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# New Strategies in the Raman Study of the Cr/$SiO_2$ Phillips Catalyst: Observation of Molecular Adducts on Cr(II) Sites

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We report the first Raman spectra of molecular adducts (CO and $N_2$) formed on Cr(II) sites dispersed on silica surface (Phillips catalyst for ethylene polymerization), thus obtaining indirect information about the metal anchored species. These results have been achieved using an ad hoc selected laser line (able to excite a ligand to Cr charge-transfer transition that does not relax in a radiative channel), and adopting as a support a silica aerogel behaving as an optically uniform medium in the region of work. These two combined strategies, never simultaneously applied before, allowed us to obtain great quality Raman spectra of surface species, demonstrating that Raman spectroscopy can have great sensitivity toward surface species present in small concentration. Raman spectroscopy thus becomes a powerful tool complementary to IR and UV−vis DRS spectroscopies for surface investigation. The improvement can be quantified by comparing published spectra of the oxidized Cr(VI)/$SiO_2$ system (the only available in the literature) with the more intense and much richer one obtained under the present experimental conditions, where new spectroscopic features (never observed before) are clearly observed.

## 1. Introduction

The Cr/$SiO_2$ Phillips catalyst, nowadays responsible for the production of more than one-third of the polyethylene worldwide,[1,2] has been the subject of much controversy since its discovery in 1958.[3,4] Numerous efforts have been devoted to determine the structure of the active sites and the real polymerization mechanism,[5−7] but a definitive conclusion is still missing.

The Phillips catalyst is commonly obtained by impregnating chromic acid onto amorphous silica and then calcining in oxygen at 923 K. A typical catalyst contains about 0.5−1.0% Cr by weight, corresponding to about 0.2−0.4 Cr atoms per $nm^2$, for a standard silica having a surface area of 400 $m^2\ g^{-1}$. It is well known that the anchoring process is an esterification reaction, in which the hydroxyl groups present on the silica surface are consumed and chromium are attached to the surface by oxygen linkages in the hexavalent state.[5,8−14] However, the anchored Cr(VI) are not yet the sites for the propagation reaction. In the industrial procedure, the formation of the active centers takes place by direct interaction of Cr(VI) with ethylene at 373−423 K. An induction time is observed prior to the onset of the polymerization, attributed to a reduction phase, during which Cr(VI) is reduced to Cr(II).[5] To discriminate between the reduction and the polymerization phases, a simplified version of the catalyst has been used since the beginning, obtained by reduction of the surface chromate precursors with CO at 623 K.[4,5,7,8,15,16] In the following, we will refer to this catalyst as the “CO-reduced” one, to distinguish it from the “oxidized” or “calcined” catalyst present before the CO-reduction. According to literature data, no significant difference in the polymerization products has been found by comparing this model CO-reduced catalyst with the ethylene-reduced one.[5,17]

Today, no doubts are present concerning the average oxidation state of the anchored chromium species: (i) VI in the oxidized catalyst,[5] and (ii) just above II in the CO-reduced catalyst, as comprised of mainly anchored Cr(II) and a variable amount of pseudo-octahedral Cr(III) species, presumably in the form of $Cr_2O_3$, whose concentration depends on the Cr loading, the silica support, the thermal treatments, etc.[2,8,18−23]

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Conversely, the molecular structure of the anchored chromium species, both in the oxidized and in the reduced form of the catalyst, is still a strong point of discussion in the literature, and several spectroscopic techniques (UV−vis, IR, Raman, XAS, XPS, etc.) have been employed to solve the problem.[6,7] The full understanding of the chromium structure on the silica surface, both in the oxidized and in the reduced catalysts, in fact, seems to play a crucial role for a deeper comprehension of the real polymerization mechanism on the Phillips catalyst, which is still an open question in the literature.[7] Concerning the oxidized form of the catalyst, several molecular structures (monochromate, dichromate, polychromate, etc.) have been proposed,[2,4,6,7,11−14,18,24,25] whose relative concentration is a function of the support type and composition, of the chromium loading, of the activation procedure, and of the presence of possible dopants. Coming to the reduced form of the catalyst, the common opinion is that the structure of the anchored Cr(II) ions is extremely heterogeneous, thus reflecting the high heterogeneity of the amorphous support.[5,7] IR spectroscopy of probe molecules has been revealed by far as the more sensitive and useful technique to discriminate among different Cr(II) sites on the silica surface.[7,26−32]

Raman spectroscopy is potentially a powerful technique to determine the molecular structure of the anchored chromium species and should offer information complementary to that obtained from other techniques. Nevertheless, few Raman works concerning the Phillips catalyst or related Cr/Silica systems (such as $Cr/SiO_2-Al_2O_3$, $Cr/SiO_2-TiO_2$, and Cr/MCM materials) appeared in the literature,[6,10,11,33−38] if compared to the large amount of results obtained with IR spectroscopy. In this regard, the seminal works of Wachs et al. have to be particularly mentioned because of their pionering character.[6,10,11,33] Furthermore, Raman spectroscopy has been applied up to now essentially to characterize the $Cr(VI)/SiO_2$ system. Few reasons could be tentatively accounted for these lacks; all are intrinsically related to the silica support and thus are apparently difficult to overcome. (i) The identification of Raman bands for the $Cr/SiO_2$ system is partially hampered by the presence of a rising baseline due to luminescence from the silica support, which has been well documented.[6,10,11] (ii) Vibrations involving the chromate groups are significantly mixed with vibrations involving the Si−O bonds of the silica support, so that it is very difficult to discriminate between the two contributions, especially for low chromium loadings.[10] (iii) To obtain direct information about the reduced $Cr(II)/SiO_2$ system, techniques able to reveal the Cr−O-support vibrations are required. This task is particular difficult, due to the partly ionic character of the Cr−O-support bond, which results in a very low Raman intensity because of the decrease of polarizability. This explains also why metal−O-support vibrations have never been observed for other supported metal oxide systems, for example, supported rhenium oxide, molybdenum oxide, and tungsten oxide.[10,39]

In this work, we have used Raman spectroscopy to characterize the Cr(VI) and Cr(II) species anchored on the amorphous silica support, trying to overcome some of the problems discussed previously. By using as a support a silica aerogel characterized by peculiar scattering properties and by working in resonant conditions, we obtained very intense Raman spectra of surface Cr species. On the oxidized Cr(VI)/$SiO_2$ system, an improved, more intense, and richer Raman spectrum, if compared to the spectra present in the literature, has been obtained. On the $Cr(II)/SiO_2$ catalyst, we report, to our knowledge for the first time, Raman spectra of probe molecules (CO and $N_2$) adsorbed on Cr(II) sites. This makes Raman spectroscopy actually complementary to the much more used IR spectroscopy.[26−32,40−42] In this way, we can obtain indirectly also information about the Cr(II) anchored species, thus overcoming the difficulty in probing the Cr−O-support vibrations. Raman experiments have been supported by UV−vis spectra and compared to IR results. We will show that the complementary use of the three spectroscopies is decisive in identifying the molecular structure of the anchored Cr(VI) and Cr(II) species on the surface of the Phillips catalyst. Our approach can be easily extended to the fraction of metal-supported systems for which limited information has been obtained with the Raman technique until now.

## 2. Experimental Section

**2.1. Raman Experiments: Sample Preparation and Experimental Setup.** The $Cr/SiO_2$ samples for Raman experiments have been prepared by impregnating fragments of silica aerogel monolite (see Figure 1) in the millimeter scale, with a solution of $CrO_3$ in $CH_3CN$, resulting in a 0.5 wt % Cr loading. The aerogel monolites

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**Figure 1.** Photo of an aerogel monolite used as a support for Raman experiments lying on a black printed blue paper. The optical transparency allows a perfect reading of the text written on the paper.

have been kindly supplied by Novara Technology Co.[43] and exhibit a surface area of about 700 m$^2$ g$^{-1}$. After the impregnation step, the aerogel fragments were dried at room temperature and then transferred into a Raman cell designed to allow thermal treatments of the sample either under high vacuum or in the presence of gases. The samples were then activated according to the following procedure: (i) activation at 923 K; (ii) calcination in O$_2$ at the same temperature for 1 h (oxidized sample, light orange); (iii) reduction in CO at 623 K (reduced sample, light blue-green), followed by CO removal at the same temperature; and (iv) cooling to room temperature.

Raman spectra were recorded by using a Renishaw micro-Raman system 1000 spectrometer. A He−Cd laser emitting at 442 nm (22 625 cm$^{-1}$) was used in which its output power was 10% of its maximum value. The photons scattered by the sample were dispersed by a 2400 lines/mm grating monochromator and simultaneously collected on a CCD camera; the collection optic was set at 20× objective. The oxidized sample (activation procedure stopped at point ii) has been measured in O$_2$ atmosphere (40 Torr), while the reduced one (completed activation) has been measured in CO or N$_2$ atmosphere (40 Torr) employing a self-made cell, which is constituted by a suprasil-quartz cuvette (Hellma, 2 mm optic path) sealed to a quartz tube.

**2.2. Diffuse Reflectance UV−Vis and FTIR Experiments: Sample Preparation and Experimental Setup.** The Cr/SiO$_2$ catalysts for diffuse reflectance (DRS) UV−vis and FTIR experiments were obtained by impregnating a silica aerosil (Degussa, surface area 400 m$^2$ g$^{-1}$) with a CrO$_3$ aqueous solution, following the procedure described elsewhere,[5,27,29,30,42,44] with a Cr loading of 0.5 wt % with respect to SiO$_2$. For IR measurements, the powder was pressed in thin pellets, while for DRS UV−vis experiments, the powder was not pressed. In both cases, the activation procedure was the same as described for the Raman experiments. The DRS UV−vis spectra were obtained with a Perkin-Elmer Lambda 19 spectrophotometer, equipped with a reflectance sphere. The FTIR spectra were collected by using a Bruker IFS66 spectrophotometer, with a resolution of 2 cm$^{-1}$.

## 3. Results and Discussion

### 3.1. The Oxidized Cr/SiO$_2$ Catalyst: Molecular Structure of Cr(VI) Species.

Figure 2a reports the DRS UV−vis spectrum of the oxidized Cr/SiO$_2$ catalyst (solid line). The spectrum is characterized by three main components at about 40 000, 30 000, and 21 600 cm$^{-1}$, which are ascribed in the literature[6,7,20,45,46] to O→Cr(VI) charge-transfer (CT) transitions. DRS UV−vis spectroscopy has been widely used to investigate the nuclearity of the chromate species present on the oxidized Cr/SiO$_2$ catalyst. The main limitation of UV−vis spectroscopy is that the spectra are particularly complex and characterized by the overlap of several intense and broad CT bands, so that it is very difficult to discriminate

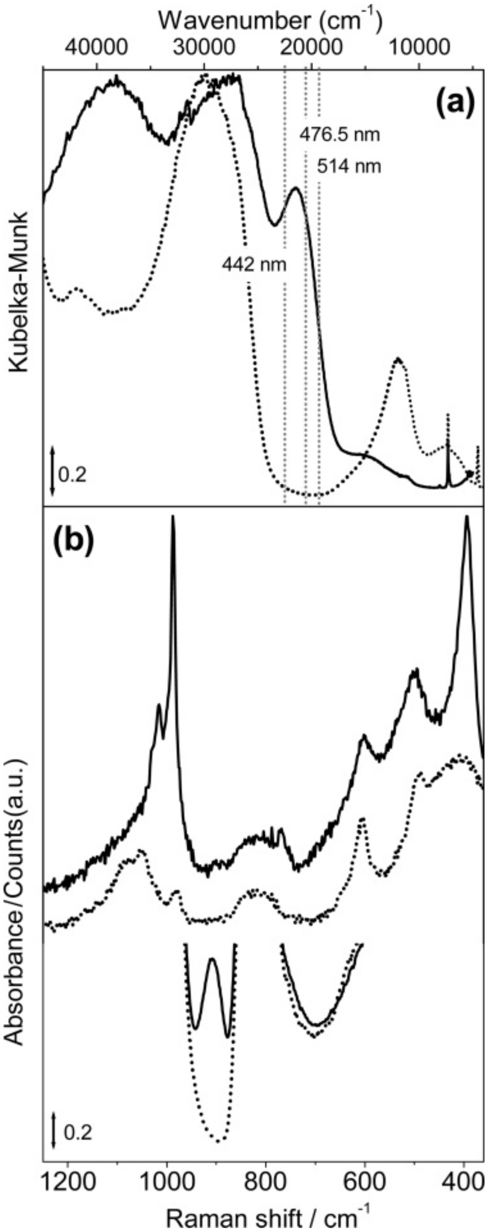

**Figure 2.** (a) DRS UV−vis spectra of a Cr/SiO$_2$-aerosil catalyst (0.5 wt %). Solid and dotted curves refer to the oxidized and the CO-reduced catalysts, respectively. The three vertical lines refer to the energy position of the Raman excitation λ used in this work (442 nm) and in the literature (476.5 and 514 nm). (b) Top part: Raman spectra of a Cr(VI)/SiO$_2$-aerogel, solid curve, and of a Cr(II)/SiO$_2$-aerogel, dotted curve. Bottom part: FTIR spectra of the Cr/SiO$_2$-aerosil catalyst (0.5 wt %). Solid and dotted curves are as in part (a).

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between different species characterized by very similar optical manifestations. Weckhuysen et al.[21] have tried to establish the monochromates/dichromates ratio by deconvolving the CT bands present in the spectra of calcined samples (monochromates, bands at 44 100, 30 600, and 20 300 cm$^{-1}$; dichromates, bands at 45 500, 36 600, and 25 000 cm$^{-1}$). They found that the main chromium species on industrial pyrogenic silica supports (Cab-O-Sil, 300 m$^2$/g) characterized by low chromium loadings are monochromates.[21]

If mono-, di-, and polychromates are characterized by very similar electronic transitions, conversely they give rise to several distinct vibrations, which differ both in frequency and in intensity. For this reason, the application of vibrational spectroscopies is mandatory to discriminate between different chromium molecular species. Nevertheless, IR spectroscopy is scarcely useful in the characterization of the oxidized form of the Cr/$SiO_2$ catalyst. In fact, the vibrational manifestations of Cr=O species fall in a region obscured by the intense modes of the silica support[47] (absorptions present at frequencies higher than 950 cm$^{-1}$ and lower than 880 cm$^{-1}$ in Figure 2b, bottom part). In the so-called “silica window”, only a band at 908 cm$^{-1}$ is evident. This band has already been reported in the past[8,10] and explained with the presence of terminal $CrO_3$ units, isolated or not.[10,48]

Raman spectra do not suffer of the same problems encountered in the IR, because the vibrational modes of silica in the 1300−200 cm$^{-1}$ range contribute scarcely to the inelastic light scattering. For this reason, Raman spectroscopy has been used in the past to discriminate between different Cr molecular structure on different supports ($SiO_2$, $SiO_2$−$Al_2O_3$, $SiO_2$−$TiO_2$, etc.).[6,10,11,33,35−37] Raman experiments performed in the past on calcined Cr(VI)/$SiO_2$ samples by using an excitation $\lambda$ of 514.5 nm were characterized by a single band at 986 cm$^{-1}$, which has been assigned to the stretching vibration of a Cr=O bond belonging to monochromate species.[10,33,36] No bands due to Cr−O−Cr linkages have been observed in the 820−880 cm$^{-1}$ region, at least for low Cr loadings. The Raman spectra of the calcined Cr(VI)/$SiO_2$ present in the literature suffered, however, for the presence of an increasing baseline due to the fluorescence of the silica support, as already anticipated in the Introduction, and the 986 cm$^{-1}$ band was in general rather broad. As a consequence, the observation of well-resolved Cr=O vibrations was very difficult and the presence of minor polymeric species on the silica surface could not be completely ruled out.[10,33,36]

Very recently, Dines and Inglis[34] obtained a well-defined Raman spectra on a Cr(VI)/$SiO_2$ sample with 1.0 wt % Cr loading, by means of a 476.5 nm laser excitation. They observed a single well-defined band at 990 cm$^{-1}$, which is analogous to the 986 cm$^{-1}$ band observed in previous studies.[10,33,36] Moreover, after having performed a baseline subtraction aimed to eliminate the fluorescence background, authors claimed the existence of a weak shoulder at the high energy tail of the main peak, centered at 1004 cm$^{-1}$, which has been attributed to the expected antisymmetric Cr=O stretch. The manipulation of the raw experimental data needed to appreciate this shoulder, as well as the borderline signal-to-noise ratio of the data around 1004 cm$^{-1}$, makes the claimed observation of the antisymmetric Cr=O stretching rather questionable. However, to support this weak experimental evidence, Dines and Inglis[34] complemented their work with ab initio calculations, with DFT methods using the B3-LYP functional, performed on a very simple model, involving $CrO_4$ bridging across a siloxane group, which yielded $\tilde{\nu}_s$(O=Cr=O) at 983 cm$^{-1}$ and $\tilde{\nu}_{as}$(O=Cr=O) at 1010 cm$^{-1}$, respectively (reported frequencies have been rescaled by a factor of 0.85). Other chromate vibrations, involving Cr−O stretching and O=Cr−O deformation, were predicted to be strongly mixed with vibrations of the support, giving rise to composite modes that have much lower Raman intensity.

On the basis of a critical examination of the limitations[10,11,33,36] and recent improvements[34] of the literature results presented above, we have adopted in our Raman experiments new strategies that allowed us to strongly improve the signal-to-noise ratio of the Raman spectra collected on the Cr(VI)/$SiO_2$ system. Improvements came from the choice of both the $\lambda$ of the laser source and the silica support, as discussed in the following.

In past years, it has been demonstrated that a laser excitation $\lambda$ that falls near the energy required for an electronic transition of the material may lead to a remarkable increase in the intensity of Raman bands if the resonance occurs. The resonance Raman spectroscopy has been widely used to identify the locations of titanium,[47,49−52] iron,[53] and vanadium[54,55] in microporous and mesoporous molecular sieves. Moreover, it has also been demonstrated that the use of a UV−vis line as exciting source of Raman spectroscopy can avoid the fluorescence interference from silica materials.[52,56] By using an excitation $\lambda$ of 442 nm, we eliminated the fluorescence problems, and, at the same time, we took advantage of the resonance effect, as clearly evidenced in Figure 2a. Furthermore, we have collected Raman spectra with a low laser power, to selectively enhance the Cr=O contributions over the Si−O ones. Following this experimental approach on a 0.5 wt % Cr(VI)/$SiO_2$ sample, after oxidation at 923 K, we observed a remarkable narrow and very well-resolved peak at 987 cm$^{-1}$ (fwhm = 10 cm$^{-1}$) growing on the rising baseline of the silica support (spectrum not shown for brevity). On the basis of what has been

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discussed so far, it can be understood why the quality of the spectra reported by Dines and Inglis[34] is intermediate between the earlier ones[10,11,33,36] and the new one here discussed. In fact, Dines and Inglis,[34] using a $\lambda$ of 476.5 nm (21 000 cm$^{-1}$), start to enter into the resonant conditions, the excitation line in the low energy tail of the absorption spectrum of the sample (Figure 2a). Conversely, the Raman spectra reported by Wachs and co-workers,[10,33,36] collected with a $\lambda$ of 514.5 nm (19 400 cm$^{-1}$), are almost out of the absorption edge and thus of the resonant conditions (Figure 2a).

A further improvement has been obtained by repeating the same Raman experiments on a Cr(VI)/SiO$_2$ sample prepared by anchoring Cr(VI) on a little fragment of a silica aerogel monolite (vide supra Experimental Section). Such a support is chemically equivalent to a standard aerosil, as testified by IR spectroscopy showing O−H and Si−O stretching bands comparable to those observed in the case of a silica aerosil (spectra not reported for brevity). The aerogel monolites (see Figure 1) are perfectly transparent from the near UV to the mid-IR region of the electromagnetic spectrum. This peculiar optical property arises from the coupling of (i) the absence of absorbing bands (as for all pure SiO$_2$ materials), and of (ii) the absence of intra-grain scattering processes, which is the main reason of light attenuation in the common powdered silica. In other words, aerogel monolites exhibit an optical behavior very close to that of a homogeneous liquid phase, which is the ideal medium for performing Raman experiments. Moreover, its porous nature allows one to work with a sample having a surface area comparable to (or even greater than) that of commonly used amorphous aerosil. It is finally worth noticing that the ethylene polymerization performed on both supports results in a very similar time dependence of the in situ IR spectra monitored under comparable conditions, which basically reflects a similar catalytic activity of the two systems.[7] In other words, the Cr/SiO$_2$-aerogel system represents the ideal material for spectroscopic investigations in both visible and NIR regions, without being appreciably different, on a catalytic level, from the classical Cr/SiO$_2$-aerosil system.

The finalized choice of the silica-aerogel support and of resonant conditions has permitted us to greatly improve the quality of our Raman spectra with respect of literature data,[6,7,10,11,33−38] as shown in Figure 2b, top part, solid line curve. The spectrum is particularly intense in the entire frequency region and more structured than those presented in the previous works. It is dominated by the sharp and well-resolved band at 987 cm$^{-1}$, the only component belonging to chromate species reported up to now in the literature, assigned to the $\tilde{\nu}_s$(O═Cr═O) mode, which grows on the structured background of the aerogel system. Beside this band, two other well-resolved components at 1014 and 394 cm$^{-1}$, that is, in the regions where the $\tilde{\nu}_{as}$(O═Cr═O) and $\delta$(O═Cr═O) modes are expected, not present on the unsupported aerosil system (vide infra Figure 3), are observed here for the first time. It must be noticed that the intense band at 987 cm$^{-1}$ is characterized by a shoulder at about 1000 cm$^{-1}$, that is, at a frequency very close to that obtained by deconvolution of the baseline subtracted experimental data of Dines and Inglis.[34] The presence of two signals in the frequency region where the $\tilde{\nu}_{as}$(O═Cr═O) mode is expected (well-defined band at 1014 cm$^{-1}$ and weak shoulder around 1000 cm$^{-1}$) could be a consequence of the heterogeneity of the Cr(VI) supported on the amorphous SiO$_2$.

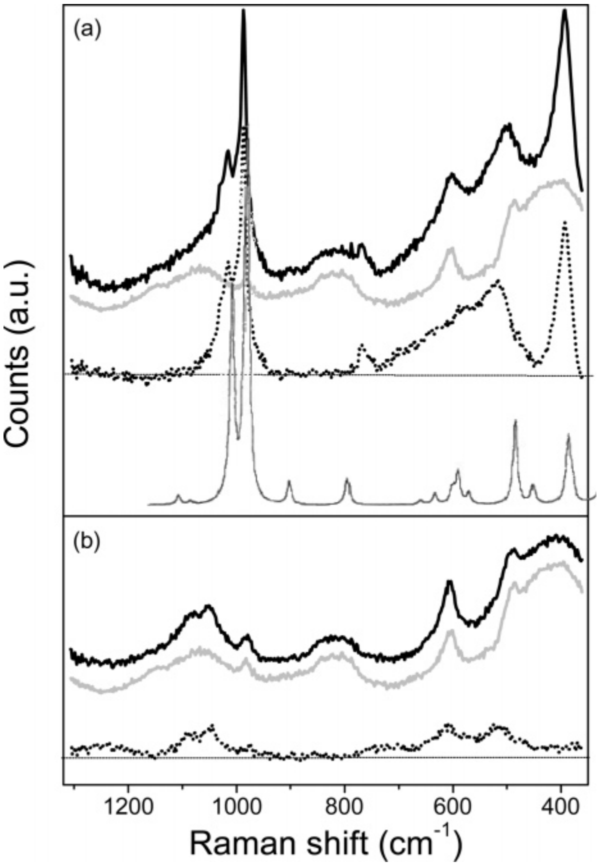

**Figure 3.** (a) Raman spectra of the oxidized Cr(VI)/SiO$_2$-aerogel catalyst (black solid curve), of the pure aerogel support (gray curve), and difference spectrum (dotted curve). For comparison also the theoretical Raman spectrum calculated by Dines and Inglis (ref 34) is reported in the bottom part of the figure. (b) Raman spectra of the CO-reduced Cr(II)/SiO$_2$-aerogel catalyst (black solid curve), of the pure aerogel support (gray curve) ,and difference spectrum (dotted curve).

By a deeper inspection and by a direct comparison of the spectrum of the Cr(VI)/SiO$_2$ sample with the spectrum of the pure silica support (before Cr impregnation), other minor features come out, as shown in Figure 3a. In particular, a little band around 770 cm$^{-1}$ and a broad absorption in the 450−650 cm$^{-1}$ interval are clearly shown in the difference spectrum (dotted curve in Figure 3a). The subtraction has been performed after having normalized the two spectra to the band at 875−740 cm$^{-1}$, where only the Si−O modes of the silica support give contributions. The silica support modes are expected to give contributions in the 875−740 and 650−350 cm$^{-1}$ regions, and to strongly couple with the Cr−O-support modes, so that it is not possible to assign these spectral features solely to the vibration of Cr−O-support or Si−O bonds. Nevertheless, the difference spectrum is extraordinarily similar to the Raman spectrum calculated by Dines and Inglis[34] (SCF-DFT B3-LYP method) in the case of a very simple model involving CrO$_4$ bridging across a siloxane group, also reproduced in Figure 3a. Skipping the modes directly related with the O═Cr═O unit, which have been discussed above, the predicted vibrational modes involving both Cr−O and Si−O bonds fall at 901, 793, 587, 566, 480, and 445 cm$^{-1}$, respectively.[34] Unfortunately, a direct comparison of the experimental and calculated Raman intensities is not feasible, because the theoretical ones cannot take into account the resonance enhancement. Notwithstanding this fact, the correspondence between computed and measured frequencies is striking.

By comparing the UV−vis, IR, and Raman results, the following considerations about the structure of Cr(VI) species anchored on the amorphous silica can be put forward. (i) The UV−vis spectroscopy alone is not able to definitely establish the molecular structure of Cr(VI) species, and the use of vibrational spectroscopies is required. However, the UV−vis technique is necessary to chose the right Raman laser excitation $\lambda$ able to induce Raman resonant conditions. (ii) The Raman bands at 987, 1014, and 394 cm$^{-1}$, the last two here experimentally observed for the first time, are consistent with a terminal $CrO_2$ unit. The absence of any other narrow bands in the 800−900 cm$^{-1}$ region, also when the silica fluorescence background has been eliminated, definitely exclude a significant presence of polymeric chromium species, at least at low chromium loadings, as already suggested (but not safely demonstrated) in the past and in contrast with the case of Cr(VI) anchored on other oxide supports.[6,10,11,33,34] (iii) The strong coupling between the Cr−O and the Si−O vibrational modes prevents any attempt to make a specific assignation of the bands which appear in the 450−800 cm$^{-1}$ interval. Nevertheless, the comparison of our Raman spectrum of the Cr(VI)/$SiO_2$-aerogel system to that predicted by Dines and Inglis[34] suggests that the presence of grafted Cr(VI) species modifies the pure silica vibrational modes. (iv) On the basis of these considerations, the band at 908 cm$^{-1}$ clearly observed in the IR spectrum (see bottom part of Figure 2b), but not visibile in the Raman one, may be reinterpreted with respect to the past[10] and assigned to a Si−O vibrational mode perturbed by the presence of the chromate units. It is worth mentioning that the highly strained siloxane bridges that are formed on the pure silica upon high-temperature dehydroxylation[7,57,58] give absorptions in the same frequency region.[7,59] The grafting of Cr(VI) may cause a similar strain on the silica surface.

**3.2. The CO-Reduced Catalyst: Direct Information about the Cr(II) Structure.** Once the nuclearity of the oxidized Cr(VI)/$SiO_2$ catalyst has been defined, the next goal is to determine the molecular structure of the CO-reduced Cr(II)/$SiO_2$ catalyst, because the comprehension of the Cr(II) structure may lead to the understanding of the polymerization mechanism on the CO-reduced model catalyst. Figure 2a (dotted curve) shows the UV−vis DRS spectrum of the CO-reduced Cr/$SiO_2$ sample (0.5 wt % Cr loading on aerosil). The spectrum is characterized by a strong absorption in the CT region (there are at least two overlapped components at about 28 000 and 30 000 cm$^{-1}$) and by two bands in the d−d region, at transition energies of about 12 000 and 7500 cm$^{-1}$, assigned in the literature to coordinatively unsaturated Cr(II) species.[7,8,11,18,20,22,26] Unfortunately, no clear inference about the coordination and symmetry of Cr(II) ions can be made from the comparison of the UV−vis results to the spectra of the rare Cr(II) homogeneous complexes carefully studied so far. The recent ab initio calculations performed by Espelid and Børve[60] suggested that the Cr(II) centers are in a pseudo-tetrahedral structure and that the ions are preferentially sensing the crystal field caused by two strong $SiO^-$ ligands, even if the possible presence of comparable amounts of pseudo-octahedral Cr(II) species cannot be excluded, because the intensities of the associated d−d bands can be very weak.

Opposite from the case of the oxidized catalyst, little direct information about the CO-reduced catalyst can be obtained by means of vibrational spectroscopies. As already anticipated in the previous sections, IR and Raman spectroscopies, in fact, are unable to distinguish between Cr−O-support vibrations and the Si−O modes. The band at 908 cm$^{-1}$, which characterizes the IR spectrum of the oxidized Cr(VI)/$SiO_2$ sample, totally disappears upon CO-reduction (dotted curve in Figure 2b, bottom part). In the same way, the Raman spectrum of the CO-reduced Cr/$SiO_2$ sample (dotted curve in Figure 2b, top part) shows the disappearance of the bands previously assigned to the monochromate species. The difference spectrum between the reduced catalyst and the pure silica support is reported in Figure 3b, dotted curve. As for the oxidized sample, also in this case a low absorption is evident in the 450−800 cm$^{-1}$ interval, together with a minor feature in the 1000−1100 cm$^{-1}$ region. The lower intensity of these components, if compared to those present in the oxidized case, suggests that the perturbation on the silica framework induced by the chromate units is greater than that caused by grafted Cr(II) ions. This fact, which explains also the absence of the band at 908 cm$^{-1}$ in the IR spectrum, is not strange, because the reduction of Cr(VI) leads certainly to a surface relaxation, to stabilize the less coordinated Cr(II) ions.

To improve the knowledge obtained by means of UV−vis spectroscopy and to better clarify the structure of Cr(II) ions on the silica surface, we have tried to use the method of the probe molecules, commonly applied in the case of IR spectroscopy,[41,42] also with UV−vis and Raman spectroscopies. Of course, it must be kept in mind that different probe molecules can give different answers (depending upon the interaction strength) and that this method is not absolute, because the probing process is necessarily associated with a perturbation of the surface. This is the reason why it is always preferable to use more than one molecule to probe the structure of surface sites: in our case, we have chosen CO and $N_2$ molecules, characterized by a rather strong and a weaker strength of interaction, respectively, which are able to adsorb to Cr(II) even at room temperature.

**3.3. Indirect Information about the Cr(II) Structure: CO Adsorption on the Cr(II)/$SiO_2$ Catalyst.** CO is an excellent probe molecule for Cr(II) sites, because its interac-

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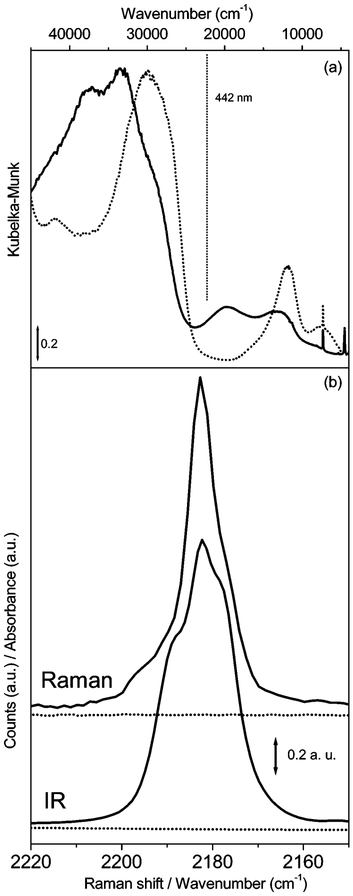

**Figure 4.** CO adsorption on the CO-reduced Cr(II)/SiO$_2$ catalyst as monitored by DRS UV−vis (a), Raman and FTIR spectroscopies (b, top and bottom, respectively). Dotted and solid curves refer to the catalyst before and after the CO interaction, respectively. CO equilibrium pressure: 40 Torr. Vertical dotted line indicates the laser line used in the Raman experiment.

tion is normally rather strong. In Figure 4a (solid curve), the DRS UV−vis spectrum of the Cr(II)/SiO$_2$ catalyst after interaction with 40 Torr of CO at room temperature is reported. The spectrum is characterized by the consumption of the two d−d bands described before (12 000 and 7500 cm$^{-1}$), by the appearance of two new d−d transitions at 12 900 and 19 700 cm$^{-1}$, and by the shift of the CT band toward higher frequencies. Without entering into detail, the evolution of the UV−vis spectrum upon CO addition can be explained in terms of an increase of the Cr(II) coordination number, due to the formation of mono- and dicarbonyl species. This phenomenon causes a shift of the d−d transitions toward the values more typical of the octahedral coordination.[7] Furthermore, in the presence of CO, which is an electron donor molecule, more energy is requested to transfer electrons from the oxygen ligands of the support to Cr(II) species; as a consequence, the O→Cr CT transition shifts at higher frequencies (from 28 000 to 30 000 to 33 700 cm$^{-1}$). At increasing CO pressure, also the CO→Cr(II) CT transition becomes visible (band at 37 400 cm$^{-1}$).

The increase of the Cr(II) coordination number upon CO adsorption is confirmed by IR spectroscopy, which has been used extensively in the past to characterize the CO-reduced Cr/SiO$_2$ system. No attempt will be made to cover the entire field here, and, in this respect, we refer to several literature papers.[7,26−32,40] Briefly, we recall that high CO coverage on Cr(II)/SiO$_2$ gives rise to the formation of the so-called "room-temperature triplet" in the 2191−2178 cm$^{-1}$ region, that is, at frequencies higher than that of CO gas (2143 cm$^{-1}$) as reported in Figure 4b, bottom part (solid curve). The observed high CO stretching frequencies indicate that CO bonding relies predominantly on electrostatic and $\sigma$-donation effects.[61] By analyzing the evolution of the $\tilde{\nu}_{CO}$ bands upon CO pressure variation, it has been stated that Cr(II) sites are distributed in two basic structural configurations, $Cr^{II}_A$ and $Cr^{II}_B$, according to the nomenclature adopted in refs 7,26−30,62,63. $Cr^{II}_B$ sites are able to coordinate only one CO molecule at room temperature, giving rise to the band at 2191 cm$^{-1}$, see Figure 4b, bottom part. $Cr^{II}_A$ sites are more coordinatively unsaturated than $Cr^{II}_B$ sites, as they are able to coordinate at room temperature up to two CO molecules, responsible for the doublet at 2183−2179 cm$^{-1}$. Furthermore, $Cr^{II}_A$ sites have a higher tendency to give d−$\pi$ interactions. The absence of bands at $\tilde{\nu} < 2100$ cm$^{-1}$ (vide infra Figure 5a) demonstrates that no bridging CO structures[64,65] are formed upon CO dosage at room temperature.[7,26−30,62,63] It has been demonstrated that the relative intensity of the three components, and thus the relative concentration of the two chromium species, strongly depends on the thermal history of the catalyst.[7]

By adopting the same strategies discussed before for the study of the oxidized catalyst, we have been able, to our knowledge for the first time, to observe the CO "room temperature triplet" also by means of Raman spectroscopy (Figure 4b, top part). It is worth noticing that the CO signal is extraordinarily intense in the Raman spectrum. In Figure 5, the IR (part a) and Raman (part b) spectra of the CO adsorbed on the Cr(II)/SiO$_2$ sample are reported and compared in an extended frequency range covering both C−O and Si−O modes. The intensity of the CO triplet in the IR spectrum is about twice that of the first harmonics of the bulk silica modes (bands in the 2000−1500 cm$^{-1}$ region), while the silica modes at frequencies below 1400 cm$^{-1}$ are so intense that they saturate the detector. Conversely, the CO triplet in the Raman spectrum is more than 2 times higher than the bulk silica modes at low frequencies. On one hand, this means that, considering the high Cr dilution, CO molecules adsorbed on surface Cr(II) species are better Raman scatterers than SiO$_4$ units by about 3 orders of magnitude. On the other hand, it is evident that the ratio of the response of surface CO versus bulk SiO$_4$ moieties is increased by several orders of magnitudes by moving from IR to Raman. This gigantic effect suggests that some resonance effects are probably occurring. For the time being, as the exciting source is in the high energy d−d transition of the Cr(II)···(CO)$_2$ complexes, a new charge distribution

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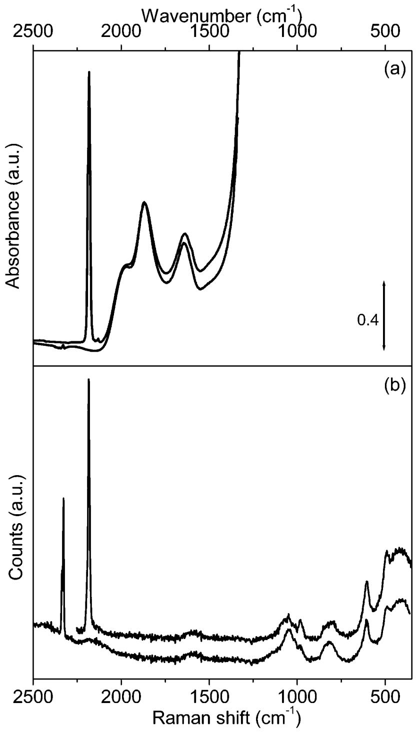

**Figure 5.** IR (a) and Raman (b) spectra of the CO (upper curves) and $N_2$ (lower curves) adsorption on the Cr(II)/$SiO_2$ catalyst. In the IR spectra, the frequency region below 1400 $cm^{-1}$ is dominated by the intense bulk modes of the silica, which saturate the detector.

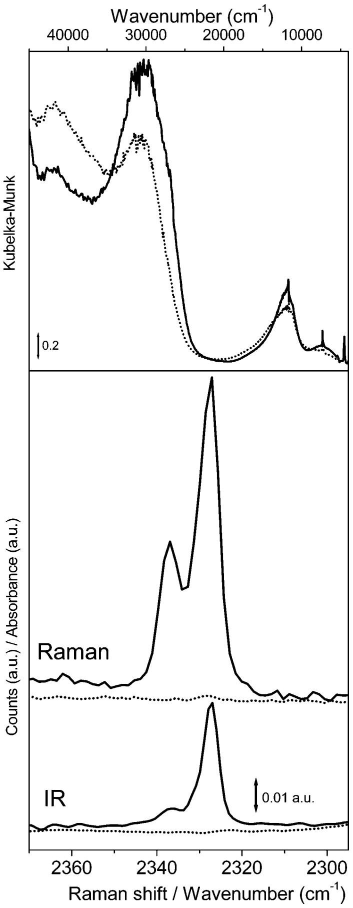

**Figure 6.** $N_2$ adsorption on the CO-reduced Cr(II)/$SiO_2$ catalyst as monitored by DRS UV−vis (a), Raman and FTIR spectroscopies (b, top and bottom, respectively). Dotted and solid curves refer to the catalyst before and after the $N_2$ interaction, respectively. $N_2$ equilibrium pressure: 40 Torr.

is expected for Cr(II) sites, which may induce a great variation of the polarizibility of the adsorbed CO molecules. However, without a systematic ab initio study, the last sentence must be considered on a purely speculative level.

Coming to a detailed discussion of the Raman CO triplet, it is characterized by an intense component at 2183 $cm^{-1}$, by a shoulder at about 2179 $cm^{-1}$, and by a less resolved component at 2191 $cm^{-1}$ (Figure 4b, solid line in the top part). The CO "room temperature triplet" obtained with IR and Raman spectroscopies is clearly characterized by a different relative intensity of the three components. This can be explained (i) by simply considering that the experimental conditions are not exactly the same and/or (ii) by taking into account the different selection rules that govern the two spectroscopies. Starting from the first point, it is important to notice that during Raman experiments the local temperature on the sample can be higher than that present during IR experiments, due to the laser irradiation. In these conditions, the stability of the CO species could change if compared to that of the same species during IR experiments. As a consequence, it is not possible to compare the relative intensity of the bands at 2191 and 2183−2179 $cm^{-1}$ in the two triplets, because it could be explained in terms of a different relative population of the two carbonyl species. Coming to the second point, we expect that some vibrational modes should be enhanced/depressed in Raman or IR spectra according to the geometry of the carbonyl species and/or the local environment, that is, the polarization ability of the Cr center. This means that the comparison between the Raman and the IR triplets should allow, in principle, one to make some considerations about the coordination geometry of the carbonyl species and the polarizing ability of the involved Cr centers. We can compare the relative intensity of the bands at 2183 and 2179 $cm^{-1}$, that is, the two bands assigned to a dicarbonyl species on $Cr^{II}_A$ centers, in the IR and Raman triplets, as they belong to the same species. From this comparison, it is clear that the band at 2183 $cm^{-1}$ is relatively more intense with respect to that at 2179 $cm^{-1}$ in the Raman spectrum. This observation strongly supports the assignment of the two bands to the symmetric and antisymmetric stretching modes of a dicarbonyl species.[7,29] The total symmetric mode at 2183 $cm^{-1}$, in fact, is strongly enhanced in the Raman spectrum, while the antisymmetric mode at 2179 $cm^{-1}$ is more active in the IR spectrum. On the basis of the intensity ratio of the symmetric and antisymmetric stretching bands of the dicarbonyl species in the IR spectrum ($I_{2183}/I_{2179} = 1.1$), and assuming a $C_{2v}$-like symmetry, an angle between the two CO molecules of about 85° is inferred.[64,66] The complexity of the situation does not allow one at the moment to extract other conclusions about the geometry of the carbonyl species and the polarizing ability of the Cr centers, and further investigations are required.

**3.4. Indirect Information about the Cr(II) Structure: $N_2$ Adsorption on the Cr(II)/$SiO_2$ Catalyst.** The adsorption of $N_2$ has an effect on the UV−vis spectrum less pronounced than that caused by the CO, as reported in Figure 6a. In this

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case, the two d−d bands characterizing the Cr(II)/$SiO_2$ sample (12 000 and 7500 $cm^{-1}$) are less eroded, and a low absorption centered at about 16 360 $cm^{-1}$ (i.e., on the tail of the more intense d−d band) appears. At the same time, the CT band at about 30 000 $cm^{-1}$ decreases, and a broad component at about 41 600 $cm^{-1}$ grows. The evolution of the UV−vis spectrum upon $N_2$ adsorption can be interpreted taking into account the fact that $N_2$ is a $\sigma-\pi$ acceptor ligand weaker than CO and thus is responsible for smaller modifications in the optical features of the sample.

The room-temperature IR spectrum of the Cr(II)/$SiO_2$ catalyst upon $N_2$ adsorption is reported in Figure 5a (bottom curve, extended region) and in Figure 6b, bottom part (solid curve, N−N region). The $N_2$ signal in the IR spectrum is negligible if compared to the high intensity of the silica modes. Nevertheless, by a deeper inspection, the spectrum is characterized by a well-defined and narrow band at 2327 $cm^{-1}$ (with an intensity of 0.04 au, accompanied by a small shoulder at about 2333 $cm^{-1}$) and by a weaker component at 2337 $cm^{-1}$. As in the case of CO, $N_2$ adsorbed on the Cr(II)/$SiO_2$ system gives rise to an intense signal in the Raman spectrum, about 1.5 higher than the bulk silica modes at low frequencies. This signal presents the same components already discussed in the case of the IR one, but with a different intensity ratio, see Figure 6b, top part. The observation of adsorbed $N_2$ species at room temperature is worth discussing, because it is known that the interaction of $N_2$ with the surface metallic sites is usually very weak and requires high-pressure and/or low-temperature conditions to be observed. The very small frequency shifts with respect to the frequency of $N_2$ gas (Raman peak at 2331 $cm^{-1}$), which characterize the two bands, both in the IR and in the Raman spectra (−4 and +6 $cm^{-1}$ respectively), suggest that the $N_2$ molecule is slightly perturbed by the Cr centers. Following the interpretation given in the case of the CO adsorption and remembering that $N_2$ is a weaker ligand, it is conceivable that only one $N_2$ molecule may adsorb both on $Cr^{II}_A$ and on $Cr^{II}_B$ sites. The peak at 2327 $cm^{-1}$ ($\Delta\tilde{\nu} = -4$ $cm^{-1}$) may be assigned to the $N_2$ adsorbed on the $Cr^{II}_A$ sites, while the band at 2337 $cm^{-1}$ ($\Delta\tilde{\nu} = +6$ $cm^{-1}$) may be due to the $N_2$ adsorbed on the $Cr^{II}_B$ sites, characterized by a higher polarization ability and/or a less tendency to give d−$\pi$ interactions with respect to the $Cr^{II}_A$ centers. As in the case of the CO spectra, also in this case the different intensity ratio of the two components in the IR and Raman spectra could be a consequence of the different experimental conditions and/or of the different selection rules governing the two techniques.

## 4. Conclusions

This work presents a combined excitation selected Raman, UV−vis DRS, and FTIR spectroscopic investigation of surface species in the Phillips catalyst. The quality of the Raman spectra has been greatly improved if compared to the literature experiments, due to the finalized choice of the silica support and of Raman resonant experimental conditions. As far as the Cr(II)/$SiO_2$ system is concerned, the method of the probe molecules, commonly applied only to IR spectroscopy, has been applied also to the UV−vis DRS and Raman techniques to indirectly determine the structure of the Cr(II) sites on the reduced catalyst. We have shown, for the first time, that CO and $N_2$ adsorbed on the Cr(II)/$SiO_2$ catalyst are clearly visible also by means of Raman spectroscopy, giving rise to manifestations more intense than those observed with IR spectroscopy and very similar in frequencies. The Raman technique can therefore be looked at as an important technique to obtain information on surface species complementary to those obtainable by means of IR and UV−vis DRS spectroscopies. Coming to the oxidized catalyst, the complementary use of the three techniques definitely demonstrates that Cr(VI) are anchored as monochromate species on the surface of the Cr/$SiO_2$ catalyst at low chromium loadings. The approach here adopted has allowed us to observe clearly, for the first time, some bands in the regions where the antisymmetric stretching and the bending vibrations of the O═Cr═O species are expected. Also, broad absorptions in the 450−800 $cm^{-1}$ range have been observed and assigned to Si−O modes modified by the presence of grafted Cr(VI) species. Finally, the approach applied here on the Cr/$SiO_2$ system could be easily extended to the fraction of metal-supported systems for which limited information has been obtained with the Raman technique until now.

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