NIR region (inset in Figure 1a). These bands are related to the alkyl groups derived from DEALE, although it is not possible to distinguish among all the putative species depicted in Scheme 1cd, namely the alkylated Cr-R sites and the AlR(OR) species grafted on silica. Indeed, the same bands are observed in the spectrum of SiO$_2$+DEALE (Figure S1). This implies that the fraction of modified Cr sites is very small and/or that the vibrational fingerprints of the modifies Cr sites do not differ from those of the Al species grafted on silica.

In addition, two important observations must be done. Although the amount of DEALE is the double of the Cr(II) sites, only ca. 30% of the Cr(II) sites seem involved in the reaction. Indeed, the two bands in the DR UV-Vis spectrum at 12000 and 7500 cm^{-1} decrease of roughly 1/3. At the same time, no specific features associable with the modified Cr sites are observed neither in the UV-Vis nor in the FT-IR spectra. The absence of peculiar spectroscopic fingerprints makes it difficult to

unravel the molecular structure of the modified Cr sites. Nevertheless, the observation that the modified Cr sites are almost invisible by UV-Vis spectroscopy might suggest that they have prevalently an octahedral coordination. Indeed, d-d transitions are formally Laporte forbidden for transition metals in octahedral symmetry [28]. Hence, the corresponding bands are expected to have a very low intensity compared to those of the unmodified Cr(II) sites.
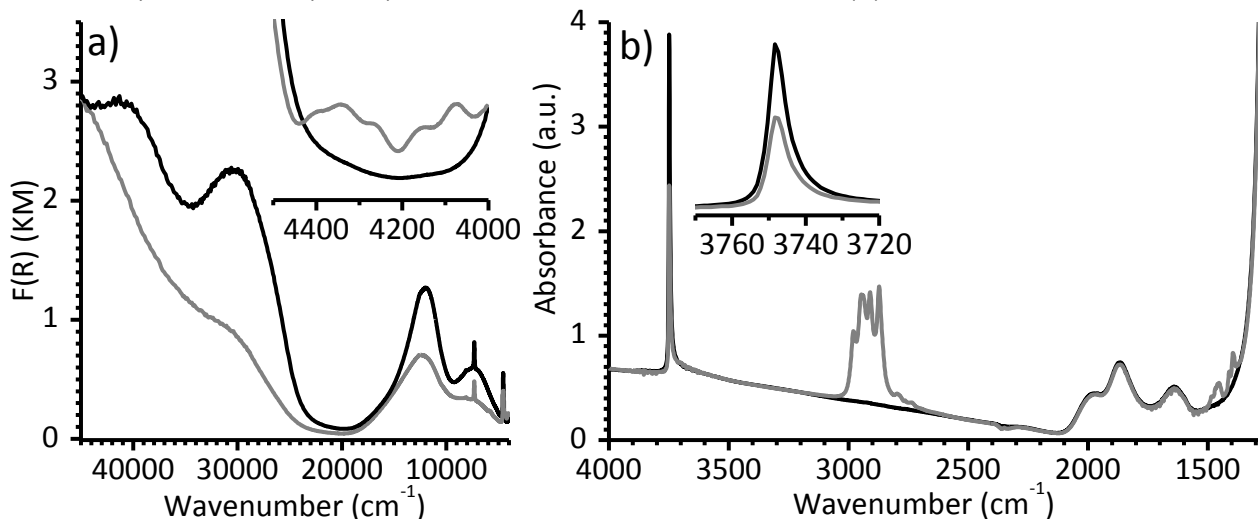

Figure 1. DR UV-Vis-NIR spectra (part a) and FT-IR spectra (part b) of CO-reduced $Cr(II)/SiO_2$ (black), and of the same sample reacted with DEALE at the stoichiometric ratio of Al/Cr = 2/1 (grey). The inset in part a) shows a magnification of the NIR region. The inset in part b) shows a magnification of the $\nu(OH)$ absorption band.

3.2 Testing the $Cr(II)/SiO_2$+DEALE catalyst in ethylene polymerization

The $Cr(II)/SiO_2$+DEALE catalyst was very active towards ethylene polymerization, even at room temperature and at mild ethylene pressure. Figure 2a shows the evolution of the FT-IR spectra collected every 12 seconds during ethylene polymerization, after subtraction of the spectrum before ethylene admission into the cell. Two absorption bands at 2920 and 2855 cm^{-1} rapidly grow and go out of scale in less than 1 minute. Simultaneously, in the $\delta(CH_2)$ region (inset in Figure 2a), two bands are observed. The first, at 1442 cm^{-1} dominates the spectra at short polymerization times and is assigned to the $\delta(CH_2)$ vibrational mode of ethylene coordinated to Cr(II) sites [29-32]. The corresponding $\nu(=CH_2)$ mode is observed at 3004 cm^{-1}. It gives an indication of the existence of a fraction of sites that do coordinate ethylene but are slow to start working (dormant sites) or do not start at all in the experimental conditions (spectators). The same band was previously reported for ethylene coordinated to the unmodified $Cr(II)/SiO_2$ catalyst [29]. The second band, initially at 1463 cm^{-1}, is due to the $\delta(CH_2)$ vibrational mode of the polyethylene chains. At longer polymerization times a third band appears at ca. 1472 cm^{-1}, which indicates the formation of crystalline polyethylene [33].

Kinetic experiments were performed to evaluate the ethylene polymerization rate on the $Cr(II)/SiO_2$+DEALE catalyst in comparison with the $Cr(II)/SiO_2$ catalyst. Figure 2b shows the decrease of ethylene pressure as a function of time for the two catalysts, monitored in the same experimental conditions and at a constant Cr loading. The data clearly demonstrate that $Cr(II)/SiO_2$+DEALE is ca. 5 times faster than the unmodified $Cr(II)/SiO_2$ catalyst. Considering that only ca. 30% of the total Cr(II) sites have been modified by DEALE, this means that they are approximately 15 times faster than the unmodified Cr(II) sites in inserting ethylene.
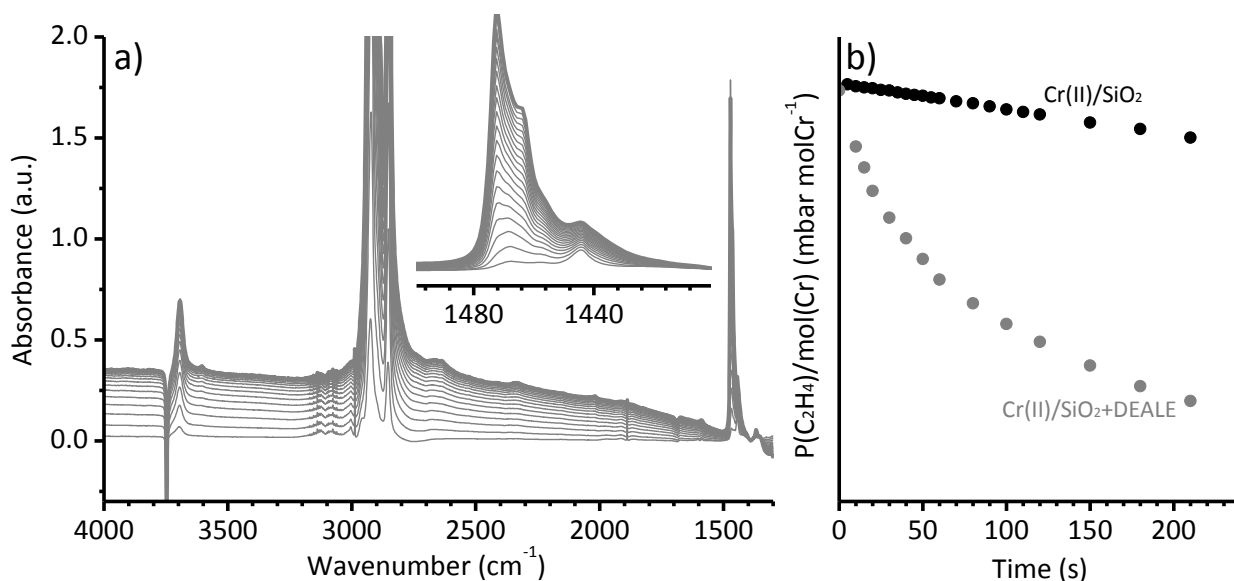
Figure 2. Part a) FT-IR spectra collected during ethylene polymerization on the Cr(II)/SiO$_2$+DEALE catalyst (PC$_2$H$_4$ = 100 mbar), after subtraction of the spectrum prior ethylene admission in the cell. The spectra were collected every 12 seconds. The last spectrum was collected after 4 minutes of reaction. The inset shows a magnification of the δ(CH$_2$) region. Part b) Kinetics of ethylene polymerisation on the Cr(II)/SiO$_2$+DEALE catalyst in comparison to that on Cr(II)/SiO$_2$, obtained by recording the ethylene equilibrium pressure as a function of time.

3.3 Probing the Cr(II) sites modified by DEALE

Successively, the accessibility of the Cr sites in Cr(II)/SiO$_2$+DEALE were investigated by means of FT-IR spectroscopy of adsorbed probe molecules. CO and CD$_3$CN were selected as suitable probes.

3.3.1 CO as a molecular probe

Figure 3 shows the evolution of the background subtracted FT-IR spectra, in the $\tilde{v}$(CO) region, for CO adsorbed at room temperature on Cr(II)/SiO$_2$+DEALE (part a) as a function of the CO coverage, compared to the same sequence of spectra collected for CO adsorbed on the unmodified Cr(II)/SiO$_2$ (part b). The same experiment was also performed for SiO$_2$+DEALE and the corresponding spectra are reported in Figure S2.

The spectra of CO adsorbed on Cr(II)/SiO$_2$+DEALE show several absorption bands in two distinct spectral regions. At the maximum CO coverage, a triplet of bands is observed at 2191, 2184 and 2178 cm^{-1}, exactly the same as those observed for CO adsorbed on unmodified Cr(II)/SiO$_2$ (Figure 2b). In the pioneering works of Zecchina et al. [34-37] they are ascribed to mono- and di-carbonyl species formed on two types of Cr(II) sites grafted on the silica surface through two siloxy monoanionic [≡SiO-] ligands and in interaction with a different number of adjacent siloxane bridges, respectively labelled as Cr$_B$ and Cr$_A$ [23, 38]. Upon decreasing the CO coverage, the 2184 and 2178 cm^{-1} doublet of the di-carbonyl species on Cr$_A$ evolves into a single band at 2180 cm^{-1} due to mono-carbonyl species [23, 38]. The tendency of the Cr(II) sites in unmodified Cr(II)/SiO$_2$ to form non-classical carbonyls (i.e. where the Cr←CO σ donation prevails over the Cr→CO π back-donation) was largely documented in the past and was attributed to the unique nature of the silica support, that acts as a macro- and multi-dentate ligand able to stabilize Cr(II) sites in geometries which are unlikely for homogeneous complexes [39]. The integrated absorbance of the "triplet" (ca. 20 a.u.) is roughly 70% of that observed for CO adsorbed on unmodified Cr(II)/SiO$_2$ (ca. 29 a.u.). This indicates

that approximately 70% of the original Cr(II) sites are not modified by DEALE, a value which is in very good agreement with that estimated by the analysis of the UV-Vis spectra (Figure 1a).
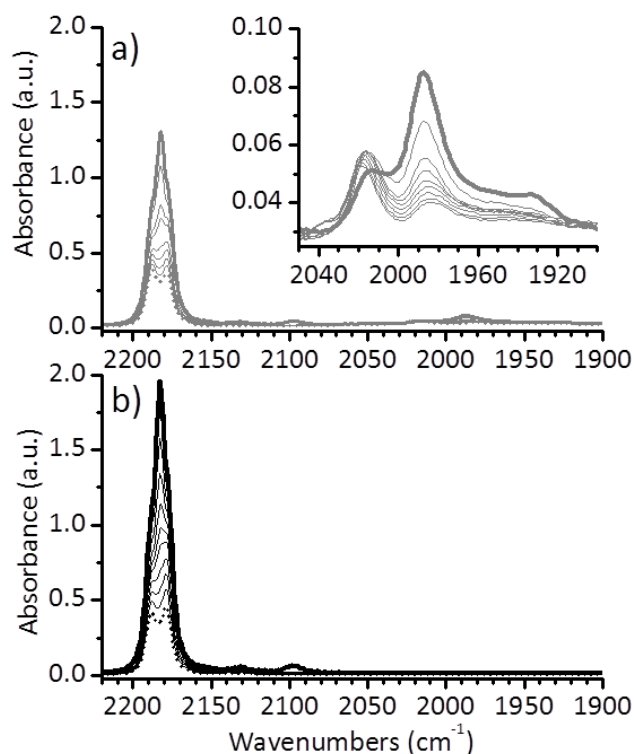

Figure 3. Evolution of the background subtracted FT-IR spectra, in the $\tilde{v}$(CO) region, for CO adsorbed at room temperature on Cr(II)/SiO$_2$+DEALE as a function of the CO coverage (part a), compared to the same sequence of spectra collected for CO adsorbed on unmodified Cr(II)/SiO$_2$ (part b). All the spectra are reported after subtraction of that collected before CO dosing. Spectra in parts a) and b) are normalized for the optical thickness of the pellet. Bold spectra: maximum CO coverage; dotted spectra: irreversible fraction of adsorbed CO. The inset in part a) shows a magnification of the 20150 – 1900 cm^{-1} region.

A second set of bands is observed in the 2100-1900 cm^{-1} region (inset of Figure 3a), which indicates the formation of classical Cr carbonyls (i.e. of carbonyls where the prevalent contribution is the Cr→CO π back-donation) [40, 41]. In particular, at the maximum CO coverage the main absorption band is centred at 1987 cm^{-1}, with a shoulder at 2014 cm^{-1}. Upon decreasing the CO pressure the former gradually diminishes in intensity and the latter shifts at 2017 cm^{-1}. While classical carbonyls are typically formed on homogeneous Cr complexes [42-45], they are much more rare for Cr species grafted on support materials. One of the very few examples reported in the literature for classical Cr carbonyls on heterogeneous Cr-based systems is represented by CO adsorption on the CO-reduced Cr(II)/SiO$_2$ catalyst modified by hydrosilanes (SiH$_4$ or R$_3$SiH) [46, 47]. In that case, the modifying agents were demonstrated to transform the bis-grafted Cr(II) sites into mono-grafted ones, having a character similar to that of homogeneous Cr complexes, and forming prevalently di-carbonyl species in the presence of CO. The $\tilde{v}$(CO) bands observed in the 2100-1900 cm^{-1} region and their evolution upon decreasing the CO coverage are very similar to those reported by Barzan et al. [46], strongly suggesting that they are related to di-carbonyl species formed on mono-grafted Cr sites. It is worth noticing that the bands in the 2100-1900 cm^{-1} region are very weak in comparison to those observed in the "triplet" region. Considering that the molar extinction coefficient for a $\tilde{v}$(CO) band increases upon decreasing $\tilde{v}$, the fraction of the modified Cr(II) sites

accessible by CO should be very small and surely not accounting for the 30% of sites as expected on the basis of the analysis of the triplet region. Notably, when the same experiment is conducted on SiO$_2$+DEALE (Figure S2), no absorption bands are observed in the whole spectral region, but only the roto-vibrational spectrum of gaseous CO. The obvious conclusion is that CO molecules at room temperature interacts only with the Cr sites.

Summarizing, the FT-IR spectra reported in Figure 3 point out the co-presence of at least three types of Cr sites in Cr(II)/SiO$_2$+DEALE:

a) a fraction of unmodified Cr(II) sites, accounting for ca. 70 % of the originally accessible Cr sites (a value determined by integrating the area behind the "CO triplet");

b) a first type of modified Cr(II) sites, which are accessible to CO, and are likely mono-grafted to silica, as previously demonstrated for the sites obtained upon reacting Cr(II)/SiO$_2$ with hydrosilanes;

c) a second type of modified Cr(II) sites, which are not accessible by CO, probably because shielded by sterically encumbering ligands nearby.

3.2.2 CD$_3$CN as a molecular probe

To obtain a more complete description of the Cr(II)/SiO$_2$+DEALE system, the accessibility of the Cr sites was successively probed by the adsorption of CD$_3$CN at room temperature. This molecule has been largely employed to probe both acid and basic sites on metal oxides and zeolites [48-57]. Curiously it was never used in the characterization of the Phillips catalyst. Since both Cr(II) and Al(III) sites are Lewis acids (i.e. prone to accept electrons), acetonitrile is expected to interact with both of them as a soft Lewis base by sharing the nitrogen lone-pair, according to equation (1):

$$CD_3CN\text{:} + M(surf) \rightarrow [CD_3CN\text{:}\cdots M(surf)]_{ads} \tag{1}$$

where M(surf) = Cr(II) or Al(III).

As a consequence of this interaction, the $\tilde{v}(C\equiv N)$ vibration is expected to increase, proportionally to the strength of the Lewis acid-base couple. In general, d-acetonitrile is employed to avoid the occurrence of an annoying Fermi resonance effect [58].

Figure 4 shows the evolution of the background subtracted FT-IR spectra in the $\tilde{v}(C\equiv N)$ region for d-acetonitrile adsorbed at room temperature on Cr(II)/SiO$_2$+DEALE (part a), Cr(II)/SiO$_2$ (part b) and SiO$_2$+DEALE (part c), as a function of the CD$_3$CN coverage. The data in all the spectral range are reported in Figure S3. Differently from CO, d-acetonitrile interacts not only with the Cr sites, but also with the silica surface. This is clearly evident by looking to the spectra of CD$_3$CN adsorbed on SiO$_2$+DEALE (Figure 4c). Two bands are observed in the $\tilde{v}(C\equiv N)$ region, at 2276 and 2267 cm^{-1}, which are assigned to CD$_3$CN adsorbed on the OH groups and to liquid-like acetonitrile, respectively [48, 50, 51, 57]. Both bands decrease rapidly in intensity upon degassing up to disappear, indicating that the interaction of d-acetonitrile with the silica surface is quite weak and fully reversible. A minor band is hardly observable at ca. 2318 cm^{-1}, which is due to d-acetonitrile in interaction with an almost negligible amount of Al(III) species. The majority of Al(III) sites are inaccessible to the probe probably because of steric reasons. In this respect it is worth mentioning that most of the Al-alkyls have the tendency to dimerize [59], and this is likely to happen also between the AlR$_x$ species grafted at the silica surface and the DEALE in excess. The same two bands at 2275 and 2265 cm^{-1} are observed when CD$_3$CN is dosed on Cr(II)/SiO$_2$ (Figure 3b), although with a

reversed intensity. However, this time the spectra are dominated by an intense and broad band centred at ca. 2305 cm^{-1} (integrated absorbance of ca. 8.9 a.u.), which is straightforwardly ascribed to CD$_3$CN in interaction with the Cr(II) sites. This band is only slightly affected by degassing, indicating that the interaction is very strong. The strength of that interaction is the reason why CD$_3$CN does not discriminate between the Cr$_A$ and Cr$_B$ sites, as done by CO, which is a much weaker (and hence more selective) probe.

The spectra of CD$_3$CN adsorbed on Cr(II)/SiO$_2$+DEALE (Figure 4a) are very similar to those of CD$_3$CN adsorbed on Cr(II)/SiO$_2$ (Figure 4b), except that the absorption band ascribed to d-acetonitrile in interaction with Cr(II) sites is even broader and with an evident shoulder at ca. 2316 cm^{-1}. By deconvolving this absorption band two contributions can be found, the first centred at 2305 cm^{-1} (integrated absorbance of ca. 5.8 a.u.), and the second at 2316 cm^{-1} (integrated absorbance of ca. 1.6 a.u.). The former is ascribed to d-acetonitrile adsorbed on the fraction of unmodified Cr(II) sites, and accounts for about 65% of the total Cr(II) sites, in excellent agreement with the values determined by the previous analysis. The latter is assigned to d-acetonitrile adsorbed on the modified Cr(II) sites. Opposite to CO, d-acetonitrile is able to probe a larger number of modified Cr(II) sites, although perhaps not all of them, but it is unable to discriminate among them. The position of the $\tilde{v}$(C≡N) band indicates that these sites are more acidic than the unmodified ones.

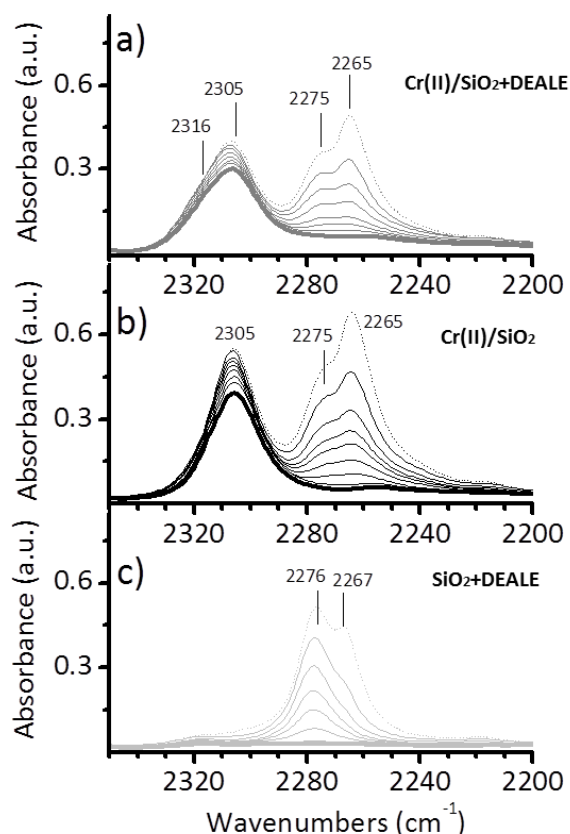**Figure 4.** Evolution of the background subtracted FT-IR spectra, in the $\tilde{v}$(C≡N) region, for CD$_3$CN adsorbed at room temperature on Cr(II)/SiO$_2$+DEALE as a function of the CO coverage (part a), compared to the same sequence of spectra collected for CD$_3$CN adsorbed on unmodified Cr(II)/SiO$_2$ (part b), and on SiO$_2$+DEALE (part c). All the spectra are reported after subtraction of that collected before CD$_3$CN dosing. The spectra are all normalized for the optical thickness of the pellet. Dotted spectra: maximum CD$_3$CN coverage; bold spectra: irreversible fraction of adsorbed CD$_3$CN.

4. Conclusions

The whole set of spectroscopic data discussed so far allowed to make the following conclusions regarding the reactivity of Cr(II)/SiO$_2$ with DEALE.

1. DEALE reacts both with the Cr(II) sites and the silica surface, involving both isolated silanols and siloxane bridges.

2. Even when DEALE is used in excess with respect to the Cr sites (stoichiometric ratio Al/Cr = 2/1), only a fraction of the Cr(II) sites are modified, accounting for about 30 − 35% of the total. This finding has two important consequences. The first is that in Cr(II)/SiO$_2$+DEALE a substantial fraction of unmodified Cr(II) sites are always co-present with the modified ones, creating the premises for the development of a tandem catalysis. The second consequence is that there is an abundance of DEALE-derived species at the silica surface, that become part of the environment of the modified Cr(II) sites, affecting their properties in a similar way as the ancillary ligands do in homogeneous catalysis.

3. That this is the case is demonstrated by the observation that the modified Cr(II) sites are scarcely accessible by CO, that is notoriously a weak probe, while they are more accessible to d-acetonitrile, which is a stronger Lewis base. As already demonstrated in the past, the information conveyed by a certain probe molecule is often a compromise between the ability to probe as many sites as possible and the sensibility of discriminating their small differences.

4. Neither CO nor d-acetonitrile interact with the Al(III) of the DEALE-derived species grafted at the silica surface. This suggests that the Al-grafted species are in the form of small clusters.

5. As far as the modified Cr(II) sites are concerned, they look more acidic than the unmodified Cr(II) sites, and they are likely mono-grafted to the silica surface, i.e. of the type ≡Si–O-Cr-L, where L stands either for an alkyl (R) or an alkoxy group (OR). The presence of the Al-grafted species nearby is essential for their stabilization.

6. Finally, kinetic experiments indicate that the modified Cr(II) sites are ca. 15 times faster in inserting ethylene than the unmodified Cr(II) sites. Several reasons might account for their faster activity, among which the simplest is that they are already alkylated (i.e. the first Cr-C bond is already present). However, it should be noticed that a similar fast kinetic profile is shown also by CO-reduced Cr/Al$_2$O$_3$ in the absence of any activator [5], and recently ascribed to the presence of Al(III) sites in close proximity of the Cr(II) sites [27], a situation very similar to that found for Cr(II)/SiO$_2$+DEALE.

As a general conclusion, the results discussed in this work demonstrate once more that the intrinsic activity of the Cr sites in Phillips-type catalysts does depend not only on their molecular structure, but also on the concurrence of several other phenomena involving the support and the surroundings of the active sites [60].

References

[1] Nowlin TE Business and Technology of the Global Polyethylene Industry Wiley-Scrivener New York (2014) 432

[2] Market Report: Global Catalyst Market Acmite Market Intelligence Ratingen, Germany (2015) 542

[3] Hutley TJ, Ouederni M "Polyolefins - The History and Economic Impact" in Polyolefin Compounds and materials Springer Switzerland (2016)

[4] Hogan JP, Banks RL U.S. Patent 2, 825, 721 (1958)

[5] McDaniel MP (2010) Adv. Catal. 53:123-606

[6] Cicmil D, Meeuwissen J, Vantomme A, Wang J, van Ravenhorst IK, van der Bij HE, Munoz-Murillo A, Weckhuysen BM (2015) Angew. Chem. 54:13073-13079

[7] Schwerdtfeger E., Buck R., McDaniel M. (2012) Appl. Catal. A 423-424, 491.

[8] Bent BE, Nuzzo RG, Dubois LH (1989) J. Am. Chem. Soc. 111 1634

[9] Klepper KB, Nilsen O, Fjellvåg H (2010) Dalton Trans. 39:11628

[10] Kerber RN, Kermagoret A, Callens E, Florian P, Massiot D, Lesage A, Coperet C, Delbecq F, Rozanska X, Sautet P (2012) J. Am. Chem. Soc. 134:6767-6775

[11] Li JH, DiVerdi JA, Maciel GE (2006) J. Am. Chem. Soc. 128:17093-17101

[12] Pelletier J, Espinas J, Vu N, Norsic S, Baudouin A, Delevoye L, Trebosc J, Le Roux E, Santini C, Basset J-M, Gauvin RM, Taoufik M (2011) Chem. Commun. 47:2979

[13] Sauer J, Ugliengo P, Garrone E, Saunders VR (1994) Chem. Rev. 94:2095-2160

[14] Zhuravlev LT (2000) Colloid Surf. A 173:1-38

[15] Barzan C, Bordiga S, Groppo E (2016) ACS Catal. 6:2918-2922

[16] Liu BP, Terano M (2001) J. Mol. Catal. A 172:227-240

[17] Liu B, Šindelář P, Fang Y, Hasebe K, Terano M (2005) J Mol Catal A Chem 238:142-150

[18] Liu H, Fang Y, Nakatani H, Terano M (2004) Macromol Symp. 213:37-46

[19] Xia W, Liu B, Fang Y, Hasebe K, Terano M (2006) J Mol Catal A Chem 256:301-308

[20] Cicmil D, Meeuwissen J, Vantomme A, Weckhuysen BM (2016) ChemCatChem 8:1937-1944

[21] Cicmil D, van Ravenhorst IK, Meeuwissen J, Vantomme A, Weckhuysen BM (2016) Catal Sci Technol 6:731-743

[22] Xia W, Tonosaki K, Taniike T, Terano M, Fujitani T, Liu BP (2009) J. Appl. Polym. Sci. 111:1869–1877

[23] Groppo E, Lamberti C, Bordiga S, Spoto G, Zecchina A (2005) Chem. Rev. 105:115-183

[24] McDaniel M, Welch MB, Dreiling MJ (1983) J. Catal. 82:118-126

[25] Liu B., Šindelář P. , FangY., Hasebe K. , Terano M. (2005) J. Mol. Catal. A: Chem. 238:142-150

[26] Groppo E, Damin A, Otero Arean C, Zecchina A (2011) Chem. Eur. J. 17:11110 – 11114

[27] Martino GA, Barzan C, Piovano A, Budnyk A, Groppo E (2018) J. Catal. 357:206-212

[28] Figgis BN Introduction to ligand fields John Wiley & Sons New York (1966)

[29] Groppo E, Lamberti C, Bordiga S, Spoto G, Zecchina A (2005) J. Phys. Chem. B 109:15024-15031

[30] Ghiotti G, Garrone E, Zecchina A (1991) J. Mol. Catal. 65:73-83

[31] Vikulov K, Spoto G, Coluccia S, Zecchina A (1992) Catal. Lett. 16:117-122

[32] Bade OM, Blom R, Dahl IM, Karlsson A (1998) J. Catal. 173:460-469

[33] Chelazzi D, Ceppatelli M, Santoro M, Bini R, Schettino V (2004) Nat. Mater. 3:470-475

[34] Spoto G, Bordiga S, Garrone E, Ghiotti G, Zecchina A, Petrini G, Leofanti G (1992) J. Mol. Catal. 74:175-184

[35] Zecchina A, Bordiga S, Spoto G, Marchese L, Petrini G, Leofanti G, Padovan M (1992) J. Phys. Chem. 96:4991-4997

[36] Zecchina A, Garrone E, Ghiotti G, Coluccia S (1975) J. Phys. Chem. 79:972-978

[37] Zecchina A, Groppo E (2012) Proc. R. Soc. A-Math. Phys. Eng. Sci. 468:2087-2098

[38] Lamberti C, Zecchina A, Groppo E, Bordiga S (2010) Chem. Soc. Rev. 39:4951–5001

[39] Gianolio D, Groppo E, Vitillo JG, Damin A, Bordiga S, Zecchina A, Lamberti C (2010) Chem. Commun. 46:976–978

[40] Lupinetti AJ, Frenking G, Strauss SH (1998) Angew. Chem. -Int. Edit. 37:2113-2116

[41] Lupinetti AJ, Strauss SH, Frenking G (2001) Progr. Inorg. Chem. 49:1-112

[42] Braterman PS Metal Carbonyl Spectra Academic Press London (1975)

[43] Zhou MF, Andrews L, Bauschlicher CW (2001) Chem. Rev. 101:1931-1961

[44] Estephane J, Groppo E, Vitillo JG, Damin A, Gianolio D, Lamberti C, Bordiga S, Quadrelli EA, Basset JM, Kervern G, Emsley L, Pintacuda G, Zecchina A (2010) J. Phys. Chem. C 114:4451-4458

[45] Estephane J, Groppo E, Vitillo JG, Damin A, Lamberti C, Bordiga S, Zecchina A (2009) Phys.Chem.Chem.Phys. 11:2218-2227

[46] Barzan C, Gianolio D, Groppo E, Lamberti C, Monteil V, Quadrelli EA, Bordiga S (2013) Chem. Eur. J. 19:17277-17282

[47] Barzan C, Groppo E, Quadrelli EA, Monteil V, Bordiga S (2012) Phys.Chem.Chem.Phys. 14:2239–2245

[48] Morterra C, Mentruit MP, Cerrato G (2002) PCCP 4:676-687

[49] Cerruti M, Morterra C, Ugliengo P (2005) Chemistry of Materials 17:1416-1423

[50] Morterra C, Cerrato G, Novarino E, Mentruit MP (2003) Langmuir 19:5708-5721

[51] Platero EE, Mentruit MP, Morterra C (1999) Langmuir 15:5079-5087

[52] Arean CO, Platero EE, Mentruit MP, Delgado MR, Xamena F, Garcia-Raso A, Morterra C (2000) Micropor Mesopor Mat 34:55-60

[53] Sempels RE, Rouxhet PG (1976) J Colloid Interface Sci 55:263-273

[54] Pelmenschikov AG, Van Santen RA, Jänchen J, Meijer E (1993) J.Phys.Chem. 97:11071-11074

[55] Chen J, Thomas JM, Sankar G (1994) J. Chem. Soc., Faraday Trans. 90:3455-3459

[56] Aboulayt A, Binet C, Lavalley J (1995) J. Chem. Soc., Faraday Trans. 91:2913-2920

[57] Cerruti M, Bolis V, Magnacca G, Morterra C (2004) PCCP 6:2468-2479

[58] Knoezinger H, Krietenbrink H (1975) J. Chem. Soc., Faraday Trans. 1, 71:2421-2430

[59] Jeffery EA, Mole T (1968) Aust J Chem 21:2683-2686

[60] Barzan C, Piovano A, Braglia L, Martino GA, Lamberti C, Bordiga S, Groppo E (2017) J. Am. Chem. Soc. 139:17064-17073