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Ethylene, propylene and ethylene oxide in situ polymerization on the $Cr(II)/SiO_2$ system: A temperature- and pressure-dependent investigation

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Abstract

The $Cr(II)/SiO_2$ system was found to be able to activate and polymerize at room temperature not only light olefins (such as ethylene and propylene), but also a cyclic molecule such as ethylene oxide, which does not contain a C–C unsaturation. The polymerization of ethylene, propylene and ethylene oxide on the $Cr(II)/SiO_2$ system have been followed in situ by means of temperature- and pressure-resolved FTIR spectroscopy. This method allowed to ''freeze'' the precursors of the reaction and the intermediate species, even when their amount is low in comparison with spectator species, and in some cases to determine the initiation mechanism. Information about the energy barrier associated with the polymerization reaction (temperature at which the reaction starts) and about the kinetic of the process (time dependence of the experiment) have been obtained in the three cases.

Keywords: Polymerization; in-situ FTIR spectroscopy; Phillips catalyst

1. Introduction

The nature of the precursor species and the mechanism of ethylene polymerization on the $Cr(II)/SiO_2$ Phillips catalyst [1] have been the subject of a deep investigation in the past [2–4], due to the unique ability of this system to polymerize ethylene without the intervention of any activator [4]. However, notwithstanding the importance of this system in the polyethylene (PE) world-production [5], these questions have been clearly highlighted only very recently [6]. Temperature- and pressure-resolved in situ FTIR experiments have been fundamental in this field [7]. In fact, at room temperature (RT), the ethylene coordination to the Cr(II) centres, which are the precursor of the active sites, is rapidly followed by a very fast polymerization reaction (high turnover frequency) [2,4,8,9]. For this reason, the study of the $Cr(II)\cdots(C_2H_4)_n$ complexes and of the deriving intermediate species can be achieved only by lowering the temperature down to a value where kT is lower than the activation barrier of the first step of the polymerization reaction [7,10,11]. Furthermore, only a small fraction of all the Cr(II) sites is active in the ethylene polymerization [12], making the identification of the real intermediates a challenge for spectroscopic methods. In this respect, the study of the initiation steps of the ethylene polymerization on the $Cr(II)/SiO_2$ system is a good example to illustrate the problems encountered when dealing with the hunting of few intermediate species characterized by a very short lifetime [7].

Temperature- and pressure-resolved in situ FTIR spectroscopy revealed that the first step in the ethylene polymerization on the $Cr(II)/SiO_2$ system is the formation of $Cr(II)\cdots(C_2H_4)_n$ π-bonded complexes [6,7,10,11], followed by the formation of metallacycle intermediate species, characterized by a structural strain decreasing with increasing ring dimension [6]. The strength of the $Cr(II)–C_2H_4$ interaction, which can be evaluated by measuring the perturbation of the C═C stretching frequency in comparison with that of the free ethylene molecule, is related to the stability of the $Cr(II)\cdots(C_2H_4)_n$ π-bonded complexes, and thus to the rate of formation of the metallacycle species and of the subsequent polymerization reaction.

It is known that the Phillips catalyst is able to polymerize not only ethylene, but also propylene and other higher α-olefins

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[13], even if the polymerization mechanism has not been determined so far. In analogy with the ethylene polymerization, it is expected that also in these cases the reaction should occur through the formation of π-bonded complexes, followed by the construction of the active site. In this work the interaction of propylene with the Cr(II)/SiO_2 system has been studied by adopting the same experimental procedure used for ethylene polymerization [6,7,10,11]. Temperature- and pressure-resolved FTIR experiment allowed to identify the Cr(II)···(C_3H_6) π-bonded complexes and to follow the first step of the polymerization reaction. It is demonstrated that the propylene polymerization rate is lower than that of ethylene polymerization, suggesting that the presence of an additional CH_3 group in the monomer molecule has strong influence in the formation and stability of the Cr(II) π-bonded complexes.

The high affinity and/or reactivity of the highly uncoordinated Cr(II) sites in the Cr(II)/SiO_2 system towards molecules containing unsaturated C–C bonds is demonstrated also by their ability to instantaneously trimerize acetylene and methylacetylene, which result in the immediate formation of benzene and 1,3,5-trimethylbenzene, respectively [14]. Up to now, the presence of an unsaturated C–C bond able to form Cr(II) π-bonded complexes with different relative stability and reactivity seemed mandatory in order to observe oligomerization/polymerization reaction on the Phillips catalyst. However, quite surprisingly, in this work we have discovered that the Cr(II)/SiO_2 system is able to activate and slowly polymerize at RT also a cyclic molecule such as ethylene oxide, which does not contain a C–C unsaturation. The temperature-resolved FTIR spectra of the interaction of ethylene oxide with Cr(II)/SiO_2 have been extremely useful in the understanding of the nature of the products obtained by reacting with oxygen the intermediate species of the ethylene polymerization reaction [6].

This work demonstrates that temperature- and pressure-resolved FTIR spectroscopy is a technique extremely useful to follow chemical reaction that are fast at room temperature, such as polymerizations. By changing the experimental conditions in a suitable way, in fact, it is possible ‘‘to freeze’’ the precursor and the intermediate species, even when their amount is low in comparison with spectator species, thus allowing, in some cases, the identification of the initiation mechanism. The comparison between ethylene, propylene and ethylene oxide polymerizations allowed to understand the requisite that the Cr(II) active sites should present to guarantee a fast reaction.

2. Experimental

The Cr(II)/SiO_2 samples (1 wt.% Cr) have been prepared following the procedure described elsewhere [4,8,10,15]. An amorphous silica-aerogel (surface area of ~700 $m^2 g^{-1}$) [16] was impregnated with a solution of CrO_3 in CH_3CN, dried at RT, and pressed into a thick pellet (~0.5 mm). The silica-aerogel guarantees an almost complete transparency of the sample in the IR region in the 4500–1800 cm^{-1} range [15], because of the absence of scattering, also in the case of a thick pellet. This fact, together with the high surface area characterizing the silica-aerogel, allowed to increase the number of Cr sites probed by the IR beam by more than one order of magnitude with respect to the past experiments. The pellet has been then transferred into an IR cell designed to allow thermal treatments of the sample in the 1000–77 K range, either under vacuum or in presence of a desired equilibrium pressure of gases. The samples were activated according to the following three steps [4,11,17]: (i) activation at 923 K and calcination in O_2 at the same temperature for 1 h, after which Cr is grafted in a hexavalent state, with a chromate structure [4,15]; (ii) reduction in CO at 623 K, followed by CO removal at the same temperature, after which Cr(VI) species are almost all reduced to Cr(II) [4,10,11,17]; (iii) cooling down to RT. The FTIR spectra have been collected on a Bruker IFS-66 spectrophotometer, at 2 cm^{-1} resolution.

3. Results and discussion

3.1. Temperature- and pressure-dependent experiments

The interaction of ethylene, propylene, and ethylene oxide with the Cr(II)/SiO_2 system has been monitored by means of in situ FTIR spectroscopy according with the same procedure. A monomer pressure (~15 Torr) was dosed on the sample previously cooled at about 100 K and then the temperature was allowed to increase. Under such conditions two main thermodynamic variables play a role: temperature (T) and pressure (P). T increases gradually in the ~100–300 K range. P increases from nearly zero up to about 15 Torr in the ~100–200 K range, whereas it gradually decreases in the 200–300 K range, due to the consumption of the monomer molecules during the polymerization reaction.

Ethylene and propylene show a similar behaviour, which is therefore discussed in general terms in the following. At 100 K all the monomer molecules are adsorbed on the metallic part of the cell (sample holder) and no detectable amount of gas is able to reach the sample (dotted curves in Figs. 1–4). In the ~100–250 K range, the monomer progressively vaporizes and originate an equilibrium pressure of about 15 Torr. Under these conditions the monomer is adsorbed on both silanols (dominating contribution) and on the Cr(II) sites (sequence of light grey curves in Figs. 1–4). At about 250 K, the interaction of monomer with silanols becomes negligible, but the temperature is still too low to allow polymerization to start (bold grey curve in Figs. 1–4). This means that we are here in presence of the Cr(II) molecular precursors, which can later originate the polymeric products. Finally, when the temperature is allowed to grow from about 250 to 300 K, the polymerization reaction slowly takes place (sequence of black curves in Figs. 1–4). The temperature at which each of these phases starts gives an information on the energy barrier associated with the corresponding phenomenon [7]. Conversely, the time dependence of each phase is related with the kinetic of the process.

The ethylene oxide interaction with the Cr(II)/SiO_2 system is characterized by a more complex T/P dependence, and it will be discussed in details in Section 3.4.

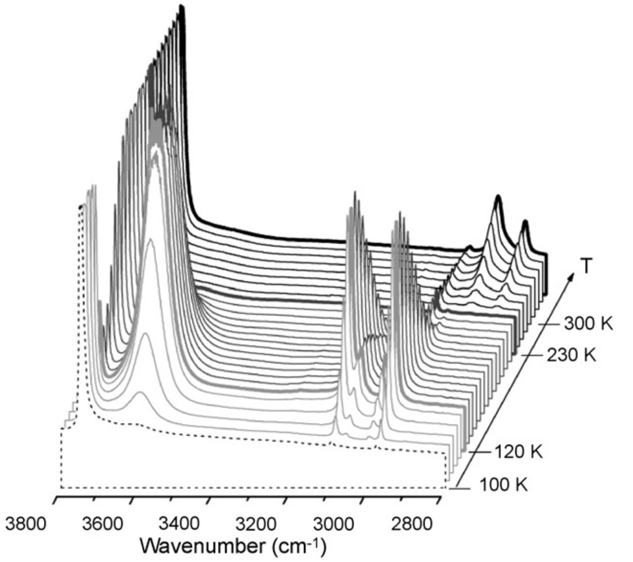

Fig. 1. Temperature-, time- and pressure-resolved C_2H_4 polymerization on the Cr(II)/SiO_2 catalyst in the 100–300 K range, in the O–H and C–H stretching regions. Dotted spectrum refers to the sample at ~100 K prior contact with ethylene. Light grey spectra are dominated by ethylene physisorption, the bold light grey one corresponding to the maximum erosion of the silanol band. Grey spectra correspond to the gradual disappearance of the manifestations of the SiOH···C_2H_4 complexes, in absence of polymerization. Black spectra monitor the polymerization reaction. The bold black spectrum corresponds to a polymerization time of about 10 min (RT has been already reached).

3.2. The C_2H_4–Cr(II)/SiO_2 system

The sequence of temperature- and pressure-resolved spectra of the Cr(II)/SiO_2 sample upon C_2H_4 adsorption and reaction are reported in Fig. 1 (O–H and C–H stretching regions) and Fig. 2 (C–H and C=C stretching and CH_2 bending in parts a and b, respectively). In the 100–120 K interval (light grey curves in Fig. 1) the spectra are dominated by the vibrational manifestations of the SiOH···C_2H_4 complexes, which overshadow the weaker manifestation of the significantly less abundant Cr(II)···$(C_2H_4)_n$ complexes. This is testified by the erosion of the silanol band at 3745 cm^{-1}, accompanied by the simultaneous growth of an intense band at about 3610 cm^{-1}, $\Delta\tilde{\nu}$(O–H) = −135 cm^{-1}, due to the OH vibration of the silanol groups in interaction with ethylene molecules [10,11]. Contemporarily, four main bands can be distinguished in the CH_2 stretching region, at 3096 cm^{-1} (vs), 3068 cm^{-1} (m), 3006 cm^{-1} (m) and 2978 cm^{-1} (vs), easily assigned to the antisymmetric and symmetric CH_2 stretching modes of the physisorbed C_2H_4 molecules (see Table 1 for the assignment) [10]. The medium intensity bands correspond to the Raman active modes of gaseous ethylene, made IR active by the reduction of symmetry induced by the adsorption. The adsorption makes also the ν(C=C) stretching mode IR active (band at 1618 cm^{-1}, the Raman band of the unperturbed molecule being at 1623 cm^{-1}), as evident in Fig. 2b (light grey curve) together with the intense band at 1440 cm^{-1}, due to the $\delta(CH_2)$ mode.

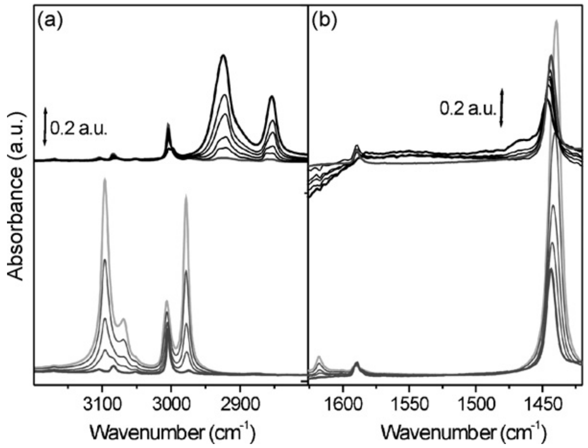

Fig. 2. Enlarged view, in the $\nu(CH_2)$ and in the ν(C=C) and $\delta(CH_2)$ regions (parts a and b, respectively) of some of the spectra reported in Fig. 1, after subtraction of the spectrum before C_2H_4 dosage (dotted line in Fig. 1). The same colour code has been adopted.

Both the shift to low frequency of the silanol band at 3745 cm^{-1} and the perturbation of the vibrational modes of adsorbed ethylene can be explained on the basis of the formation of a 1:1 π-complex [10,13]. Formation of hydrogen-bonded ethylene π-complexes characterized by similar manifestations were previously reported for ethylene adsorption on the acidic Brønsted sites of zeolites [18]. In the ν(C=C) stretching region, a second weaker component is observed at 1590 cm^{-1}, $\Delta\tilde{\nu}$(C=C) = −33 cm^{-1}. As this feature is absent in the same experiment performed on the bare silica surface, it is ascribed to Cr(II)···$(C_2H_4)_n$ complexes.

An increase of the temperature from ~120 to ~230 K (grey curves in Figs. 1 and 2) leads to the gradual disappearance of all the manifestations of the SiOH···C_2H_4 complexes and to the gradual restoration of the unperturbed silanols (peak at 3745 cm^{-1}). In this way, the new, less intense bands associated with the Cr(II)···$(C_2H_4)_n$ complexes become clearly visible (bold grey curve in Figs. 1 and 2). In these conditions, T is sufficiently high that the spectrum does not present any component due to the ethylene in interaction with the surface of the silica support (disappearance of the ν(C=C) band at 1618 cm^{-1}, see Fig. 2b), but it is still too low to start the polymerization reaction. In the CH_2 stretching region five bands can be distinguished, at 3104 cm^{-1} (w), 3084 cm^{-1} (w), 3052 cm^{-1} (vw), 3004 cm^{-1} (m) and 2974 cm^{-1} (vw) which, on the basis of the comparison with the Cr(II)···$(C_2D_4)_n$ system, have been ascribed to the $\nu(CH_2)$ of Cr(II)···$(C_2H_4)_2$ complexes [10]. The lower frequency region is characterized by the already discussed band at 1590 cm^{-1} of the IR activated ν(C=C) mode and by the 1444 cm^{-1} component of the δ(CH) mode. It is worth noticing that not all the Cr(II)···$(C_2H_4)_2$ complexes could evolve into an active site. In other words, we are not able at this point to distinguish between spectator and really active sites.

When the temperature is allowed to grow from ~230 K (bold grey curve in Figs. 1 and 2) to 300 K (black curves in Figs. 1 and 2), the polymerization reaction slowly takes place, as evidenced by the appearance of two intense absorption bands around 2925 and 2855 cm^{-1} (black curves in Figs. 1 and 2), due to the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes of the living polymeric

Table 1
Most relevant spectroscopic features of gaseous C_2H_4 and of $SiOH\cdots C_2H_4$ π-complexes in the $\nu(CH_2)$, $\nu(C{=}C)$ and $\delta(CH_2)$ regions

Assignment	C_2H_4 (gas), $\tilde{\nu}$ (cm^{-1})	$SiOH\cdots C_2H_4$ π-complexes	
		$\tilde{\nu}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})
$\nu_{as}(CH_2)$	3106 (IR)	3096 (vs)	−10
$\nu_{as}(CH_2)$	3103 (R)	3068 (m)	−35
$\nu_s(CH_2)$	3026 (R)	3006 (m)	−20
$\nu_s(CH_2)$	2988 (IR)	2978 (vs)	−10
$\nu(C{=}C)$	1623 (R)	1618 (w)	−5
$\delta(CH_2)$	1444 (IR)	1440 (vs)	−4

For the π-complexes, the $\Delta\tilde{\nu}$ with respect to the gas phase are also reported. IR: IR active; R: Raman active. The intensity scale is as following—w: weak; m: medium; s: strong; vs: very strong.

chains [4,8,17,19]. The two weak bands at 2931 and 2860 cm^{-1}, evident at short polymerization times and already reported by Bordiga et al. [11], have been recently associated with some small precursor species having a metallacycle structure, which are characterized by a structural strain decreasing with increasing ring dimension [6]. In the ethylene stretching region, we observe that the set of bands at 3104, 3084 and 3004 cm^{-1}, assigned to $Cr(II)\cdots(C_2H_4)_2$ complexes, begin to decrease when the monomer pressure declines (due to the polymerization process), evolving in a new set of bands at 3096, 3078 and 2998 cm^{-1}, which have been ascribed to a mono-ethylene complex [10]. Conversely, if the ethylene pressure is maintained sufficiently high, these bands remain quite unaltered. These observations lead to the following conclusions: (i) the bands related with the di-ethylene complexes reflect the majority of spectator species; (ii) the di-ethylene complexes are stable only in presence of a high monomer pressure [10]. Finally, by looking at the time scale, the final spectrum (bold black curve in Figs. 1 and 2) corresponds to a polymerization time of about 10 min.

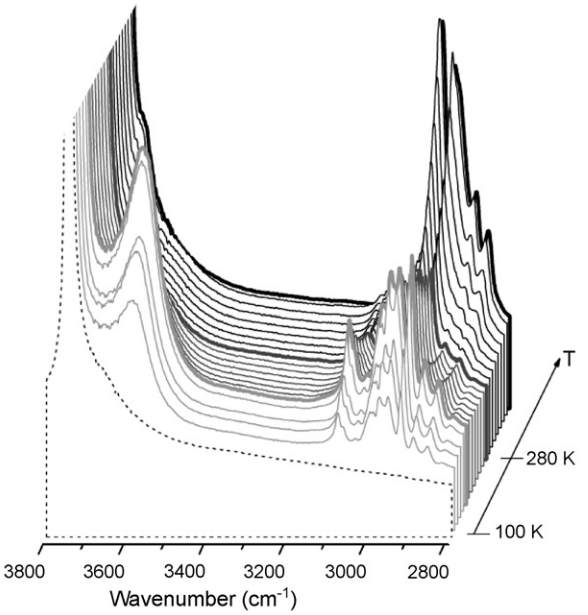

Fig. 3. Temperature-, time- and pressure-resolved C_3H_6 polymerization on the $Cr(II)/SiO_2$ catalyst in the 100–300 K range, in the O–H and C–H stretching regions. Dotted spectrum refers to the sample at ∼100 K prior contact with propylene. Light grey spectra are dominated by propylene physisorption, the bold light grey one corresponding to the maximum erosion of the silanol band. Grey spectra correspond to the gradual disappearance of the manifestations of the $SiOH\cdots C_2H_4$ complexes, in absence of polymerization. Black spectra monitor the polymerization reaction. The bold black spectrum corresponds to a polymerization time of about 30 min.

3.3. The C_3H_6–$Cr(II)/SiO_2$ system

Fig. 3 shows, in the O–H and C–H stretching region, the IR spectra of the pressure- and temperature-dependent interaction of propylene on the $Cr(II)/SiO_2$ system, according to the procedure discussed above. Dotted spectrum was collected at 100 K before propylene dosage. The subsequent spectra were collected upon increasing progressively the temperature up to 300 K. As far as the high frequency zone is concerned, we observe that the sharp and well defined band due to the O–H stretching mode of the free silanols at 3745 cm^{-1} is progressively eroded with the parallel appearance of an intense band centred around 3590 cm^{-1}, $\Delta\tilde{\nu}(O{-}H) = -160\ cm^{-1}$, testifying the formation of $SiOH\cdots C_3H_6$ complexes (light grey spectra in Fig. 3). The bold light grey spectrum corresponds to the maximum erosion of the silanol band (highest intensity of the 3590 cm^{-1} band), which occurs around 230 K. In these conditions, the spectrum is dominated by the vibrational features of propylene physisorbed on the silica surface, as testified by the close similarity of this spectrum with that of liquid propylene (see dashed spectrum in Fig. 4), both in the C–H stretching region (part a) and in the C=C stretching and C–H bending regions (part b).

The complete assignment of all the vibrational features characterizing the $SiOH\cdots C_3H_6$ complexes is outside the aim of this work. It is only stressed here that the presence of an additional CH_3 group with respect to the C_2H_4 case, causes a

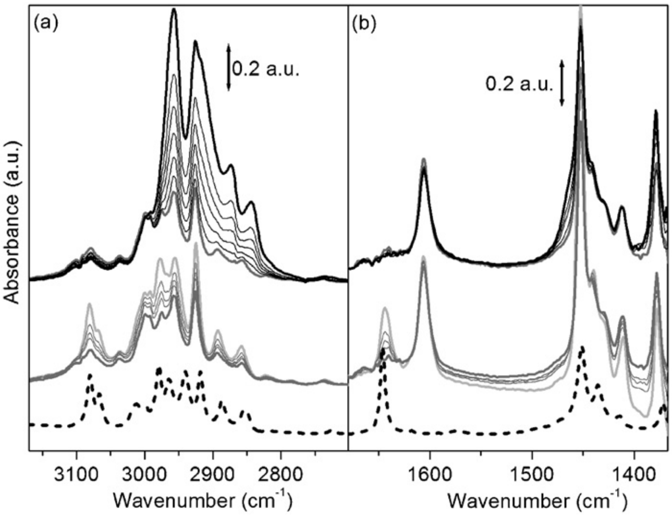

Fig. 4. Enlarged view, in the $\nu(CH)$ and in the $\nu(C{=}C)$ and $\delta(CH)$ regions (parts a and b, respectively) of some of the spectra reported in Fig. 3, after subtraction of the spectrum before C_3H_6 dosage (dotted line in Fig. 3). The same colour code has been adopted. Dashed spectrum refers to liquid propylene.

Table 2
Most relevant IR spectroscopic features of gaseous C_3H_6 and of $SiOH\cdots C_3H_6$ π-complexes in the ν(CH), ν(C═C) and δ(CH) regions

Assignment	C_3H_6 (gas), $\tilde{\nu}$ (cm^{-1})	$SiOH\cdots C_3H_6$ complexes	
		$\tilde{\nu}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})
$\nu_{as}(CH_2)$	3081	3081 (m)	0
$\nu(CH) + \nu_s(CH_2)$	3012	2998 (w)	−14
$\nu_s(CH_2)$	2979	2977 (m)	−2
$\nu(CH) + \nu_{as}(CH_3)$	2960	2956 (m)	−4
$\nu_{as}(CH_3)$	2916	2925 (m)	+9
$\nu_s(CH_3)$	2852	2858 (w)	+6
ν(C═C)	1647	1644 (m)	−3
$\delta_{as}(CH_3) + \delta(CH_2)$	1472	1473 (vw)	+1
$\delta_{as}(CH_3)$	1448	1452 (vs)	+4
$\delta(CH_2)$	1416	1412 (w)	−4
$\delta_s(CH_3)$	1399	1378 (m)	−21

For the π-complexes, the $\Delta\tilde{\nu}$ with respect to the gas phase are also reported. The intensity scale is as following—vw: very weak; w: weak; m: medium; s: strong; vs: very strong.

dramatic increase in the complexity of the spectrum. The most relevant spectroscopic features of the C_3H_6–Cr(II)/SiO_2 system are summarized in Table 2. Finally, it is worth noticing that hydrogen-bonded propylene π-complexes characterized by similar manifestations were previously reported for the acidic Brønsted sites of zeolites [18]. In the ν(C═C) stretching region, a second quite intense component is observed at 1605 cm^{-1}, $\Delta\tilde{\nu}$(C═C) = −39 cm^{-1}, which can be ascribed to Cr(II)$\cdots(C_3H_6)_n$ complexes. The downward shift of the ν(C═C) mode testifies that the propylene molecules are strongly perturbed by the Cr(II) centers.

At higher temperatures (grey spectra in Figs. 3 and 4), the desorption process of propylene from the labile $SiOH\cdots C_3H_6$ complexes becomes dominant, causing the almost total restoration of the band due to the free silanols. At about ∼280 K the spectrum does not show any component due to propylene interaction with silica (disappearance of the $\tilde{\nu}$(C═C) band at 1644 cm^{-1}), but the polymerization reaction is not started yet. In these conditions (bold grey spectrum in Figs. 3 and 4) the spectrum is characterized only by the features of the Cr(II)$\cdots(C_3H_6)_n$ complexes, which are similar to those of physisorbed propylene, with the only exception of the already discussed $\tilde{\nu}$(C═C) mode at 1605 cm^{-1}. At this point the polymerization reaction slowly starts (black spectra in Figs. 3 and 4), as evidenced by the growing of four bands at 2956–2875 cm^{-1}, due to the $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ modes of the polymeric chains, and at 2918–2844 cm^{-1}, due to the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes, respectively.

The fact that the propylene polymerization reaction starts at a temperature definitely higher than that of ethylene polymerization (∼280 K versus ∼230 K) suggests that the activation barrier associated with the first reaction is higher than that characterizing the second one. Furthermore, it is important to observe that the propylene polymerization rate is extremely low if compared with the ethylene polymerization one, also when the temperature reaches 300 K. The bold black spectrum reported in Figs. 3 and 4 has been collected after a polymerization time of about 30 min. These observations suggest that the presence of an additional methyl group in the monomer molecule strongly affects the energetic barrier associated with the monomer insertion and thus the reactivity of the Cr(II)$\cdots$(α-olefin) systems. In particular, the CH_3 group may have both an electronic and a sterical influence.

3.4. The C_2H_4O–Cr(II)/SiO_2 system

The interaction of ethylene oxide with the Cr(II)/SiO_2 system in the 100–300 K range is reported in Figs. 5 and 6. Differently from ethylene and propylene, ethylene oxide strongly interacts with the silica surface already at room temperature. The strong affinity of this molecule towards silica is testified by the consumption of the band at 3745 cm^{-1} due to the free silanol groups (consumption not evident in Fig. 5 because this band is out of the reported scale), which is accompanied by the growth of an intense and broad band centred at ∼3410 cm^{-1}, $\Delta\tilde{\nu}$(O–H) = −335 cm^{-1}, associated with the formation of $SiOH\cdots C_2H_4O$ complexes. The bold light grey spectrum corresponds to the maximum erosion of the silanols band, which occurs at about 200 K. In these conditions, the spectrum is dominated by the manifestations of the $SiOH\cdots C_2H_4O$ complexes, the most relevant ones being reported in Table 3. In the high frequency region two main components at 3085 and 3018 cm^{-1} characterize the $SiOH\cdots C_2H_4O$ complexes, due to the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes, respectively. Both bands are at frequencies higher than those of the gas phase (see the narrow peaks in both Figs. 5 and 6). In the 1500–1300 cm^{-1} region, the $SiOH\cdots C_2H_4O$ complexes show two $\delta(CH_2)$ modes, at 1493 and 1468 cm^{-1}.

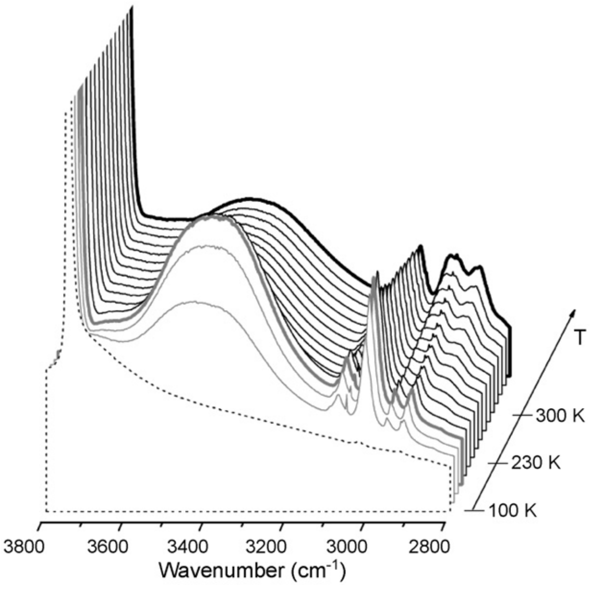

Fig. 5. Temperature-resolved C_2H_4O adsorption and polymerization on the Cr(II)/SiO_2 catalyst in the 100–300 K range, in the O–H and C–H stretching regions. Dotted spectrum refers to the sample at ∼100 K prior contact with ethylene oxide. Light grey spectra are dominated by ethylene oxide physisorption, the bold light grey one corresponding to the maximum erosion of the silanol band. Black spectra monitor the polymerization reaction. The bold black spectrum corresponds to a polymerization time of about 1 h and 30 min.

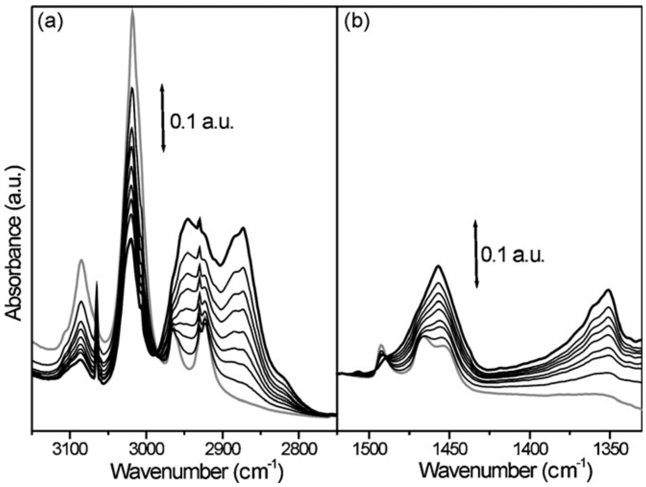

Fig. 6. Enlarged view, in the $\nu(CH_2)$ and in the $\delta(CH_2)$ regions (parts a and b, respectively) of some of the spectra reported in Fig. 5, after subtraction of the spectrum before C_2H_4O dosage (dotted line in Fig. 5). The same colour code has been adopted.

Table 3
Most relevant spectroscopic features of gaseous C_2H_4O and of $SiOH\cdots C_2H_4O$ complexes in the $\nu(CH_2)$ and $\delta(CH_2)$ regions

Assignment	C_2H_4O (gas), $\tilde{\nu}$ (cm^{-1})	$SiOH\cdots C_2H_4O$ complexes	
		$\tilde{\nu}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})
$\nu_{as}(CH_2)$	3065	3085 (m)	+20
$\nu_s(CH_2)$	3006	3018 (vs)	+12
$\delta(CH_2)$	1498	1493 (w)	−5
$\delta(CH_2)$	1472	1468 (w)	−4

For the complexes, the $\Delta\tilde{\nu}$ with respect to the gas phase are also reported. The intensity scale is as following—w: weak; m: medium; s: strong; vs: very strong.

Together with the bands related to the physisorbed C_2H_4O, the bold light grey spectrum in Figs. 5 and 6 presents other less intense components, at 2965, 2923 and 1453 cm^{-1}, which can be tentatively assigned to the $\nu(CH_2)$ and $\delta(CH_2)$ modes of the $Cr(II)\cdots(C_2H_4O)_n$ σ-complexes. Since the Cr(II) are characterized by a high degree of coordinative unsaturation, the coordination of more than one C_2H_4O molecule seems possible. Coordination through the heteroatom to a positive centre is known to perturb the vibrational properties of several coordinated molecules [20]. Normally, the perturbation is restricted to the low frequency modes, the CH stretching and bending modes being fairly insensitive to coordination effects. However, the case of ethylene oxide is anomalous, because the exceptional ring strain makes also these modes extremely sensitive to the electronic modifications occurring at the heteroatom. It is worth noticing that ethylene oxide was found to bond via the oxygen atom to the Ag(1 1 0) [21] and Pt(1 1 1) [22] surfaces, with the C–C bond axis parallel to the metal surface and C_{2v} symmetry, resulting in an important downward shift of the $\nu(CH_2)$ modes with respect to the gas phase (−58 and −63 cm^{-1} for ethylene oxide adsorbed on Ag(1 1 0) and on Pt(1 1 1), respectively).

Upon increasing the temperature, two phenomena occur simultaneously. A fraction of ethylene oxide gradually desorbs from the silica surface, as testified by the consumption of the broad band at ∼3410 cm^{-1}. At the same time, a slow but constant polymerization process starts, as demonstrated by the slow parallel increase of three complex absorptions centred at ∼2945, ∼2880 and at 1355 cm^{-1}, which can be associated with $(CH_2–O–CH_2)_n$ oligomeric/polymeric chains. Similar bands were previously reported for the ethylene oxide polymerization on the MgO surface [23]. Once that the system has reached a temperature of 300 K, the formation of these species is accompanied by the progressive disappearance of the bands due to the physisorbed ethylene oxide, a fact which can be explained in terms of a displacement of the monomer molecules due to the incoming polymeric chains. It is worth noticing that no polymerization is observed on the bare silica support, testifying the catalytic role played by the Cr sites.

To our knowledge, the observation of ethylene oxide polymerization on the $Cr(II)/SiO_2$ system has never been reported so far. A large proportion of the heterogeneous systems reported to catalyze the polymerization of ethylene oxide to high molecular weight polyethylene oxide (PEO) are alkaline earth oxides [23–25]. In the homogeneous phase, alkyls and alkoxides of various metals (such as Zn, Mg, and Ca) have a combination of properties that makes them predisposed to catalyze polymerization of energetic monomers such as ethylene oxide [26–28]. The common feature of all these catalysts seem to be the ability to promote polymerization via a ring opening anionic mechanism. The intervention of basic oxygen have been also claimed to occur during ethylene oxide polymerization on the MgO surface [23]. As for the $Cr(II)/SiO_2$ system is concerned, the presence of basic oxygen can be ruled out; hence the polymerization mechanism likely not proceeds via anionic intermediates, and further investigations are required to understand it.

4. Conclusions

Temperature- and pressure-resolved FTIR spectroscopy has been revealed fundamental in order to deeply investigate the polymerization of ethylene and propylene on the $Cr(II)/SiO_2$ Phillips catalyst, starting from the identification of the $Cr(II)\cdots$(α-olefin) π-precursors, through the detection of intermediate species, to the observation of the final polymeric products. In the case of ethylene, we have been able to distinguish between spectator species and real intermediates of the polymerization reaction. It has been found that the propylene polymerization starts at a temperature about 50 K higher than that of ethylene polymerization (∼280 K versus ∼230 K), implying that the corresponding activation barrier is higher. Furthermore, the propylene polymerization rate is extremely low if compared with the ethylene polymerization one, also at room temperature. These observations suggest that the presence of an additional methyl group in the monomer molecule strongly affects the reactivity of the $Cr(II)\cdots$(α-olefin) system.

Moreover, it has been discovered that the $Cr(II)/SiO_2$ system is able to activate and slowly polymerize at room temperature also a cyclic molecule such as ethylene oxide, which does not contain a C–C unsaturation. Temperature- and pressure-resolved FTIR spectroscopy allowed the identification of the vibrational manifestation of the $Cr(II)\cdots C_2H_4O$ σ-complexes and of the following $(CH_2–O–CH_2)_n$ oligomeric/polymeric chains.

Notes added in proofs

Very recently it has been shown [29] that interaction of the $Cr(II)/SiO_2$ system with CH_2Cl_2 under well defined conditions results in the deactivation of the more active and abundant Cr(II) sites, and in the simultaneous selective modification of the remaining ones, that are converted into highly active polymerization sites. The resulting system shows a much higher polymerization activity in comparison to the standard Phillips catalyst.

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