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Ethylene polymerization on SiH_4-modified Phillips catalyst: detection of in situ produced α-olefins by operando FT-IR spectroscopy

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Ethylene polymerization on model Cr(II) Phillips catalyst modified with gas phase SiH_4 leads to a waxy product containing in a bimodal MW distribution α-olefins ($M_w < 3000$ g/mol) and a highly branched polyethylene, LLDPE (M_w ca. 10^5 g/mol, $T_m = 123$ °C), contrary to the unmodified catalyst which gives a linear and more dense PE, HDPE ($M_w = 86000$ g/mol (PDI = 7), $T_m = 134$ °C). Pressure and temperature resolved FT-IR spectroscopy in operando conditions (T = 130-230 K) allows us to detect α –olefins, and in particular 1-hexene and 1-butene (characteristic IR absorption bands at 3581-3574, 1638 and 1598 cm^{-1}) as intermediate species before their incorporation in the polymer chains. Polymerization rate is estimated using time resolved FT-IR spectroscopy to be 7 times higher on SiH_4- modified Phillips catalyst with respect to the unmodified one.

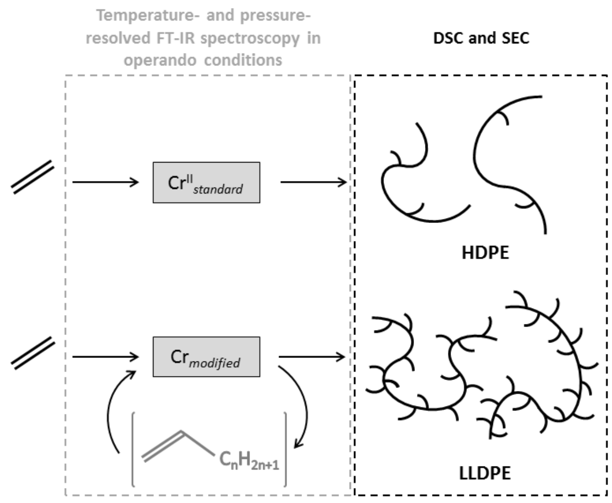
1. Introduction

The Cr/SiO_2 Phillips catalyst, used in industrial plants since the 1960's, is well known for manufacturing linear polyethylenes having different grades, accounting for more than one-third of all the polyethylene supply.[1,2] In particular, this catalyst produces 40-50% of all the High Density Polyethylene (HDPE) sold worldwide; and it has also a large share of Linear Low Density Polyethylene (LLDPE), which is a linear polyethylene having a large amount of short branches in the main polymer chains. Short branches, which are obtained by co-polymerization of ethylene with a small amount (0-4 mol%) of different α-olefins, are excluded from the crystalline regions of the polymer and therefore lower the polyethylene density; moreover, they increase the flexibility, toughness and elongation, all properties that are useful for specific applications.

Commercial processes for making LLDPE were initially based on the addition of α-olefins to the ethylene feedstock. More recently, a new technique that has received a lot of interest is tandem catalysis, wherein two catalysts are involved: the first oligomerizes ethylene to the desired comonomer (usually 1-butene) and the second copolymerizes ethylene and the comonomer to LLDPE.[3,4] This one-pot approach presents some obvious advantages, in particular the comonomer does not need to be separately prepared, purified, and transported to site, with a consequent lowering of the manufacturing costs. However, some difficulties must be overcome, such as the interference between the two catalysts and matching of the activities such that the comonomer concentration can be maintained as desired. Another possibility is the co-production of α-olefins in situ by the same catalyst responsible of polymerization.[2] This process, called in situ branching, has even more advantages than the tandem catalysis. In situ produced α-olefins are incorporated about two to four times more efficiently than in ordinary catalytic copolymerization with α-olefins added from external sources.[2] This increased incorporation efficiency provides a major benefit during the manufacture of polyethylene, such that the in situ branching process has become the basis for some unique low-density commercial polymer grades introduced during the early 1990's.[5-8]

The Cr/SiO_2 Phillips catalyst is able to produce LLDPE via in situ branching when treated with metal alkyl "cocatalysts" such as AlR_3, BR_3, ZnR_2; among all, the most effective for in situ α-olefins generation are the hydrosilanes (provided that they contain at least a Si-H group).[2] These cocatalysts are very effective even at very low concentration, suggesting that they are highly selective in their reaction with the catalyst, reacting preferentially with potentially active sites. However, the effect of hydrosilanes in affecting the structure of the Cr sites was never investigated in details, and only a few hypothesis have been advanced in the specialized literature.[2] The in situ production of α-olefins with Phillips catalyst in presence of hydrosilanes is claimed on the basis of the analysis of the final polymer product (amount of branching in the polymer, density, MW distribution), but there are no direct experimental evidences of the processes occurring on the active sites at a molecular level.

Herein, we propose a detailed spectroscopic study of ethylene polymerization with a SiH_4-modified Phillips catalyst in operando conditions, with the final aim to detect the in situ produced α-olefins before their incorporation in the growing polymer chains. On the basis of our past experience, among all of the spectroscopic techniques, FT-IR spectroscopy is the most versatile and has enough sensitivity to identify the intermediates of a reaction, being able to directly discern between the vibrational manifestations of different species even under operando condition and in presence of very diluted system.[9,10]



Scheme 1 Products of ethylene polymerization on *standard* and *modified* catalyst and the proposed experimental approach.

This was the case for the standard CO-reduced Cr(II)/SiO_2 catalyst, on which FT-IR spectroscopy, either in the conventional and temperature-resolved versions, was fundamental in the identification of the intermediate species involved in the very first steps of ethylene polymerization.[11-13] Temperature and pressure-resolved FT-IR spectroscopy would demonstrate to be very informative also in the present case. Complementary results on the type of produced PE are obtained by means of differential scanning calorimetry (DSC) and size exclusion chromatography (SEC), as schematically shown in Scheme 1.

2. Experimental

The Cr/SiO_2 catalyst (1 wt.% Cr) was prepared by impregnation of a silica-aerosil (surface area about 380 m^2/g) with chromic acid (from CrO_3 in distilled water). The activation procedure involved the following steps: i) evacuation at 973 K followed by calcination in O_2 at the same temperature for 1 hour; ii) reduction in CO at 623 K for 1 hour followed by evacuation at the same temperature; and iii) cooling down to room temperature in dynamic vacuum. It was previously demonstrated that step i) provides Cr sites in a hexavalent state having a chromate structure,[14-16] which are completely reduced to Cr(II) by CO (step ii));[14,16,17] hereafter, we will call this sample *standard* catalyst. Further details concerning this procedure can be found elsewhere.[11]

Modification of the Phillips catalyst with SiH_4 was performed by contacting the *standard* catalyst with a mixture of silane (5000 ppm) in argon at room temperature, resulting in the hereafter called *SiH_4-modified* catalyst. SiH_4 was dosed in a 1:1 molar ratio with respect to the chromium sites and was left in contact with the catalyst for about 45 minutes. This contact time was determined to be necessary for a complete reactivity of SiH_4 with Cr/SiO_2.

FT-IR experiments were performed *in-situ* and in controlled atmosphere on thin self-supported wafers place inside an IR cell designed to allow thermal treatments in the 1000-77 K range. In this way the samples were activated directly into the IR cell where FT-IR experiments were conducted, avoiding any catalyst poisoning. The FT-IR spectra were collected on a Bruker Vertex 70 spectrophotometer at 2 cm^{-1} resolution. For ethylene polymerization experiments at room temperature a time resolution of the order of 8 s was used. Temperature and pressure-resolved FT-IR experiments were performed according to the procedure described elsewhere.[13,18]

A characterization of the obtained polymer by DSC and SEC analysis is also proposed as completion of the IR experimental data. Size Exclusion Chromatography (SEC) analysis provides data related to the molecular weight of the polymer (M_n, M_w) and the broadness of the molecular weight distribution (polydispersity index –PDI–). PE samples coming from polymerization during FT-IR experiments were first extracted from the matrix in pure 1,2,4-trichlorobenzene (TCB) at 150 °C and filtered with Teflon filters and then analyzed by SEC using a Waters Alliance GPCV 2000 instrument (columns: PLgel Olexis); two detectors (viscosimeter and refractometer) in trichlorobenzene (flow rate: 1 mL/min) at 150°C. The system was calibrated with polystyrene standards using universal calibration. According to the density of the polyethylene it is possible to distinguish via Differential Scanning Calorimetry (DSC) between a high density and linear low density PE with regard to their melting temperature, T_m (°C); DSC measurements were performed on both PE samples produced on *standard* and SiH_4 *modified* catalysts during FT-IR experiments. The analyses were performed on a Mettler Toledo DSC1 at a heating rate of 2 K/min, with two successive heating and cooling steps in the range of temperature from 50 to 150 °C. The values of T_m were taken from the second heating ramp, to have no traces of the thermal history of the polymer.

3. Results and Discussion

3.1 Interaction of SiH_4 with Cr/SiO_2

Before following by FT-IR spectroscopy in *operando* conditions the ethylene polymerization reaction with both, *standard* and *SiH_4-modified* catalysts, it is worth to briefly discuss the spectroscopic features of the *SiH_4-modified* sample. Figure 1 shows the IR spectrum of Cr(II)/SiO_2 before (black) and after interaction with silane (gray). The IR spectrum of Cr(II)/SiO_2 is characterized by the spectroscopic fingerprints of a high surface area SiO_2 activated at high temperature,[19-21] *i.e.* a narrow IR absorption band at 3745 cm^{-1} due to ν(OH) of isolated silanol groups, weak absorption bands at 1980, 1868 and 1640 cm^{-1} assigned to the first overtones of framework vibrational modes and a strong and out-of-scale absorption at frequencies below 1300 cm^{-1} due to the Si-O vibrations of the bulk. Beside these vibrational features, the IR spectrum of the *SiH_4-modified* catalyst is characterized by several IR absorption bands in the 2300-2100 cm^{-1} region (see inset in Figure 1), where ν(Si-H) vibrational modes are expected. A detailed assignment of these bands is out of the scope of this work; however, the following observations can be done. (i) The presence of several (broad) IR absorption bands in the 2300-2100 cm^{-1} region is indicative of a heterogeneity of SiH_x species, not necessarily related to the surface Cr sites. In particular, IR absorption bands below 2200 cm^{-1} were previously assigned to ν(Si-H) of $(SiH_x)_n$ oligomeric species,[22] whereas IR bands above 2200 cm^{-1} were assigned to ν(Si-H) of SiH_x species bonded to a more electronegative atom (such as O).[23,24] (ii) SiH_4 does not react with a pure SiO_2 pre-activated at 973 K (spectra not shown): therefore, it must be assumed that Cr(II) sites catalyze the reactivity of SiH_4 with SiO_2.

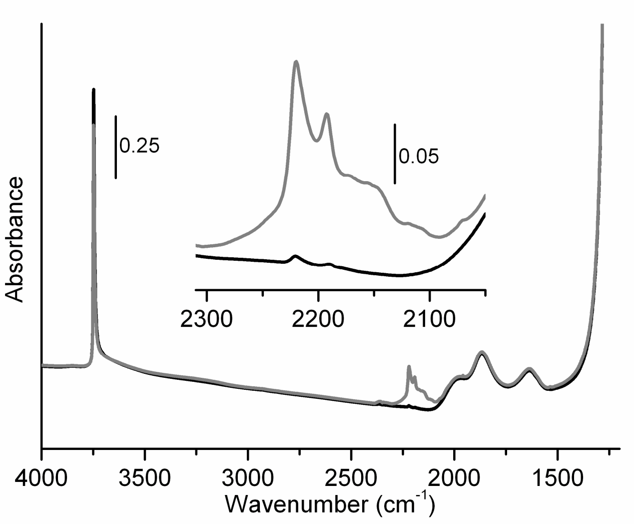


Fig. 1 FT-IR spectra of Cr(II)/SiO_2 before (black) and after (grey) interaction with SiH_4 at room temperature. The inset shows a magnification of the frequency region where ν(Si-H) modes give a contribution.

Some hypothesis on the structure of Cr(II) sites after modification by SiH_4 (or hydrosilanes) were advanced in the recent literature. In particular it has been proposed that Si-H reacts with Cr-O-Si bonds to transfer the hydride to chromium.[2] However, the FT-IR data shown herein are not able to support neither to discard anyone of the previous hypothesis and further experimental evidences are necessary to understand the role of SiH_4 as modifying agent.

3.2 Ethylene polymerization at room temperature monitored by operando FT-IR spectroscopy: evaluation of the catalyst activity and of the PE product

In this section FT-IR spectroscopy will be applied to follow in situ ethylene polymerization at room temperature on both *standard* and *SiH_4-modified* Phillips catalyst, in order to get information on both, the relative polymerization rate and the type of PE produced. Figure 2 shows the FT-IR spectra collected within the first eight minutes of ethylene polymerization at room temperature on the two catalysts, in the ν(CH_x) (parts a and c) and in the δ(CH_x) (parts b and d) regions, respectively. The spectra were recorded at a time resolution of 8 s and at constant ethylene pressure (200 mbar). By comparing the two sequences of FT-IR spectra two main differences are immediately visible: i) ethylene polymerization is much faster on the *SiH_4-modified* catalyst, so that the ν(CH_2) IR absorption bands go immediately out-of-scale; and ii) the formed polyethylene is different, as testified by the corresponding IR absorption bands.

Starting from point i), the relative polymerization rate of the two catalysts can be estimated by evaluating the intensity of the IR absorption bands characteristic of the growing polyethylene chains as a function of time (once that the spectra have been normalized for the thickness of the pellet).[25]

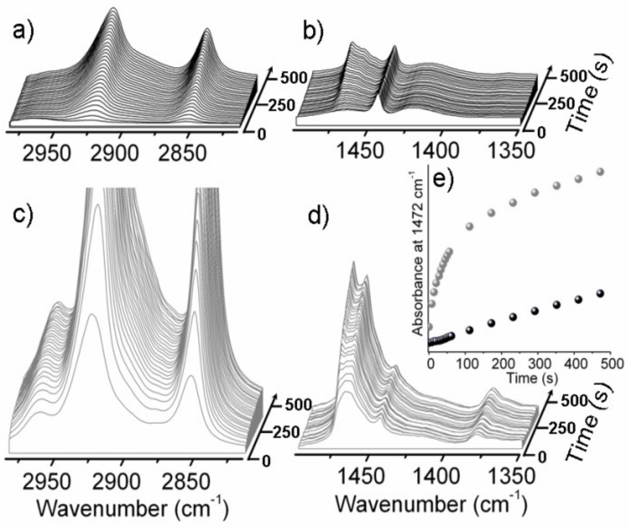


Fig. 2 Ethylene polymerization experiments on *standard* (black) and *SiH_4-modified* (grey) Cr/SiO_2 catalysts, as followed by FT-IR spectroscopy at room temperature. FT-IR spectra collected within the first eight minutes of reaction are shown in the ν(CH_2) (parts a and c) and δ(CH_2) (parts b and d) regions, respectively. The intensity of the δ(CH_2) IR absorption band at 1472 cm^{-1} is reported versus time in part (e).

The intensity of the δ(CH_2) absorption band at 1472 cm^{-1} (preferred to the ν(CH_2) ones because it remains in scale for longer time) is plotted versus time in Figure 2e. It is evident that ethylene polymerization on the *SiH_4-modified* catalyst starts without the short induction period observed on the *standard* catalyst[1,2,11,25] and proceeds at a higher rate. In particular, the initial slope of the two curves shown in Figure 2e gives an indication of the relative polymerization rate, which is about 7 times greater on the *SiH_4-modified* catalyst than on the *standard* one. Note that on the former catalyst the polymerization rate slowdowns after the first two minutes of reaction, possibly as a consequence of the diffusion limitation caused by the layer of polymer formed on the FT-IR pellet, which blocks the accessibility of the monomer to the surface Cr sites. The role of hydrosilanes in enhancing the ethylene polymerization rate on the Phillips catalyst is known in the industrial practice;[2,26] nevertheless, the results shown in Figure 2 are, to our knowledge, the first spectroscopic data obtained during ethylene polymerization on a Phillips catalyst modified by SiH_4.

The FT-IR spectra shown in Figure 2 provide information also on the type of polyethylene produced. On the *standard* catalyst, the growing polyethylene chains are characterized by two IR absorption bands at 2920 and 2851 cm^{-1} (Figure 2a), assigned to the asymmetric and symmetric ν(CH_2) modes characteristic of HDPE. Besides these bands, on the *SiH_4-modified* catalyst two additional IR absorption bands are observed in the ν(CH_x) region at 2965 and 2877 cm^{-1} (Figure 2c, the former well evident, the latter rapidly hidden by the more intense IR absorption bands due to CH_2 species, which are clearly visible during the low temperature experiments, Fig. 4 c and f), which are assigned to the asymmetric and symmetric stretching modes of CH_3 groups, respectively; the corresponding δ(CH_3) band occurs at 1379 cm^{-1} (Figure 2d, absent in Figure 2b). The presence of IR absorption bands characteristic of methyl groups demonstrates that the PE formed with the *SiH$_4$-modified* catalyst contains more CH$_3$ moieties than that formed on the *standard* catalyst, indicating either higher branching and/or shorter CH$_3$-terminated chains.

An additional insight was gained by SEC and DSC analysis of the polymers produced with the two catalysts. Figure 3a shows the MW distribution of the polymer that was recovered after ethylene polymerization performed during spectroscopic measurements, whereas Figure 3b shows the corresponding DSC curves. The MW distribution of the polymer made with the *standard* catalyst is quite broad and results into a polydispersity index (PDI) of about 7.0, as usually found for a Phillips PE.[2] The corresponding DSC curve shows a melting peak at 134 °C characteristic of HDPE having a negligible level of branching. On the contrary, the solid product obtained with *SiH$_4$-modified* catalyst is characterized by a very large MW distribution (Figure 3a, gray), having an essentially bimodal molecular weight distribution, with two components: the heavier one similar to the one obtained with the *standard* catalyst, and a very low MW fraction centered at about 10^3 g/mol (ca. 2.7 on logarithmic MW scale). The corresponding PDI is in the 30-90 range. This polymer melts at a much lower temperature (123 °C, Figure 3b, gray), which is in agreement with LLDPE.[27]

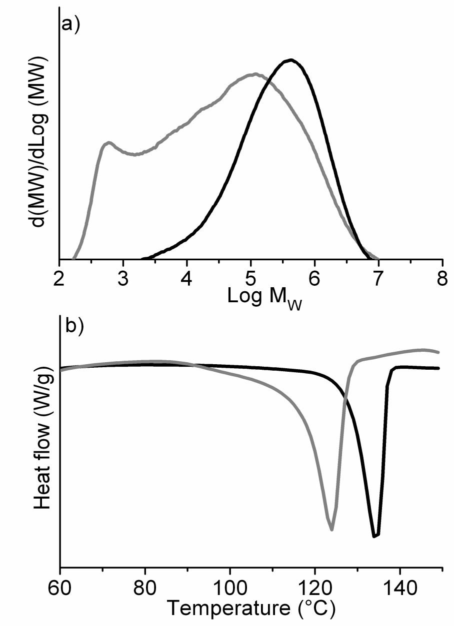


Fig. 3 Molecular weight distributions (from size exclusion chromatography, part a) and DSC signals (part b) of the polymers produced with the *standard* Cr(II)/SiO$_2$ (black) and with the *SiH$_4$-modified* catalyst (grey).

The in situ FT-IR spectra shown in Figure 2, together with SEC and DSC analysis conducted on the produced polymers (Figure 3), demonstrate that SiH$_4$ modifies the performances of the Phillips catalyst, enhancing the polymerization rate and changing the type of polyethylene produced. These results are in pretty good agreement with those obtained on polyethylenes made at the industrial scale with both *standard* and hydrosilane-*modified* Phillips catalysts.[2] We can thus conclude that, although our spectroscopic data are obtained at low ethylene pressure and room temperature, they are well representative of the phenomena occurring at the industrial level.

3.3 Observation of intermediate species by means of temperature- and pressure-resolved FT-IR spectroscopy in operando conditions

In the previous section, we have followed by FT-IR spectroscopy the ethylene polymerization at room temperature on both *standard* and *SiH$_4$-modified* Phillips catalyst and we have proven with the help of PE thermal properties that with the latter LLDPE is produced, while HDPE is obtained with the former. As a matter of fact, hydrosilanes are used in the industrial practice as highly efficient co-catalysts for producing in situ branching.[2,26] In presence of hydrosilanes, α-olefins are increasingly found along with the polymer; therefore, it is thought that introduction of branching in polyethylene chains arises from co-polymerization of ethylene with in situ produced light α-olefins.[2] In other words, the *SiH$_4$-modified* catalyst do not only polymerize, but also oligomerize, ethylene. However, the time-resolved FT-IR spectra shown in Figure 2 do not allow the detection of any light α-olefin, because the high rate of monomer insertion prevents the observation of intermediate species. The same problem was encountered many years ago during investigation of the initiation mechanism of ethylene polymerization on the *standard* Cr(II)/SiO$_2$ catalyst.[11,18,28,29] The solution was found more recently, and is based on temperature and pressure-resolved FT-IR experiments. By working in controlled pressure and temperature conditions it was possible to freeze precursors (C$_2$H$_4$···Cr(II) π-complexes)[13,30] and intermediate (metallacycles) species,[12,13] and therefore to obtain relevant information on the initiation mechanism of ethylene polymerization. Herein, we apply a similar strategy to catch the in situ α-olefins formation on the *SiH$_4$-modified* catalyst before their incorporation in the growing polymer chains.

Figure 4 shows the sequence of temperature- and pressure-resolved FT-IR spectra collected during ethylene polymerization on *standard* Cr(II)/SiO$_2$ catalyst in the ν(OH) (parts a and d), ν(CH$_x$) (parts c and f) and ν(C=C) (parts b and e) regions, respectively. The spectra evolution was already discussed in our previous works[12,13] and therefore only a few relevant details are commented hereafter. At very low temperature (about 130 K, bold light gray spectrum in Figure 4a), C$_2$H$_4$ is physisorbed on the silica surface, as testified by the consumption of the IR absorption band at 3745 cm^{-1} due to free isolated hydroxyl groups and the appearance of a broad band centered at 3620 cm^{-1} (Δν(OH): -125 cm^{-1}), previously assigned to the ν(OH) vibration of silanols interacting with ethylene molecules.[13,18,30,31] Formation of SiOH···C$_2$H$_4$ 1:1 π-complexes reduces the ethylene symmetry and makes the C=C stretching mode of adsorbed ethylene IR active (very weak absorption band at 1618 cm^{-1}, Figure 4b). At this temperature, ethylene molecules interact also with the surface Cr(II) sites, forming Cr(II)···C$_2$H$_4$ π-complexes characterized by weaker IR absorption bands at 3004 cm^{-1} and 1590 cm^{-1} (due to ν$_{symm}$(CH$_2$) and ν(C=C) vibrational modes, respectively, see asterisks in Figure 4b and 4c). The intensity of these vibrational features is much lower than that of the

$SiOH\cdots C_2H_4$ complexes, in fair agreement with the ratio of the surface silanols over Cr(II) species under the adopted activation conditions.

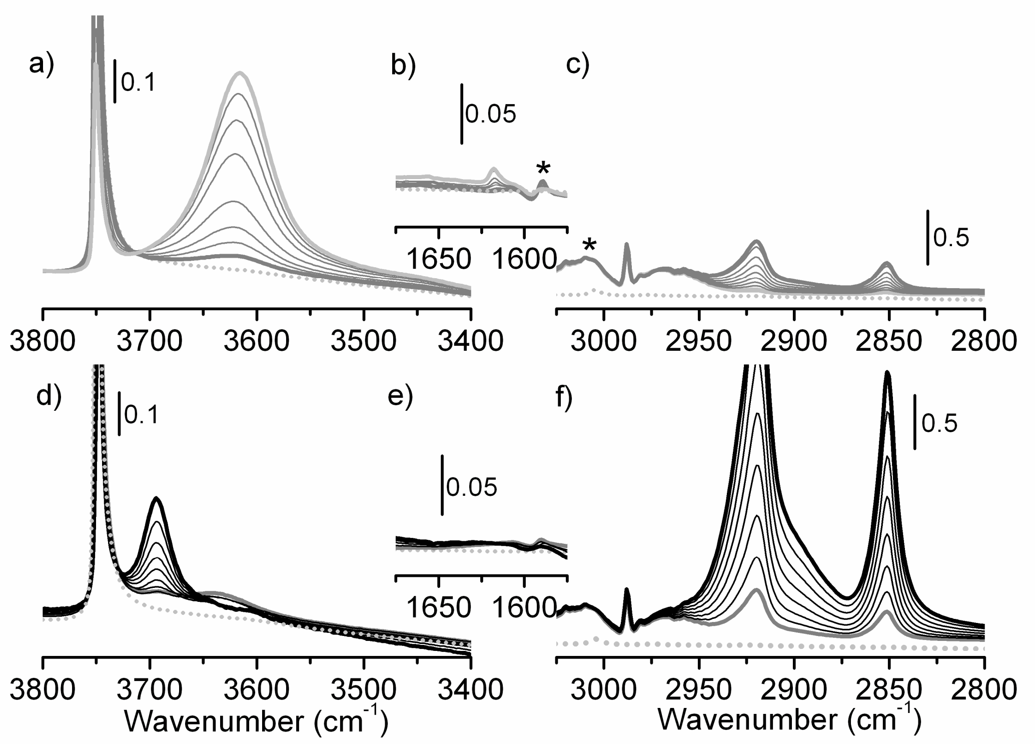


Fig. 4 Ethylene polymerization experiment on *standard* $Cr(II)/SiO_2$ catalysts, as followed by temperature- and pressure-resolved FT-IR spectroscopy, in the ν(OH) (parts a and d), $\nu(CH_x)$ (parts c and f) and ν(C=C) (parts b and e) regions, respectively. Dotted spectrum refers to the sample at about 100 K prior ethylene contact. Bold light grey spectrum is recorded at about 130 K and is dominated by ethylene physisorption. Dark grey spectra are collected at increasing temperature in the 130 – 230 K range and show the gradual disappearance of the IR manifestation of $SiOH\cdots C_2H_4$ π-complexes in presence of a modest polymerization. Black spectra are collected at increasing temperature in the 230 – 300 K range and monitor the occurrence of ethylene polymerization reaction.

Upon increasing temperature (Figure 4d-f), the IR absorption bands characteristic of $SiOH\cdots C_2H_4$ π-complexes gradually disappear and ethylene polymerization slowly takes place, as testified by the growth of the two absorption bands at 2925 and 2855 cm^{-1} due to the symmetric and asymmetric CH_2 stretching modes, respectively. At longer polymerization times black spectra in Figure 4d-f), the polyethylene chains start to interact via H-bonding with surface silanols, causing a shift of the corresponding IR absorption band down to 3694 cm^{-1} (Figure 4d). Note that the Δν(OH) value (-51 cm^{-1}) is smaller than that observed for the $SiOH\cdots C_2H_4$ π-complexes, because the C-C single bonds in the polymer are less basic than the double bond of ethylene molecule.

A similar temperature- and pressure-resolved experiment was performed on the *SiH_4-modified* catalyst and the corresponding FT-IR spectra are shown in Figure 5. As already discussed for the unmodified catalyst, at very low temperature (light grey spectra in Figure 5a-c), $SiOH\cdots C_2H_4$ 1:1 π-complexes are formed, as testified by the shift of the ν(OH) absorption band down to 3620 cm^{-1}, and the appearance of a very weak absorption band at 1618 cm^{-1} due to the ν(C=C) vibrational mode of physisorbed ethylene (see asterisk in Figure 5b). It is worth noticing that the vibrational manifestation of $Cr(II)\cdots C_2H_4$ π-complexes are scarcely visile, demonstrating that SiH_4 modified the large majority of the Cr(II)sites. Upon increasing temperature (dark grey spectra in Figure 5a-c), the IR absorption bands assigned to $SiOH\cdots C_2H_4$ π-complexes gradually disappear and ethylene polymerization slowly takes place, as testified by the appearance of the characteristic IR absorption bands in the $\nu(CH_x)$ region. Since the very beginning, both $\nu(CH_2)$ (bands at 2920 and 2850 cm^{-1}) and $\nu(CH_3)$ (band around 2970 and 2880 cm^{-1}) vibrational manifestations are present. Simultaneously, and differently from the previous case, new IR absorption bands appear in both ν(OH) (at 3577 cm^{-1}) and ν(C=C) (bands at 1638 and 1598 cm^{-1}) vibrational regions. A further increase in temperature (black spectra in Figure 5d-f) causes a further downward shift of the ν(OH) absorption band (down to 3534 cm^{-1}) that decreases in intensity. Ethylene polymerization proceeds at a higher rate, as testified by the fast growth of the IR bands in the $\nu(CH_x)$ region and by the appearance of the IR absorption band at 3693 cm^{-1} due to the polyethylene chains in interaction with the silanol groups. The sequence of FT-IR spectra shown in Figure 5 can be interpreted by considering that during ethylene polymerization new α-olefins are formed and progressively interact with both, the silica surface and the small fraction of un-modified Cr(II) sites. As a matter of fact, it was found previously that the ν(OH) stretching frequency of different SiOH···olefin 1:1 π-complexes is downward shifted with respect to that of free silanol groups, as a consequence of the hydrogen-bonding interaction.[13,31]

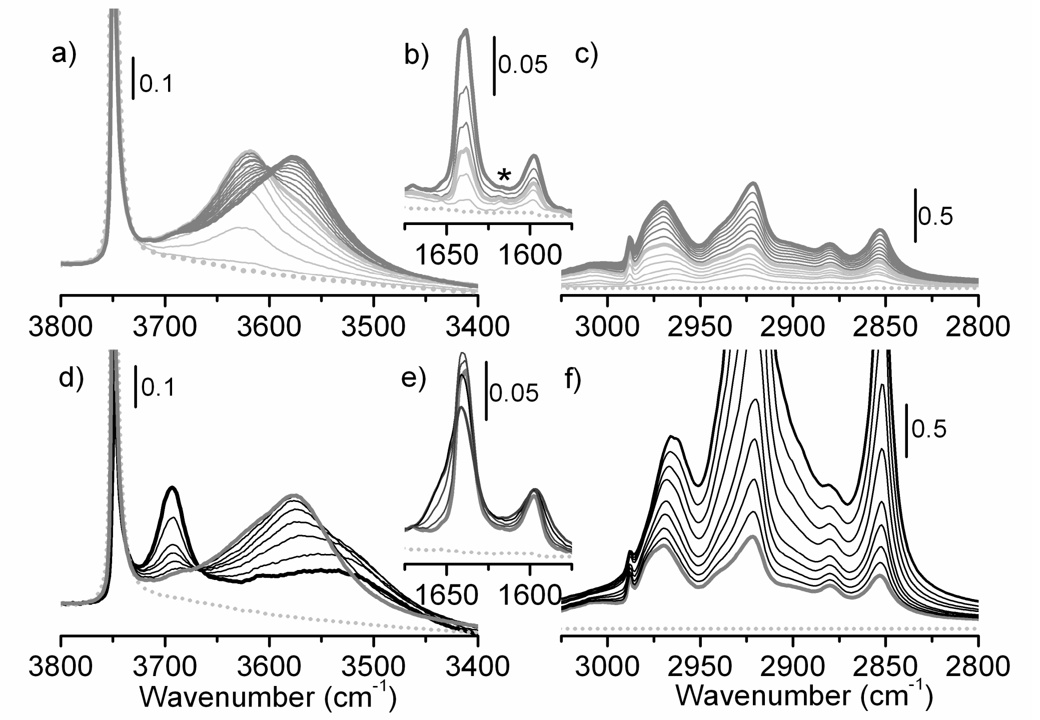


Fig. 5 Ethylene polymerization experiment on *SiH4-modified* Cr/SiO$_2$ catalysts, as followed by temperature- and pressure-resolved FT-IR spectroscopy, in the ν(OH) (parts a and d), ν(CH$_x$) (parts c and f) and ν(C=C) (parts b and e) regions, respectively. Dotted spectrum refers to the sample at about 100 K prior ethylene contact. Bold light grey spectrum is recorded at about 130 K and is dominated by ethylene physisorption. Dark grey spectra are collected at increasing temperature in the 130 – 230 K range and show the gradual disappearance of the IR manifestation of SiOH···C$_2$H$_4$ π-complexes, and the simultaneous appearance of the IR absorption bands due to SiOH···(light α-olefin) π-complexes, in presence of a modest polymerization. Black spectra are collected at increasing temperature in the 230 – 300 K range and monitor the occurrence of both, polymerization and oligomerization reaction.

Simultaneously, the vibrational modes of the adsorbed olefin are also perturbed with respect to those of the gas phase; in particular, the ν(C=C) vibrational mode downward shifts as a consequence of the weakening of the C=C double bond.[13,31] The shift of the ν(C=C) is even larger for the Cr(II)···C$_2$H$_4$ π-complexes.[30]

This is clearly demonstrated in Figure 6, which shows the FT-IR spectra of different α-olefins adsorbed on *standard* Cr(II)/SiO$_2$ in the ν(OH) and ν(C=C) regions, respectively. The spectra were collected at low temperature, when interaction with silica is maximized. The most relevant spectroscopic features are summarized in Table 1. It is clear that both Δν(OH) and Δν(C=C) of SiOH···olefin 1:1 π-complexes, as well as the Δν(C=C) of Cr(II)···α-olefin π-complexes, are characteristic of the adsorbed α-olefin. In particular, the ν(OH) absorption band is the most sensitive parameter, since Δν(OH) increases upon increasing the olefin length. By comparing the results shown in Figure 6 and summarized in Table 1 with the sequence of spectra shown in Figure 5, it can be concluded that during ethylene polymerization on *SiH$_4$-modified* catalyst 1-hexene and 1-butene are mainly formed (characteristic IR absorption bands at 3581-3574, 1638 and 1598 cm^{-1}), along with a small amount of longer α-olefins.

These results, which are the first direct spectroscopic evidence of α-olefins in situ generation on a Phillips catalyst, are in good agreement with the conclusions arising from observation of the final products in the commercial processes. Indeed, it has been reported that the α-olefins generated in situ on a Phillips catalyst in presence of hydrosilanes consist of a sharp Shulz-Flory distribution of even-numbered linear α-olefins with little additional 1-hexene.[2] The simplest way to explain the tendency to chain termination for the modified chromium sites is to invoke the occurrence of a standard Cossee mechanism on Cr-H sites. The same mechanism was recently claim to be responsible for polymer production at the Phillips catalyst.[32] However, the data at our disposal do not allow to support this hypothesis, neither to discard it; the fully characterization of the modified Cr sites would the object of an incoming paper.

Table 1 Frequency position (in cm^{-1}) of the main IR absorption bands characteristic of different 1:1 π-complexes of olefin with SiOH groups and with Cr(II) sites at the Cr(II)/SiO$_2$ surface. The values in parenthesis indicate the Δν(OH) shift with respect to free silanol groups, and the Δν(C=C) with respect to the olefin in the gas phase.

α-olefin	SiOH···C$_n$H$_{2n}$ complexes		Cr(II) ···C$_n$H$_{2n}$ complexes
	ν(OH)	ν(C=C)	ν(C=C)
Ethylene	3620 (-125)	1618 (-5)	1590 (-33)
Propylene	3587 (-158)	1645 (-3)	1607 (-40)
1-Butene	3581 (-164)	1638 (-7)	1599 (-46)
1-Hexene	3574 (-171)	1638 (-4)	1598 (-44)

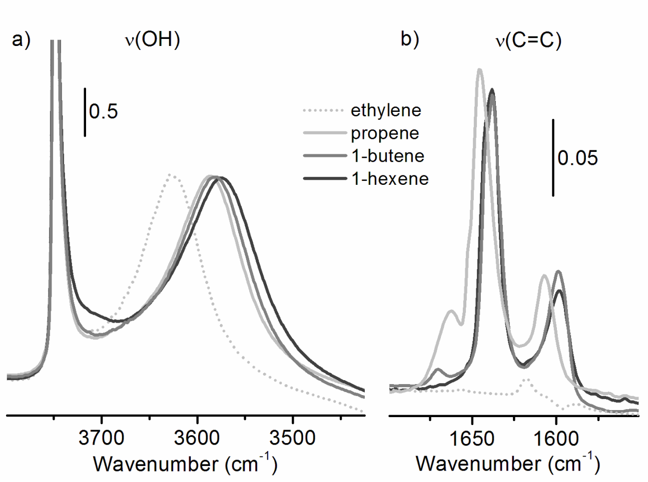


Fig. 6 FT-IR spectra of different α-olefins adsorbed at low temperature on *standard* Cr(II)/SiO_2 in the ν(OH) and (C=C) regions (parts a and b, respectively).

4. Conclusions

FT-IR spectroscopy applied in operando conditions was used to investigate ethylene polymerization on a *SiH_4-modified* Phillips catalyst, in comparison with the *standard* one. Time-resolved FT-IR spectra collected at room temperature allowed us to estimate that ethylene polymerization rate is 7 times higher on the *SiH_4-modified* catalyst than on the *standard* one. Moreover, it was found that the produced PE contains more CH_3 moieties than that formed on the *standard* catalyst; SEC and DSC analysis demonstrated that the produced PE is a LLDPE, in good agreement with the literature results. However, the high rate of monomer insertion at room temperature prevented the observation of reaction intermediate species on the *SiH_4-modified* Phillips catalyst; only the application of temperature- and pressure-resolved FT-IR spectroscopy allowed the detection of in situ produced α-olefins, before their incorporation in the polymer chains. The results shown herein offer a direct spectroscopic insight into the in situ branching process, which is at the basis of the LLDPE production with a hydrosilane-*modified* Phillips catalyst.

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