



On the first stages of the ethylene polymerization on $\text{Cr}^{2+}/\text{SiO}_2$ Phillips catalyst: time and temperature resolved IR studies

S. Bordiga^{a,b,c,*}, S. Bertarione^{a,b}, A. Damini^{a,b}, C. Prestipino^{a,c},
G. Spoto^{a,b}, C. Lamberti^{a,b,c}, A. Zecchina^{a,b}

^a Department of Inorganic, Physical and Materials Chemistry, University of Turin,
Via P. Giuria 7, 10125 Torino, Italy

^b INSTM UdR Torino Università, Torino, Italy

^c INFN UdR Torino Università, Torino, Italy

Received 23 October 2002; received in revised form 20 January 2003; accepted 4 February 2003

Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

IR spectroscopy, even in the time resolved mode, failed up to now in the identification of the species formed during the initiation of the ethylene polymerization step on the $\text{Cr}^{2+}/\text{SiO}_2$ Phillips catalyst. To overcome this problem in this investigation we have designed and performed new experiments allowing to collect IR spectra at lower T or/and in presence of a poison (CO), which are both experimental conditions where the polymerization rate is so highly depressed to hopefully allow the detection of the species formed in the initiation stage. Time, pressure and temperature dependent IR spectra collected in the 173–300 K range on the $\text{Cr}^{2+}/\text{SiO}_2$ catalyst in $\text{CO}/\text{C}_2\text{H}_4$ atmosphere show, at the lowest temperatures, the formation of mixed $\text{Cr}^{2+} \cdots (\text{CO})(\text{C}_2\text{H}_4)$ physisorbed complexes and, upon increasing the temperature the switching on of the C_2H_4 polymerization. A 5–10% fraction of Cr^{2+} sites forming the mixed $\text{Cr}^{2+} \cdots (\text{CO})(\text{C}_2\text{H}_4)$ is sufficient to greatly inhibit the polymerization activity. This suggests that the Cr^{2+} sites active at 300 K represent a small fraction of the total number of Cr^{2+} sites present on the surface of the catalyst.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Phillips catalyst; Time resolved FTIR; In situ spectroscopy; Ethylene oligomerization

1. Introduction

Because of its outstanding importance in ethylene polymerization reaction, the Phillips catalyst [1] ($\text{Cr}^{2+}/\text{SiO}_2$) has been widely investigated in the past, among all see e.g. [2–25]. In spite of the large number of published paper, many questions are still

open such as the structure of the active sites and the initiation of the ethylene polymerisation reaction. The difficulties encountered in the determination of the structure of the active sites are likely associated with the high heterogeneity of the surface structures present on the amorphous silica support. Similarly the exact determination of the structure of the species formed in the initiation step has been prevented by the high the polymerization rate (high turnover number) characterizing the active site, a fact which makes the observation of the first polymerisation

* Corresponding author. Tel.: +39-011-6797855;

fax: +39-011-6797855.

E-mail address: silvia.bordiga@unito.it (S. Bordiga).

products (at least under normal reaction conditions) troublesome.

The heterogeneous character of the $\text{Cr}^{2+}/\text{SiO}_2$ catalyst can be understood if we consider in detail the most plausible mechanism of the anchoring process which involves the reaction of surface silanols (weakly acidic) with the metal oxide, with subsequent formation of grafted active species (in this case Cr^{2+}). In fact on the surface of the amorphous silica support, numerous locations of the anchored Cr^{2+} ions are conceivable, which differ in the number of ligands (two oxygen atoms of the $\equiv\text{SiO}^-$ groups and a variable number of oxygen atoms of the $(\equiv\text{SiO}^{\delta-}\text{Si}\equiv)$ bridges in adjacent position. In other words on amorphous SiO_2 many type of Cr^{2+} structures differing in the structure of the first coordination sphere are simultaneously present. The problem associated with the presence of a distribution of sites (heterogeneity of Cr^{2+} centers), directly connected with the amorphous nature of silica, is difficult to be overcome. It is known however that thermal treatments at high temperature decreases the population of the grafted Cr^{2+} sites characterized by highest coordinative unsaturation and favors the partial penetration of the ions into the flexible framework with subsequent stabilization of more coordinated Cr species [12,25]. The study of the adsorptive properties towards CO and NO of $\text{Cr}^{2+}/\text{SiO}_2$ treated at different temperatures has allowed to partially enlighten on the structure of the sites and on their coordinative unsaturation [8,12–16,25,26]. Furthermore it has been reported that the samples annealed at high T in vacuo show the lowest polymerisation activity. On this basis it has been hypothesized that the sites with the lowest number of ligands in the immediate vicinity are characterized by highest turnover numbers, while the most coordinated sites are much less active or even inactive at RT [14,15,20,21,25]. Following this hypothesis, under RT reaction conditions, the sites characterized by highest turnover number (probably a small fraction) readily originates long or very long polymer chain upon ethylene contact while the remaining sites (perhaps the vast majority) remains silent. This explains why even the application of fast IR spectroscopy at RT (sequence of spectra taken at intervals of 2 s) was not able to single out the true IR spectrum of the species formed during the initiation step [14,25]. In conclusion, the high polymerising rate of a small fraction of low-coordinated

sites represents the major obstacle for the study of the initiation step. To overcome this problem in this investigation we have designed and performed new experiments allowing to collect IR spectra at lower T or in presence of a poison (CO), which are both experimental conditions where the polymerization rate is so highly depressed to hopefully allow the detection of the species formed in the initiation stage.

2. Experimental

$\text{Cr}^{2+}/\text{SiO}_2$ was obtained following the procedure described elsewhere [13–15,25]. A weighted amount of SiO_2 was impregnated with a water solution of chromic acid (concentration = 2 wt.% with respect to SiO_2). After slowly drying the slurry in air at 350 K, the powder obtained was then compressed into a thin pellet and transferred to an IR cell designed to allow thermal treatments of the sample either under high vacuum or in presence of gases. The steps of the standard treatment of the sample were as follows; (i) heating step under vacuum up to 973 K, (ii) oxidation step in O_2 atmosphere at the same temperature, (iii) reduction step in CO at 673 K followed by CO removal and the same temperature, and (iv) cooling step to RT in vacuo.

The reactivity of Cr^{2+} species has been studied by dosing probe molecules able to form adducts (such as CO) or to react (such as C_2H_4). Some experiments have been carried out varying the temperature in the range 100–300 K as it will be carefully described further.

3. Results and discussion

3.1. Interaction with CO at 100 K

The IR spectra at increasing coverages of CO adsorbed at 100 K on a $\text{Cr}^{2+}/\text{SiO}_2$ system are illustrated in Fig. 1. The IR bands can be clearly grouped into two series, depending on the CO equilibrium pressure (P_{CO}).

The first series, dominating at low P_{CO} , reflects a CO/ Cr^{2+} ratio lower than 2 and is associated with the presence of several C–O stretching bands of adsorbed CO molecules characterized $\nu(\text{CO})$ frequencies higher than that of the free molecule ($\nu(\text{CO}_{\text{gas}}) =$

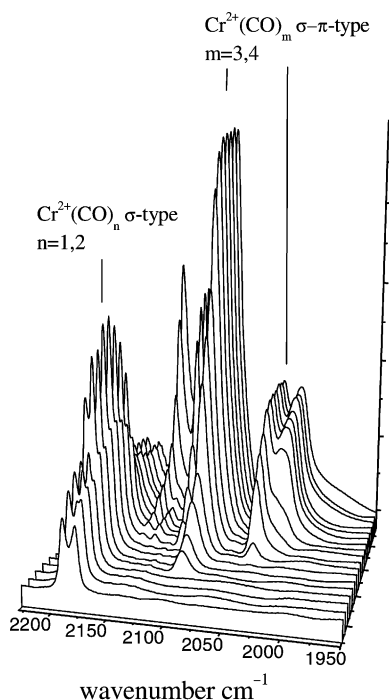


Fig. 1. Evolution of the IR spectra of CO dosed at liquid nitrogen temperature on $\text{Cr}^{2+}/\text{SiO}_2$ upon changing P_{CO} .

2143 cm^{-1}) at 2191, 2184, 2179, and 2178 cm^{-1} , which undergo a progressive intensification upon increasing P_{CO} . These bands are present even at RT and correspond to the most stable species [14,25]. An accurate analysis of their evolution with the CO equilibrium pressure has allowed to conclude that the bands at 2179 and 2191 cm^{-1} belongs to $\text{Cr}^{2+} \cdots \text{CO}$ adducts formed at two distinct sites (hereafter labeled as Cr_A and Cr_B , respectively). The two sites correspond to two different coordinative situations, exhibiting Cr_A sites an higher coordinative unsaturation with respect to Cr_B sites. Upon increasing P_{CO} a doublet at $2184\text{--}2178\text{ cm}^{-1}$ becomes predominant. This doublet has been assigned to a dicarbonyl formed at Cr_A sites. In all cases the blue shift of the observed C–O stretching bands indicates that electrostatic and σ -type overlap forces are mainly involved [25,27–29].

The second series of intense bands in the $2150\text{--}2050\text{ cm}^{-1}$ interval, dominating at high P_{CO} and corresponding to a CO/Cr^{2+} ratio higher than 2, is observed at $T \approx 100\text{ K}$ only. Their formation is accompanied by the progressive erosion of the

bands formed in the first phase. This can be interpreted only by assuming that both $\text{Cr}_A^{2+} \cdots \text{CO}$ and $\text{Cr}_B^{2+} \cdots \text{CO}$ complexes are able to bind additional CO ligands with formation of new labile $\text{Cr}^{2+} \cdots (\text{CO})_n$ ($2 \leq n \leq 4$) complexes [25]. Without going into detail in the assignment of all components, we only underline that: (i) these data demonstrate that the involved Cr_A^{2+} and Cr_B^{2+} species are both highly coordinatively unsaturated (although at different degree); (ii) the frequency of the barycentre of this intense multiplet in the $2150\text{--}2050\text{ cm}^{-1}$ interval is lower than $\nu(\text{CO}_{\text{gas}})$. The only possible explanation of this fact is that on passing from mono and dicarbonyls to polycarbonylic species an abrupt increase of the $d\text{--}p$ interaction is occurring, because only in this way both the downward frequency shift and the intensity increase can be understood [25,27–29]. Indeed metal carbonyls of the type $\text{M}(\text{CO})_n\text{X}_2$ ($\text{X} = \text{Br}, \text{Cl}$ etc.) characterized by substantial $d\text{--}\pi$ back donation have bands in the same frequency range and with similar intensity pattern [25,30].

The assignment given above seems in contradiction with the high lability of the tri- and tetra-carbonyl complexes (they decomposed by simply reducing P_{CO} at 100 K). In fact, if the reduced frequency of the involved CO groups is associated (as proposed before) with an increase of $d\text{--}\pi$ overlap contributions and hence with a strengthening of the $\text{Cr}^{2+} \cdots \text{CO}$ bonds a stability enhancement is expected (while the opposite is observed). This apparent contradiction has been solved by assuming that the addition of the third and fourth CO ligand is not simply a ligand insertion in preexisting coordinative vacancies of $\text{Cr}^{2+} \cdots (\text{CO})_n$ species but more correctly a ligand displacement reaction where the bonding of the additional CO ligands is accompanied by the simultaneous rupture of one or two weakly bonded surface ligands (presumably the bridging oxygen of the $\equiv\text{SiO}^\delta\text{--Si}\equiv$ groups). In other words, the adsorption of further CO is accompanied by surface relaxation. On this basis the total enthalpy change involved in the process may be small (and hence the removal of CO can be facile) because the energy required for the creation of a vacancy at the Cr^{2+} centers is counterbalanced by the energy release associated with the coordination of a surface ligand [25]. In conclusion, the Cr^{2+} centers on silica show some mobility and, under appropriate conditions, can change their position on the surface under the influence

of complexing agents (strong relaxation) and optimize their interaction with CO via $d-\pi$ interaction [12,25].

3.2. Ethylene coordination and polymerization: time resolved spectra recorded at room temperature

Time resolved spectra recorded at RT after admission of 15 Torr (1 Torr \approx 133.3 Pa) of ethylene (Fig. 2) on a model $\text{Cr}^{2+}/\text{SiO}_2$ sample reduced in CO following the standard procedure described before, show a doublet in the $\nu(\text{CH})$ stretching region at 2920 and 2851 cm^{-1} growing with time in a parallel way and at nearly constant rate. The first spectrum has been obtained immediately after admission of C_2H_4 and the last one has been recorded after 15 min. The assignment of these spectroscopic features is straightforward as they are undoubtedly associated to the stretching modes of the CH_2 groups of the living polymer chains [15,17,25]. The assignment is confirmed by the analysis of the $\delta(\text{CH})$ bending region (small

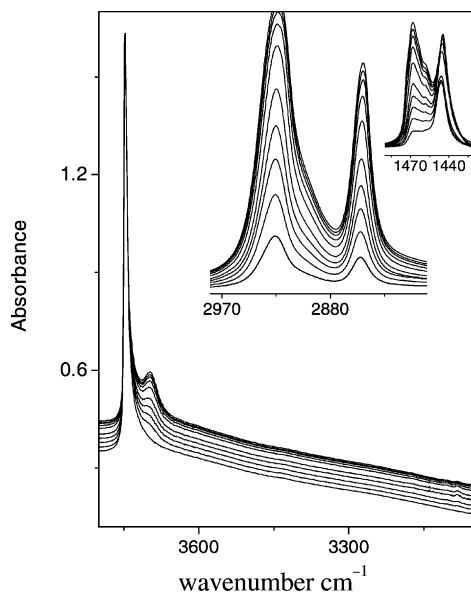


Fig. 2. Time resolved C_2H_4 polymerisation on $\text{Cr}^{2+}/\text{SiO}_2$ catalyst at RT. The reaction has been followed in the O–H stretching, C–H stretching and C–H bending regions. The first spectrum in the O–H stretching region correspond to the $\text{Cr}^{2+}/\text{SiO}_2$ system before ethylene dosage, which has been used as background for all the difference spectra reported in the C–H stretching and bending regions. The last spectrum reflects the situation after a C_2H_4 contact time of 15 min.

inset in Fig. 2), where the growth of the chain is evidenced by the appearance of the band at 1468 cm^{-1} . The band at 1445 cm^{-1} , whose intensity is not sensibly varying with time, is the $\delta(\text{CH})_2$ bending mode of C_2H_4 coordinated to Cr^{2+} centers. On the other spectroscopic properties of coordinated ethylene (CH stretching modes) we shall return in the following.

From Fig. 2 it is evident that no absorptions due to terminal groups (for instance CH_3 groups) can be seen, even in the early stages of the polymerisation, although the corresponding modes have extinction coefficient larger than those of CH_2 . Analogously no absorptions associated with carbene species (which are the other precursors hypothesized so far [8]) can be observed in the series of spectra shown in Fig. 2. Parallel to the chain growth we observe, in the O–H stretching region, the erosion of the 3750 cm^{-1} band (due to free hydroxyl groups [31–33]) and the simultaneous formation of a band at 3700 cm^{-1} , due to the hydrogen bonding interaction of silanols with the polymer chain progressively covering the surface. Due to the long dimension of the polymeric chains, the presence of polymer-silanol interaction does not necessary imply that the active Cr^{2+} centers and the SiOH groups are in adjacent position.

3.3. Ethylene coordination and polymerization: temperature resolved spectra of adsorbed ethylene in the 100–300 K range

In order to follow in greater detail the initial stages of the polymerization, we have decided to introduce ethylene (15 Torr) on the sample cooled at about 100 K (Fig. 3). Under these conditions ethylene condense on the metal part of the cell (pellet holder) and consequently no adsorption (and hence polymerisation) can occur on the sample. Under such conditions, in a temperature dependent experiment in the 100–300 K range, two main thermodynamic variables plays a role: temperature (T) and pressure (P). The latter is the most important variable in the ~ 100 –173 K range, increasing from nearly zero up to 15 Torr, while it plays a negligible role in the ~ 173 –300 K range. The first spectrum in Fig. 3 represent the catalyst at liquid nitrogen temperature before C_2H_4 dosage. In the ~ 100 –173 K range, second and third spectra in Fig. 3, the ethylene progressively vaporizes and originate an equilibrium pressure of about 15 Torr (see the gradual

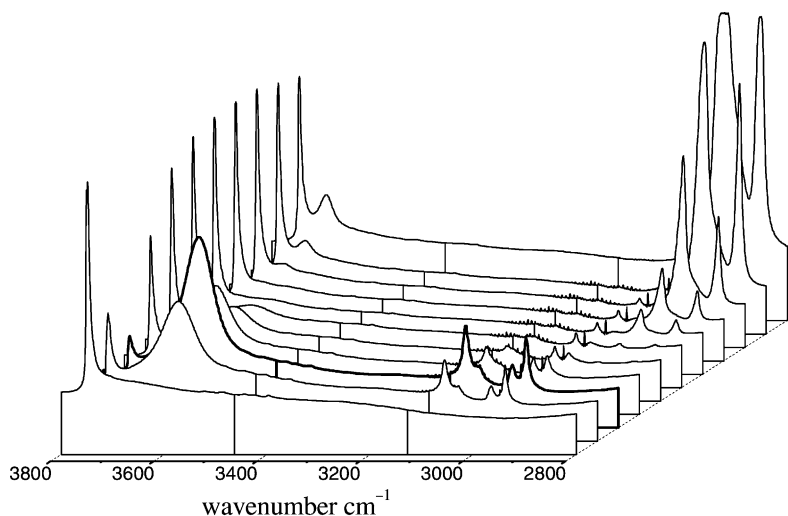


Fig. 3. Temperature resolved C_2H_4 polymerisation on Cr^{2+}/SiO_2 catalyst in the 100–300 K range in the O–H and C–H stretching regions. The first spectrum refers to the sample at 100 K prior contact with ethylene. Successive spectra refers to the temperature (and pressure) increase as described in the text. The last but two spectrum refers to the sample at 300 K, the last but one spectrum has been recorded after 15 min at 300 K, and the last one after subsequent evacuation at 300 K.

appearance of the rotovibrational spectrum of ethylene in the gas phase). Under these conditions ethylene is adsorbed on both silanols (bands at 3096 and 2978 cm^{-1} due to the $\nu(CH)_{2asym}$ and $\nu(CH)_{2sym}$ of ethylene and band at 3630 cm^{-1} , due to the hydrogen bonded silanol, and on Cr^{2+} centers (bands at 3072 and 3005 cm^{-1}). Furthermore, the temperature is so low that no polymerization can start. This means that we are here in presence only of the molecular precursors which can later originate the polymer chain.

The successive increment of T (at constant P of ethylene ~ 15 Torr: 173–300 K range) has two consequences. Firstly the $SiOH \cdots C_2H_4$ hydrogen bonded species ($\nu(CH)_2$ modes at 3096 and 2978 cm^{-1} and $\nu(OH)$ mode at 3630 cm^{-1}) gradually disappear because they are weakly adsorbed and hence they are not stable when the temperature approaches the ambient value. Secondly the bands of the $Cr^{2+} \cdots C_2H_4$ adducts ($\nu(CH)_2$ modes at 3072 and 3005 cm^{-1}) are not affected, because the complex is stable under these temperature and pressure conditions. Finally, starting from the fifth spectrum, the further T increase results in the slow and progressive start of the polymerization reaction, as demonstrated by the progressive growth of the stretching bands of the CH_2 groups of the polymer chain. In conclusion, this experiment allows at the

same the full detection of the molecular precursor and to slow down the reaction rate (as proposed initially). The bold spectrum in Fig. 3 represents the situation where C_2H_4 has formed the maximum amount of hydrogen bonded and coordinated species in absence of polymerisation. The last but one spectrum of Fig. 3 has been recovered when the sample has just reached the room temperature and after 15 min of contact at the same T ; is totally equivalent to the spectra reported in Fig. 2. In particular we observe: (i) ethylene in the gas phase (narrow rotovibrational modes) (ii) coordinated C_2H_4 (doublet at 3072 and 3005 cm^{-1}), (iii) ethylene polymer (doublet at 2920 and 2851 cm^{-1}) interacting by H-bond with silanols (band at 3630 cm^{-1}). The final curve reported in Fig. 3 has been obtained after pumping the gas phase. In this condition, all ethylene in gas phase disappear and only irreversible species are present.

We can conclude that, even in the case where the chain growth is definitely lowered, infrared spectra don't show any peculiarity that could be associated to well defined initiation species. In conclusion, this experiment although successful in showing clearly the spectroscopy of the molecular precursors, failed once again to reveal the properties of the initiation intermediates.

3.4. Ethylene coordination and polymerization: temperature resolved spectra of adsorbed ethylene in the 100–300 K recorded in presence of pre-adsorbed CO acting as polymerization inhibitor

As a final tentative to slow down the reaction rate and to observe the initial stages of C₂H₄ polymerization reaction, we have performed the following experiment. A model Cr²⁺/SiO₂ sample has been contacted with CO (40 Torr) at 100 K. In this way, we have obtained the full formation of polycarbonilic species already deeply discussed in Section 3.1 (first spectrum in Fig. 4). After this stage, 15 Torr of ethylene has been allowed to flow in. As already illustrated before (Section 3.3), under these conditions ethylene cannot reach the sample because it is completely frozen on the metallic holder. At this point the temperature has been allowed to increase gradually and the evolution has been simultaneously followed (see Fig. 4 caption for more details). As detailed in the previous experiment, at about 173 K the partial pressure of ethylene in cell has reached ~15 Torr (second spectrum in Fig. 4). After this temperature the partial pressure of

ethylene remains constant and only the temperature is changing reaching 300 K. A selection of spectra obtained during this experiment are reported in Fig. 4. Bold curve illustrate the formation of Cr²⁺... (CO)_n polycarbonils characterized as usual by intense and characteristic components in 2200–2000 cm⁻¹ range (see Section 3.1). Upon increase of the ethylene partial pressure, occurring just above the melting point of ethylene at 104 K, we observe: (i) the formation of the characteristic bands of the SiOH...C₂H₄ hydrogen bonded adducts; (ii) depletion of the peaks of the Cr²⁺... (CO)_n complexes; (iii) simultaneous formation of a new carbonyl band at 2170 cm⁻¹ due to the formation of mixed Cr²⁺... (CO)(C₂H₄) complexes. Further temperature increment of *T* causes a decrement of the band of the mixed complex (without full disappearance). As at the same time the characteristic bands in the 3100–3000 cm⁻¹ interval of the Cr²⁺...C₂H₄ complexes are reaching the maximum intensity. We so conclude that, in this temperature range ethylene is gradually displacing CO from mixed species. This displacement is not complete even when the temperature is gradually increased up to 300 K (the peak at

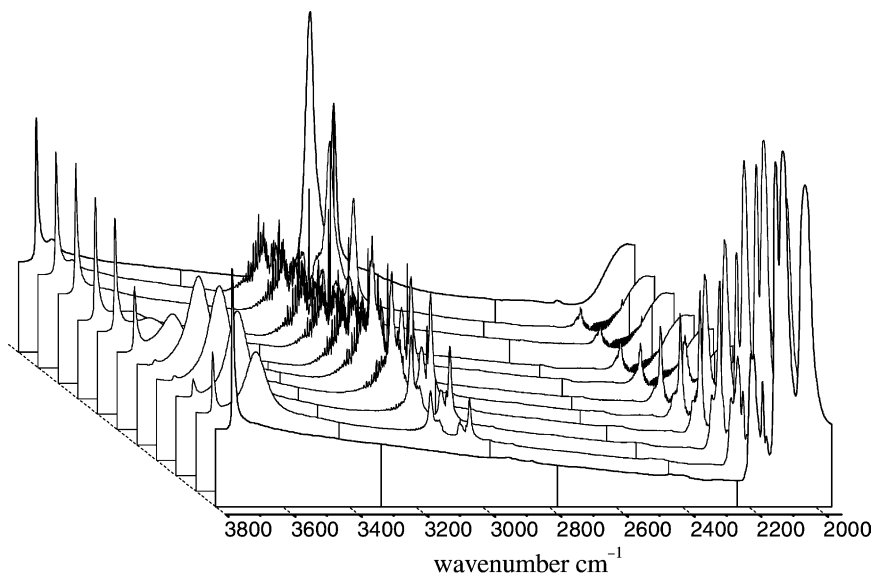


Fig. 4. Temperature resolved C₂H₄ polymerisation on Cr²⁺/SiO₂ catalyst in the 100–300 K range in presence of pre-adsorbed CO (40 Torr). The selected frequency interval covers the O–H, C–H and C–O stretching regions. First spectrum: sample in presence of CO at 100 K prior contact with ethylene. Second spectrum: sample after interaction with ethylene at ca. 173 K. Successive spectra refers to the temperature (and pressure) increase as already described for the Experiment reported in Fig. 3. The last but two spectrum refers to the sample at 300 K, the last but one spectrum has been recorded after 30 min at 300 K in CO/C₂H₄ atmosphere, and the last one after subsequent evacuation at 300 K.

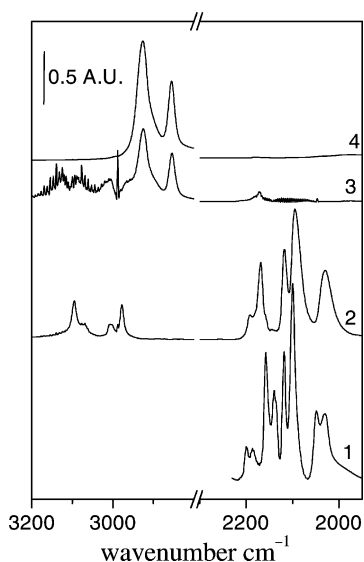


Fig. 5. Two dimensional plot of a selection of spectra reported in Fig. 4. Left and right parts refer to the O–H (and C–H) and to the C–O stretching regions respectively. Curve 1: sample in presence of CO at 100 K prior contact with ethylene (corresponding to the first spectrum in Fig. 4). Curve 2: sample at ca. 173 K in CO/C₂H₄ atmosphere before the start of the polymerisation process (corresponding to the second spectrum in Fig. 4). Curve 3: sample at 300 K (30 min in CO/C₂H₄ atmosphere) (corresponding to the last but one spectrum in Fig. 4). Curve 4: sample after subsequent evaluation at 300 K (corresponding to the last spectrum in Fig. 4). The here reported spectra have been background subtracted and vertically shifted for clarity.

2170 cm⁻¹ is remaining although with only 5–10% of the original intensity). Successive standing for a long time (30 min) of the CO/C₂H₄ mixture at 300 K leads to the slow formation of the classical polymer bands (last but one spectrum in Fig. 4). The speed of the reaction is however very slow in comparison with the previous experiment performed in absence of CO (Fig. 3). This means that CO is acting as strong poison of the polymerization activity. The polymer bands are of course not eliminated by successive pumping (last spectrum in Fig. 4). In such conditions the polymerization rate is decreased by about two order of magnitude.

A more synthetic representation of a significant selection of the same data is reported in Fig. 5. Fig. 6 reports a “temperature zoom”, between the sixth and the last but two spectra of Fig. 4, highlighting the narrow temperature range where the polymerisation

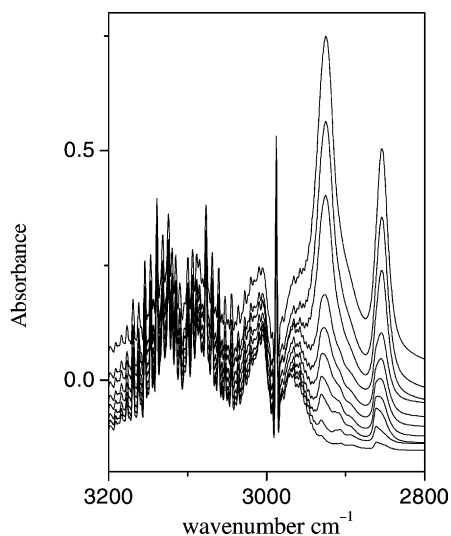


Fig. 6. Two dimensional plot, in the C–H stretching region of all the collected spectra between the sixth and the last but two spectra of Fig. 4. These data represent a “temperature zoom” highlighting the narrow temperature range where the polymerisation process, inhibited by CO, starts. All the here reported spectra have been background subtracted. The correct subtraction of the rotovibrational component of C₂H₄ in the gas phase was not possible owing to the fact that the background spectrum was collected at a lower temperature, where the ethylene equilibrium pressure was much lower.

process, inhibited by CO, starts. From the data reported in Figs. 4–6 new features can be observed which could not be evidenced in the usual polymerization experiments (Fig. 2, and even 3), presumably because the reduced rate allows the observation of shorter oligomeric chains. It is a matter of fact that, at the lowest reaction times the, $\nu(\text{CH}_2)$ peaks of the oligomer are located at 2931 and 2860 cm⁻¹ (more evident in Fig. 6), i.e. at values distinctly different from those observed in the normal experiments (2920 and 2851 cm⁻¹, see Figs. 2 and 3). Only after prolonged contact time these new components become overshadowed by the usual bands of the long polymeric chains characteristic of the normal RT experiments. This result suggests that we are finally observing the $\nu(\text{CH}_2)$ modes of the first products of the polymerization. Other noticeable features are the low intensity bands at 2907 and 2890 cm⁻¹ clearly visible in the first spectra reported in Fig. 6. For the time being we are not able to assign them unambiguously. We can only

conclude that the study of the reaction in presence of a poison is promising and must further investigated.

As final observation it is useful to underline that a 5–10% fraction of Cr^{2+} sites forming the mixed $\text{Cr}^{2+} \cdots (\text{CO})(\text{C}_2\text{H}_4)$ complexes is sufficient to greatly inhibit the polymerization activity. This suggest that the sites Cr^{2+} sites active at room temperature represent a small fraction of the total number of the Cr^{2+} sites present on the surface of the catalyst reduced in CO atmosphere, in agreement with the hypothesis that only the sites characterized by lowest coordination show catalytic activity.

4. Conclusions

We have designed and performed new experiments allowing to collect in situ IR spectra during the ethylene polymerization on the $\text{Cr}^{2+}/\text{SiO}_2$ Phillips catalyst. We have tried to single out the first stages of the polymerization process (which usually escape to conventionally time resolved spectroscopies, owing to a fast polymerization rate) by dosing ethylene at liquid nitrogen temperature or by introducing CO acting as a poison for the process. Under such experimental conditions the polymerization rate is depressed by about two order of magnitude and new IR features can be observed at the early contact times. The formation of mixed $\text{Cr}^{2+} \cdots (\text{CO})(\text{C}_2\text{H}_4)$ physisorbed complexes has been observed. A 5–10% fraction of Cr^{2+} sites forming the mixed $\text{Cr}^{2+} \cdots (\text{CO})(\text{C}_2\text{H}_4)$ is sufficient to greatly inhibit the polymerization activity. This suggest that the Cr^{2+} sites active at 300 K represent a small fraction of the total number of Cr^{2+} sites present on the surface of the catalyst.

References

- [1] J.P. Hogan, R.L. Banks, Belg. Pat. 530 617 (1955).
- [2] P. Cossee, J. Catal. 3 (1964) 80.
- [3] A. Clark, Catal. Rev. 3 (1969) 145.
- [4] J.P. Hogan, J. Polym. Sci. 8 (1970) 2637.
- [5] F.J. Karol, G.L. Karapiska, C. Wu, A.W. Dow, R.N. Johnson, W.L. Carrick, J. Polym. Sci. A 10 (1972) 2621.
- [6] F.J. Karol, G.L. Brown, J.M. Davidson, J. Polym. Sci. A 11 (1973) 413.
- [7] F.J. Karol, L. Wu, J. Polym. Sci. A 13 (1975) 1607.
- [8] K.J. Irvin, J.J. Rooney, C.D. Stewart, M.L.H. Green, R.J. Mahtab, J. Chem. Soc., Chem. Comm. (1978) 604.
- [9] G. Ghiotti, E. Garrone, G. Della Gatta, B. Fubini, E. Giamello, J. Catal. 80 (1983) 249.
- [10] M.P. McDaniel, Adv. Catal. 33 (1985) 47.
- [11] M.P. McDaniel, Ind. Eng. Chem. Res. 27 (1988) 1559.
- [12] E. Garrone, G. Ghiotti, C. Morterra, A. Zecchina, Z. Naturforsch. B 42 (1987) 728.
- [13] G. Ghiotti, E. Garrone, A. Zecchina, J. Mol. Catal. 46 (1988) 61.
- [14] A. Zecchina, G. Spoto, S. Bordiga, Faraday Discuss. Chem. Soc. 87 (1989) 162.
- [15] A. Zecchina, G. Spoto, G. Ghiotti, E. Garrone, J. Mol. Catal. 86 (1994) 423.
- [16] B. Rebenstorf, J. Mol. Catal. 56 (1989) 170.
- [17] K. Vikulov, G. Spoto, S. Cosuccia, A. Zecchina, Catal. Lett. 16 (1992) 117.
- [18] B.M. Weckhuysen, I.E. Wacks, R.A. Shonheydt, Chem. Rev. 96 (1996) 3327.
- [19] M.P. McDaniel, in Handbook of Heterogeneous Catalysis, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), vol. 5, Wiley-VCH, Weinheim, 1997, p. 2400.
- [20] V.J. Ruddick, J.P.S. Baydal, J. Phys. Chem. B 102 (1998) 2991.
- [21] B.M. Weckhuysen, R.A. Schoonheydt, Catal. Tod. 51 (1999) 215.
- [22] P.C. Thüne, C.P.J. Verhagen, M.J.G. van der Boer, J.W. Niemantsverdriet, J. Phys. Chem. B 101 (1997) 8559.
- [23] P.C. Thüne, J. Loos, P.J. Lemstra, J.W. Niemantsverdriet, J. Catal. 183 (1999) 1.
- [24] P.C. Thüne, R. Linke, W.J.H. van Gennip, A.M. de Jong, J.W. Niemantsverdriet, J. Phys. Chem. B 105 (2001) 3073.
- [25] A. Zecchina, D. Scarano, S. Bordiga, G. Spoto, C. Lamberti, Adv. Catal. 46 (2001) 265 (and references therein).
- [26] G. Spoto, S. Bordiga, E. Garrone, G. Ghiotti, A. Zecchina, J. Mol. Catal. 74 (1992) 175.
- [27] A.J. Lupinetti, S.H. Strauss, Angew. Chem. Int. Ed. 37 (1998) 2113.
- [28] S.H. Strauss, J. Chem. Soc., Dalton Trans. (2000) 1.
- [29] A.J. Lupinetti, S.H. Strauss, G. Frenking, Prog. Inorg. Chem. 49 (2001) 1.
- [30] P.S. Braterman, Metal Carbonyls Spectra, Academic Press, London, 1975.
- [31] F. Boccuzzi, S. Coluccia, G. Ghiotti, C. Morterra, A. Zecchina, J. Phys. Chem. 82 (1978) 1298.
- [32] L.M. Kustov, Y.V. Borovkov, V.B. Kazansky, J. Catal. 72 (1981) 149.
- [33] V. Bolis, C. Busco, S. Bordiga, P. Ugliengo, C. Lamberti, A. Zecchina, Appl. Surf. Sci. 196 (2002) 56.