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Photo-Induced Ethylene Polymerization on the Cr^{VI}/SiO_2 Phillips Catalyst

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Abstract

Herein we report on two photo-induced reactions occurring at the surface of the Cr^{VI}/SiO_2 Phillips catalyst. The first is the photo-reduction of Cr^{VI}/SiO_2 in CO at room temperature, that leads to the reduction of a fraction of the Cr^{VI} sites to Cr^{IV}(=O) intermediates and then to Cr^{II}. With respect to the thermal reduction of Cr^{VI}/SiO_2 in CO, the relative amount of highly uncoordinated Cr^{II} sites is larger, suggesting that the relaxation of the Cr^{II} sites at the silica surface strongly depends on the temperature at which they are formed. The second is the photo-induced ethylene polymerization on Cr^{VI}/SiO_2 at room temperature that is reported here for the first time. We demonstrate that UV-Vis light has the potential to trigger the reduction of chromates by ethylene and the successive ethylene polymerization. DR UV-Vis and FT-IR spectroscopies allowed us to identify the nature of the Cr sites involved in the polymerization (i.e. 6-fold coordinated Cr^{II}) and of the oxidized by-products remaining in their coordination sphere, which are methylformate and ethylene oxide. While the former was previously observed during the thermally-induced ethylene polymerization on Cr^{VI}/SiO_2, the latter was never observed.

1. Introduction

Chromium(VI) supported on amorphous silica is one of the most used catalyst in the petrochemical industry, affording more than one third of all the High Density Polyethylene (HDPE) produced worldwide and also a large fraction of Linear Low Density Polyethylene (LLDPE).[1-3] Due to its apparent simplicity, it has been the object of fundamental studies since more than half a century. Since the beginning, most of the efforts have been devoted to correlate the structural and electronic properties of the chromium sites to the peculiar performances of this catalyst in ethylene polymerization,[4-10] such as its ability to polymerize ethylene without any activator or the very broad molecular weight distribution of the produced HDPE. These properties place the Phillips catalyst in an unique position in the polyethylene market when compared to its competitors.[1] Direct spectroscopic methods applied on model versions of the catalyst – such as the CO-reduced form (Cr^{II}/SiO_2),[6,8,11-17] or systems obtained from well-defined Cr^{VI-n} organometallic precursors,[18-24] or even planar models suitable for surface science investigation[25-33] – have played the major role in the characterization of the active sites at a molecular level, while the mechanism of ethylene polymerization has been mainly investigated by means of theoretical calculation.[23,34-43]

A crucial feature that distinguishes the Phillips catalyst from most of its competitors in olefin polymerization is its capability to start the polymerization reaction in the absence of any Al-alkyl activator, a fact that simplifies its handling in the polymerization reactor, but also opens some question on the polymerization mechanism and on the nature of the active sites. The Phillips catalyst enters the polymerization reactor after being activated in oxidizing conditions at a temperature higher than 600 °C. This procedure mainly gives isolated hexavalent chromates[6,8,11,44-48] (hereafter Cr^{VI}), and possibly also a small amount of mono-oxo CrO_5,[40,49-54] grafted on the surface of a highly dehydroxylated silica. Hence, the catalyst is not alkylated when it goes into the reactor, that is, it has no Cr–alkyl bond into which ethylene may be inserted. The Cr^{VI} sites are slowly reduced by ethylene at the reaction temperature (ca. 100 °C) during a variable induction time that can last also some hours, and successively transformed into the (alkylated) active sites. Although the two steps (reduction and alkylation) cannot be separated in the industrial reactor, many experimental evidences have been accumulated in the academic laboratories indicating that, during the reduction step, the Cr^{VI} sites are reduced to Cr^{II} precursors.[1,4,6,9,10,55-58] For a long time it was considered that the oxidized by-products deriving from ethylene oxidation left the surface of the catalyst at the reaction temperature and that therefore the precursors of the active sites were low-coordinated Cr^{II} species, similar to those obtained by reducing the Cr^{VI}/SiO_2 in CO at 350 °C.[59-62] Only recently this concept has been revolutionized, due to the observation that the oxidized by-

products (ketones, aldehydes, carboxylates or esters) do not desorb into the gas phase at temperatures below 250 °C, which suggests that under commercial polymerization conditions oxygenates may remain attached to the chromium sites.[63,64]

On the whole, it is clear that the reducing ability of ethylene towards the chromates is quite poor. This is one of the reason why often, in the industrial practice, specific reducing agents are added in the reactor before or together with the ethylene injection, aimed at shortening (or even eliminating) the induction time, and/or at performing ethylene polymerization at lower temperature.[1,65-69] In this work we explore, for the first time, the use of UV-Vis light to trigger the ethylene polymerization on the Cr^{VI}/SiO_2 catalyst at room temperature, without the addition of any activator. The idea had the inception from the documented knowledge that highly dispersed and isolated Cr^{VI} sites in the form of monochromates supported on silica can operate as efficient photocatalysts for a wide range of reactions under visible light irradiation, such as for the decomposition of NO, for the partial oxidation of propane with molecular oxygen and for the selective oxidation of CO in the presence of H_2.[70-74] In particular, it has been demonstrated that visible-light irradiation of tetrahedrally coordinated $Cr^{VI}(=O)_2$ species produces the excited triplet state $Cr^{V}(=O)(O^{-})$*, which behaves as an active site for oxidation. Moreover, more than 20 years ago, Kohler and Ekerdt demonstrated the possibility to photoreduce the Cr^{VI}/SiO_2 catalyst in CO.[75] These examples prompted us to develop an experimental set-up to monitor the Cr^{VI}/SiO_2 catalyst *during* the UV-Vis light irradiation in the presence of ethylene at room temperature, by means of FT-IR and DR UV-Vis spectroscopies. By combining these two sensitive methods, we have been able to: 1) observe the gradual reduction of the chromates; 2) investigate the properties of the reduced chromium sites; 3) detect the by-products of ethylene oxidation, and 4) demonstrate the occurrence of ethylene polymerization at room temperature.

2. Experimental

The Cr^{VI}/SiO_2 sample (Cr loading 1 wt%) was prepared by wet-impregnation of a pyrogenic silica (Aerosil, surface area *ca.* 380 m^2g^{-1}) employing CrO_3 as chromium precursor. The catalyst was activated directly inside the measurement cells, to avoid any type of contamination. The activation procedure consisted in two main steps: i) activation at 650 °C in dynamic vacuum (residual pressure < 10^{-4} mbar) in order to dehydroxylate the silica surface, and ii) subsequent oxidation in O_2 (equilibrium pressure ca. 100 mbar, twice) at the same temperature to graft the Cr species in the form of monochromates.[6,8,11,44-46] The Cr^{II}/SiO_2 reference sample was obtained from Cr^{VI}/SiO_2 after further reduction in CO (equilibrium pressure ca. 100 mbar, twice) at 350 °C, followed by degassing at the same temperature.[6] For both FT-IR and DR UV-Vis-NIR measurements the sample was prepared in the form of a self-supporting pellet, having a surface density of ca. 10 mg cm^{-2} and 60 mg cm^{-2}, respectively.

The FT-IR spectra were recorded on a Bruker IFS 28 FTIR spectrometer, equipped with a MCT cryogenic detector, averaging 64 interferograms recorded at 2 cm^{-1} resolution. Diffuse reflectance (DR) UV-Vis-NIR spectra were recorded on a Cary 5000 Varian spectrophotometer equipped with a reflectance sphere. In both cases, UV-Vis irradiation was performed using a Newport 500 W Hg(Xe) arc lamp, equipped with a water filter to eliminate the infrared portion of the spectrum. For *in situ* UV-Vis irradiation during the FT-IR experiments, the radiation was focused on the sample using an aspherical fiber bundle focusing assembly and a large core liquid light guide.[76-78] This experimental set-up reduces the amount of photons reaching the sample, but allows collecting FT-IR spectra during continuous UV-Vis irradiation. In contrast, for UV-Vis irradiation during the DR UV-Vis-NIR experiments, the radiation was not focused. This experimental set-up maximizes the number of photons reaching the sample, but does not allow collecting DR UV-Vis-NIR spectra simultaneously to the irradiation.

3. Results and discussion

3.1 Photo-reduction of Cr^{VI}/SiO_2 in CO at room temperature

Initially, we followed by *in situ* FT-IR spectroscopy the photo-reduction of Cr^{VI}/SiO_2 under UV-Vis irradiation in the presence of CO (P_{CO} = 100 mbar) at room temperature, aimed at validating our experimental set-up. Figure 1a shows the FT-IR spectrum of Cr^{VI}/SiO_2 before (spectrum 1) and after 60 minutes of irradiation in CO (spectrum 2), while Figure 1a' shows all the spectra collected at intermediate irradiation time, in the ν(CO) region and after subtraction of spectrum 1. The spectrum of Cr^{VI}/SiO_2 is characterized by a narrow band at 3745 cm^{-1} ascribed to the ν(OH) vibration of isolated silanols, and three broad bands at ca. 1980, 1870 and 1635 cm^{-1} which are due to the overtones and combinations

of the fundamental vibrational modes of silica, contributing below 1300 cm^{-1}. The only spectroscopic manifestation of the Cr^{VI} sites is a weak absorption band at 1980 cm^{-1} (Figure 1a''), assigned to the first overtone of the ν(Cr=O) modes,[8,47,48,63,79,80] which are obscured in the IR by the intense absorption due to the silica framework vibrations, but were detected at 982 – 990 cm^{-1} by Raman spectroscopy.[5,12,49,81-85]

During UV-Vis irradiation in CO a series of bands slowly appear in the ν(CO) region (Figure 1a'), concurrently to the disappearing of the band at 1980 cm^{-1} (Figure 1a''), which indicates the slow reduction of the Cr^{VI} sites and the formation of Cr-carbonyls on the reduced Cr sites. The first band to appear is centered at 2201 cm^{-1}, and reaches the maximum intensity after about 10 minutes of irradiation. A similar absorption band was previously observed by Kohler and Ekerdt during the photo-reduction of a 2 wt% Cr^{VI}/SiO_2 in CO,[75] and by some of us upon adsorption of CO on a Cr^{II}/SiO_2 sample selectively modified by N_2O.[79] In both cases it was ascribed to mono-carbonyl species formed on Cr^{IV}=O (chromyl) sites. After a few minutes of UV-Vis irradiation, also a triplet of bands at 2189, 2183 and 2177 cm^{-1} starts growing, which is known to arise from the vibrational modes of mono-carbonyls and di-carbonyls (symmetric and asymmetric modes) formed on two types of coordinatively unsaturated Cr^{II} sites (Cr^{II}_B and Cr^{II}_A, respectively).[6-8,58] A weak band is also visible at 2096 cm^{-1}, and assigned to multi-carbonyls formed on a small fraction of even more uncoordinated Cr^{II} sites.[6,8,86]

The experiment reported in Figure 1a demonstrates that when Cr^{VI}/SiO_2 is irradiated by UV-Vis light in presence of CO at room temperature the Cr^{VI} sites are gradually reduced, initially to Cr^{IV} and successively to Cr^{II}, in well agreement with the pioneering work of Kohler and Ekerdt.[75] The photo-reduction in CO is less efficient than the thermal reduction in CO at 350 °C. This is evident by looking at Figure 1b, that compares the FT-IR spectrum of Cr^{VI}/SiO_2 photo-reduced in presence of CO (spectrum 2), to that of CO adsorbed at room temperature on a Cr^{II}/SiO_2 sample (i.e. obtained upon thermal reduction of Cr^{VI}/SiO_2 in CO at 350 °C, spectrum 3). The spectra have been normalized to the optical thickness of the pellets, hence their total intensity can be quantitatively compared. Spectrum 2 is ca. 4 times less intense than spectrum 3. Since it has been demonstrated that the thermal reduction of Cr^{VI}/SiO_2 in CO at 350 °C leads to the stoichiometric conversion of all the Cr^{VI} sites to Cr^{II},[1] Figure 1b indicates that only ca. ¼ of the total Cr^{VI} sites are reduced after 60 minutes of UV-Vis irradiation in the presence of CO, partially to Cr^{IV} and partially to Cr^{II}.

It is also of interest the observation that the intensity of the weak band at 2096 cm^{-1} with respect to the triplet centered at 2180 cm^{-1} is higher for spectrum 2 than for spectrum 3. This means that the relative amount of highly uncoordinated Cr^{II} sites capable of forming multi-carbonyls in presence of CO

at room temperature is much higher when the Cr^{II} sites are obtained by photo-reduction of Cr^{VI}. This is probably a consequence of a different strain at the silica surface.[87] When the reduction of Cr^{VI}/SiO_2 is accomplished at high temperature (350 °C) the obtained Cr^{II} sites have the possibility to relax. Reduction of Cr^{VI}/SiO_2 in milder conditions does not permit the relaxation of the Cr^{II} sites, that remain more accessible to the incoming molecules. This might have important consequences in terms of catalytic performances. Indeed, it has been recently demonstrated that the Cr coordination environment influences both the ethylene insertion and the chain transfer energies, with immediate consequences on the molecular weight distribution of the obtained polyethylene.[43,88]

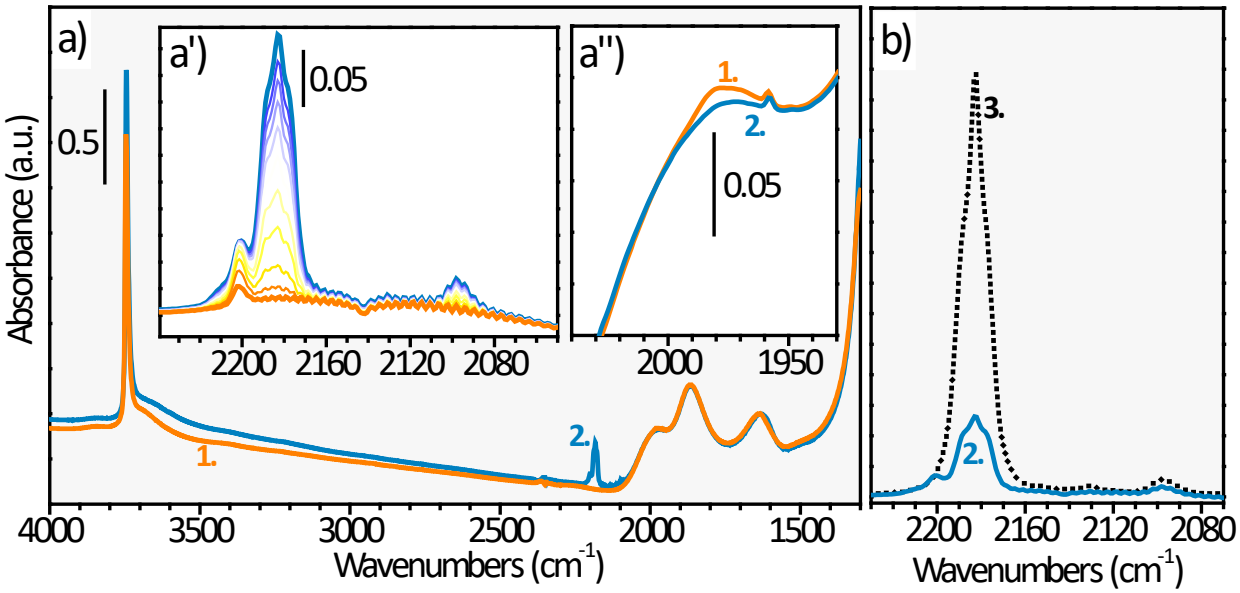

Figure 1. Part a): FT-IR spectra of Cr^{VI}/SiO_2 before (spectrum 1), and after 60 minutes of in situ UV irradiation in CO (spectrum 2) at room temperature (P_{CO} = 100 mbar). Inset a' shows the whole sequence of FT-IR spectra collected at intermediate irradiation time after subtraction of spectrum 1. Inset a'' shows a magnification of the spectral region where the only spectroscopic fingerprint of the Cr^{VI} sites appears. Part b): The same spectrum 2 as in part a, compared to the FT-IR spectrum, in the ν(CO) region, of CO adsorbed on a Cr^{II}/SiO_2 sample obtained upon thermal reduction in CO at 350 °C (spectrum 3).

3.2 Photo-induced ethylene polymerization on Cr^{VI}/SiO_2

Also ethylene (i.e. the monomer of the polymerization reaction) may act as reducing agent for Cr^{VI}/SiO_2. However, as for CO, the reaction does not occur at room temperature but needs ca. 100 °C, and also at that temperature it requires a certain induction time that can vary from minutes to hours, depending on the experimental conditions.[1] Ethylene polymerization starts on these reduced Cr sites and the steady state is reached only after several hours. Inspired by the results discussed above for the photo-induced CO-reduction of Cr^{VI}/SiO_2, we decided to investigate whether UV-Vis light irradiation can be exploited for performing ethylene polymerization on Cr^{VI}/SiO_2 at room temperature. The experiments were

performed in static conditions, at room temperature and low ethylene pressure (P_{C2H4} = 100 mbar), and were followed by means of both DR UV-Vis-NIR and FT-IR spectroscopies.

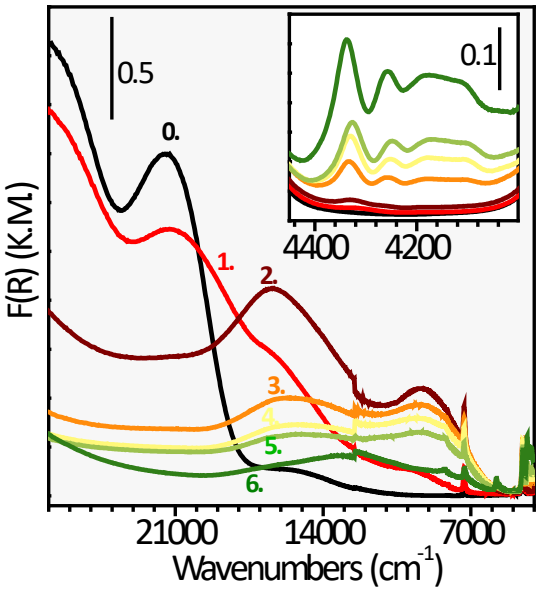

Figure 2. DR UV-Vis spectra of Cr^{VI}/SiO_2 before (spectrum 0, black) and after UV irradiation in presence of ethylene (P_{C2H4} = 100 mbar) at room temperature for increasing times (1 = 20 s, 2 = 40 s, 3 = 50 s, 4 = 1 min, 5 =2 min, 6 = 5 min). The inset shows a magnification of the NIR region, where polyethylene contributes with a series of bands due to the overtones and combinations of the $\nu(CH_2)$ and $\delta(CH_2)$ vibrational modes.

Figure 2 shows the DR UV-Vis-NIR spectra of the Cr^{VI}/SiO_2 sample before (spectrum 0) and after (spectra 1 – 6) UV-Vis irradiation in presence of ethylene at room temperature for increasing times. The spectrum of Cr^{VI}/SiO_2 (spectrum 0) is dominated by two intense bands at ca. 28000 and 21500 cm^{-1}, due to the $O \rightarrow Cr^{VI}$ charge-transfer transitions characteristic of monochromates.[5,8,11,44,45] The spectra rapidly change upon UV-Vis irradiation in presence of ethylene, and two subsequent events can be distinguished. After less than 50 seconds of irradiation (spectra 1 and 2), the spectroscopic fingerprints of the monochromates decrease in intensity, concurrently to the appearance of two bands at ca. 16500 and 9500 cm^{-1}, which indicate the reduction of the Cr^{VI} sites (d^0 species) to low-valent Cr sites (d^n species). The same bands were observed during the thermal reduction of Cr^{VI}/SiO_2 in ethylene, and ascribed to d-d transitions of Cr^{II} sites having a 6-fold coordination geometry, determined by the presence of oxidized by-products in their coordination sphere.[63] The assignment was corroborated by the observation of very similar spectra for Cr^{VI}/SiO_2 reduced by cyclohexene, a cyclic olefin that mimics the reactivity of ethylene without polymerizing.[69] During this step no ethylene polymerization occurs, as testified by the absence of any absorption band in the 4400 – 4050 cm^{-1} range (inset in Figure 2), that is where polyethylene contributes with a series of bands due to the overtones and combinations of the

$\nu(CH_2)$ and $\delta(CH_2)$ vibrational modes. Ethylene polymerization is observed after only 50 seconds of UV-Vis irradiation (spectrum 3), and efficiently proceeds for longer irradiation time. The global effect is the decrease in intensity of the d-d bands at 16500 and 9500 cm^{-1}, and in general of the whole spectrum. The same phenomenon was observed during the thermally induced ethylene polymerization on Cr^{VI}/SiO_2 and explained in terms of formation of a layer of polymer on the surface of the catalyst particles, which diffuses the incident light preventing the observation of the active Cr sites.[63]

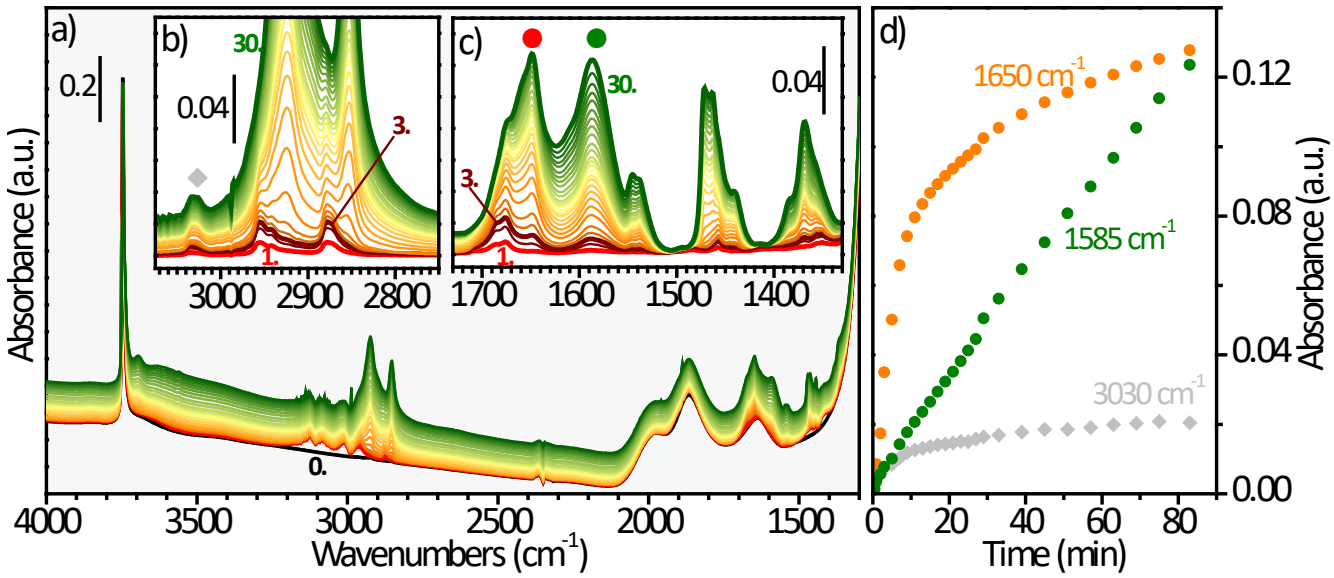

Figure 3. Part a): FT-IR spectra of Cr^{VI}/SiO_2 (spectrum 0, black) and of the same sample during continuous UV irradiation in presence of ethylene (P_{C2H4} = 100 mbar) at room temperature for increasing times (1 = 30 s, 3 = 1 min, 30 = 90 min). Part b): magnification of the same spectra reported in part a), after subtraction of spectrum 0 and of the contribution due to gaseous ethylene, in the $\nu(CH_x)$ region. Part c): as part b) in the 1730- 1330 cm^{-1}. Part d): Time evolution of the intensity of the absorption bands at 3030 cm^{-1} (ethylene oxide), 1650 cm^{-1} (methylformate ligated through the C=O moiety) and 1585 cm^{-1} (methylformate ligated in a bidentate fashion).

The DR UV-Vis-NIR experiment discussed above clearly indicates that ethylene has the potential to reduce the Cr^{VI} sites at room temperature under UV-Vis irradiation, and is then polymerized in mild conditions. Figure 3a shows the complementary experiment performed by FT-IR spectroscopy, aimed at monitoring the formation of polyethylene and of the oxidized by-products to identify their nature. The FT-IR spectrum of Cr^{VI}/SiO_2 before reaction with ethylene (Figure 3, spectrum 0) has been commented above. During the first minute of UV-Vis irradiation, a series of well-defined IR absorption bands appear in the $\nu(CH_x)$ stretching region (Figure 3b, spectra 1-3) and in the 1750-1300 cm^{-1} range (Figure 3c, spectra 1-3). In particular, the most evident bands are observed at ca. 3030, 2955 and 2877 cm^{-1} (Figure 3b) and at 1677, 1650 and 1585 cm^{-1} (Figure 3c). These bands are clearly not attributable to polyethylene and reveal the formation of surface by-products resulting from the oxidation of ethylene by

monochromates. According to the UV-Vis-NIR spectra (Figure 2) these by-products remain in the coordination sphere of the reduced Cr^{II} sites. The onset of ethylene polymerization occurs after ca. 2 minutes of continuous UV-Vis irradiation in presence of ethylene, as testified by the constant growth of two bands at 2922 and 2853 cm^{-1} (Figure 3b, spectra 4-30), which are due to the $\nu_{asymm}(CH_2)$ and $\nu_{symm}(CH_2)$ modes of polyethylene, and of the corresponding $\delta(CH_2)$ band at ca. 1470 cm^{-1} (Figure 3c, spectra 4-30).

A closer inspection to the spectra collected prior the onset of ethylene polymerization (spectra 1-3) might give indication on the nature of the by-products, and hence on the mechanism of initiation of ethylene polymerization under UV-Vis irradiation. In this respect, it is useful to recall here that methylformate (formed through the Tischenko reaction of two formaldehyde molecules at the same Cr^{II} site) has been identified as the main by-product of ethylene oxidation during the thermally induced ethylene polymerization on Cr^{VI}/SiO_2.[63] For this reason, in Figure 4 we have compared the spectrum collected after 1 minute of UV-Vis irradiation of Cr^{VI}/SiO_2 in presence of ethylene (spectrum 3, the same as in Figure 3) with two reference spectra collected with independent experiments. Spectrum 1 corresponds to methylformate adsorbed on Cr^{II}/SiO_2 (after removal of the physisorbed molecules). The spectrum is characterized by very weak bands in the $\nu(CH_x)$ region (Figure 4a), whereas it is dominated by two intense bands at ca. 1660 cm^{-1} (with a pronounced tail at high wavenumbers) and 1597 cm^{-1} (Figure 4b). Based on the literature of methylformate adsorbed on other systems,[89,90] both bands are assigned to the ν(C=O) vibration of methylformate adsorbed on Cr^{II} sites differing in their adsorption geometry: the former is ascribed to methylformate ligated through the C=O moiety, whereas the latter is due to methylformate ligated in a bidentate fashion. The similarity of spectrum 3 to spectrum 1 in this spectral region suggests that also in this case methylformate is one of the by-products of chromate reduction. As already discussed for the thermally induced ethylene polymerization, methylformate originates from the disproportion of two formaldehyde molecules formed at the same Cr site.[63] On the other hand, spectrum 2 was obtained by dosing a limited amount of O_2 on a Cr^{II}/SiO_2 catalyst at the very beginning of the ethylene polymerization. This spectrum, which is characterized by quite intense absorption bands in the 3050 – 2800 cm^{-1} region (Figure 4a) but shows negligible features at lower wavenumbers (Figure 4b), was assigned to ethylene oxide adsorbed on partially oxidized $Cr^{IV}(=O)/SiO_2$.[91] The close similarity of spectrum 1 to spectrum 3 in the $\nu(CH_x)$ region indicates that a second reaction is taking place during the UV-Vis irradiation of Cr^{VI}/SiO_2 in ethylene, involving the formation of ethylene oxide.

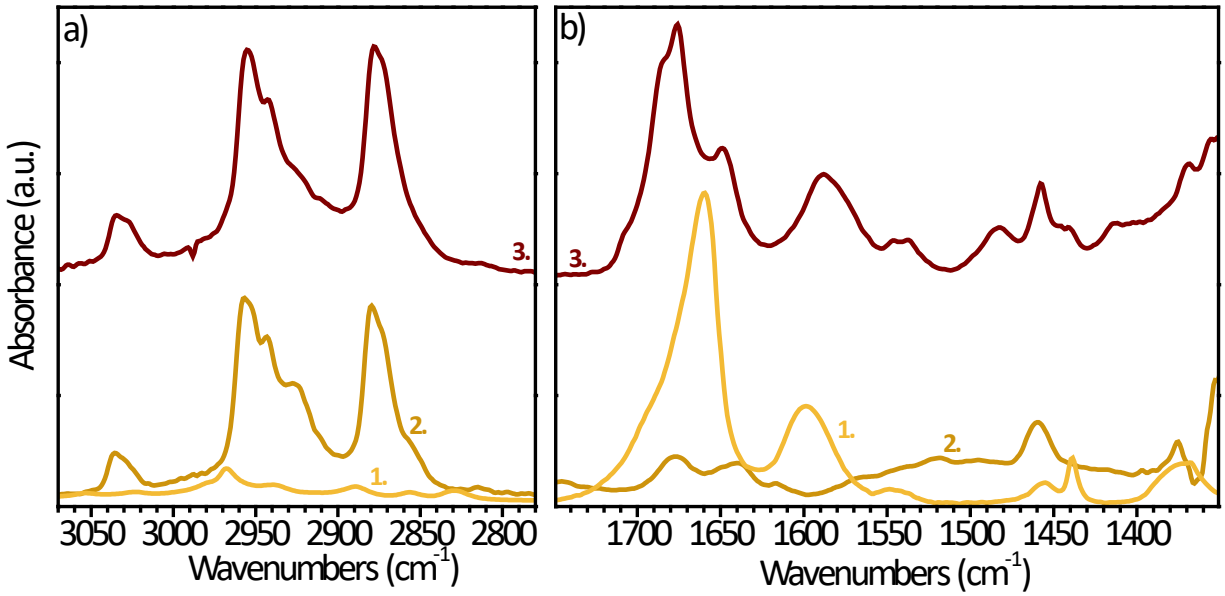

Figure 4. FT-IR spectra of methylformate adsorbed on Cr^{II}/SiO_2 (spectrum 1), the product of reacting a limited amount of O_2 on a Cr^{II}/SiO_2 catalyst at the very beginning of the ethylene polymerization, previously ascribed to ethylene oxide on Cr^{II}/SiO_2 (spectrum 2), compared to the spectrum collected after 1 minute of UV-Vis irradiation of Cr^{VI}/SiO_2 in presence of ethylene (spectrum 3, the same as in Figure 3). Parts a) and b) show the $\nu(CH_x)$ and $\nu(C{=}O)$ regions, respectively.

In summary, the FT-IR data shown in Figure 3 and Figure 4 indicate the formation of two different oxidized by-products during the initial steps of photo-induced ethylene polymerization on Cr^{VI}/SiO_2 at room temperature: ethylene oxide and methylformate. Interestingly, the absorption bands associated with methylformate keep on growing also during ethylene polymerization (Figure 3d, orange and green circles), although with a different relative intensity. In particular, the band at ca. 1585 cm^{-1} (green circles) grows faster than that at ca. 1650 cm^{-1} (orange circles) and becomes the dominant one at longer irradiation/reaction time. This behavior suggests a slow conversion of the methylformate species ligated to the Cr^{II} sites trough the C=O moiety into the most stable bidentate species. In contrast, the absorption bands associated to ethylene oxide apparently do not increase in intensity during ethylene polymerization. This is evident by looking to the band at ca. 3030 cm^{-1} (Figure 3d, grey diamond), which does not overlap with any bands due to the growing polyethylene. As a final comment, the evolution of the FT-IR spectra reported in Figure 3 clearly indicates that: 1) ethylene polymerization is photo-initiated on Cr^{VI}/SiO_2 in the presence of a substantial amount of Cr^{VI} sites which are slower to be reduced, as already reported for the thermally induced ethylene polymerization;[63] and 2) ethylene polymerization starts and proceeds in the presence of both types of oxidized by-products, that evidently remain adsorbed at the catalyst surface during the initiation of the reaction, contributing to define the ligands sphere around the active Cr sites.

4. Conclusions

In this work we have presented two examples of photo-induced reactions on the Cr^{VI}/SiO_2 Phillips catalyst. At first, we found that irradiation of Cr^{VI}/SiO_2 with UV-Vis light in the presence of CO leads to its partial reduction already at room temperature, first to a $Cr^{IV}(=O)$ intermediate, and then further to Cr^{II}, in well agreement with the pioneering work of Kohler and Ekerdt.[75] Although the photo-reduction is less efficient than the thermal one (i.e. a lower fraction of Cr^{VI} sites is reduced), notably it brings about the formation of a larger amount of highly uncoordinated Cr^{II} sites able to form multi-carbonyls in presence of CO. This finding highlights the role of the strain at the silica surface in affecting the properties of the Cr sites, and might have important consequences in terms of catalytic performances.

Second, and novel, we demonstrated that UV-Vis light efficiently triggers the ethylene polymerization on the Cr^{VI}/SiO_2 catalyst already at room temperature. By means of DR UV-Vis-NIR and FT-IR spectroscopies we have been able to discriminate between the two fundamental steps involved in the initiation of the reaction, namely the Cr^{VI} reduction by ethylene and the successive polymerization. With respect to the thermally induced ethylene polymerization, the induction time is drastically reduced. Moreover, two types of oxidized by-products deriving from the oxidation of ethylene by chromates have been detected: methylformate and ethylene oxide. While the former was found also during the thermally induced ethylene polymerization, the latter was never observed. The reason might be due to the specific photo-activation mechanism for Cr^{VI} that, according to the literature, involves a single oxygen per time passing through the formation of a $Cr^{V}(=O)(O^{-})$* excited state. Alternatively, we might consider the possibility that ethylene oxide is formed also during the thermally-induced ethylene polymerization but not detected because it desorbs from the Cr sites at the reaction temperature. This different polymerization mechanism with respect to the thermally induced process could also result in a polymer with peculiar characteristics. However, the limited amount of polyethylene produced in our setup prevented at the moment a more thorough *ex situ* characterization of the products by differential scanning calorimetry or size exclusion chromatography, which will be the object of a future work.

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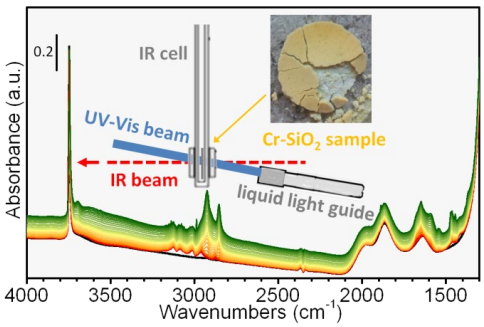
TOC Graphic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IR cell
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Cr-SiO2 sample
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Absorbance (a.u.)
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Wavenumbers (cm-1)