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A DRIFTS Study of the Cr(II)/SiO$_2$ Catalyst

Ethylene Coordination and Early Stages of Polymerisation

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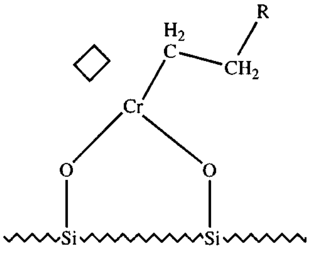
Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been used to study the reduced Cr/SiO$_2$ polymerisation catalyst during reaction with ethylene, isobutene, and carbon monoxide at ambient temperature and at 100°C. When ethylene is added to the catalyst at ambient temperature, two kinds of coordinated ethylene are detected. Relatively stable ethylene–chromium complexes are formed prior to polymerisation which are stable during polymerisation. Also a more labile ethylene–chromium complex is detected by a transient band at 3004 cm^{-1}. The intensity of this band is reduced simultaneous to the growth in the intensity of bands stemming from the polymer formed. Gel permeation chromatography (GPC) analysis of the polymer formed with an ethylene to chromium molar ratio of 1.0 shows that only 0.1% of the chromium is active at the conditions used. The low abundance of active sites suggests that the lack of observable end groups is due to the low number of end groups present. It also means that mechanistic investigation of this catalyst system by spectroscopic methods is difficult and that misinterpretations may easily be done. Saturation of the catalyst with a non-polymerising olefin such as isobutene before introducing ethylene shows that isobutene coordinates in a similar manner as ethylene does. However, coordinated isobutene does not block ethylene polymerisation, and a similar transient ethylene species is observed for the catalysts saturated with isobutene.

1. INTRODUCTION

The Phillips polymerisation catalyst, which consists of chromium ions dispersed on silica, has since the 1950s been widely used for production of polyethylene. Despite numerous investigations of the catalyst, no general agreement concerning the structure of the active catalytic sites and initial polymerisation mechanism exist.

It is generally accepted that the catalyst produces polyethylene where the individual polymer molecules have one methyl and one vinyl end group (1). The predominant termination mechanism is suggested to be β-hydrogen transfer to an incoming monomer (2), and in most cases a standard Cossee (3) type of propagation mechanism is assumed. The structure of the active species of the working catalyst has therefore often been expected to be



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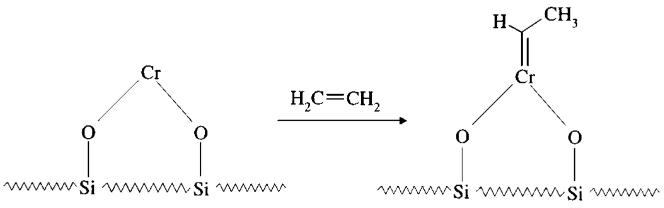
The main problem has been to explain the initiation of the first chain. In order to reach a structure similar to the one above with only ethylene added, an additional hydrogen is needed. Silanol groups have been suggested as a possible hydrogen source (4, 5); however, this has been refuted by McDaniel and Welch by obtaining high catalytic activity even when using completely dehydroxylated supports (6).

A carbene mechanism for olefin polymerisation has early been proposed by Ivin *et al.* (7). Recently, Kantcheva and co-workers also suggested a carbene mechanism for the Cr(II)/SiO$_2$ catalyst on the basis of infrared spectroscopy results (8). They assigned a band at 3016 cm^{-1} in the initial polymerisation stage to ν(C–H) of Cr=CH–R groups. This mechanism,



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has the advantage not to need an extra hydrogen for initiation.

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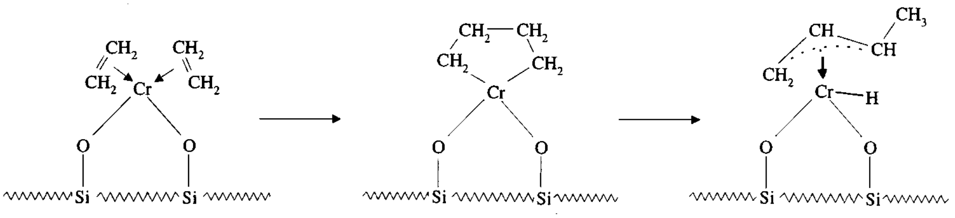
Ghiotti and co-workers proposed an alternative carbene mechanism, where the carbene was formed during a reversible hydrogen abstraction from the α-CH_2 group to a surface oxygen atom (9). In the following propagation step, the same hydrogen is transferred back to its host carbon, which closes the catalytic cycle. Their support for the carbene species was the observation of a broad band at about 2750 cm^{-1}, which was assigned to ν(C–H) of a carbene group in an agostic interaction with the active center. As opposed to the former carbene mechanism, the latter avoids hydrogen scrambling, and is in that way consistent with earlier work by McDaniel and co-workers using isotope labeled ethylene (10).

Another possible initiation mechanism which avoids additional hydrogens includes formation of metallacyclic species and allylic species as shown in (11, 12)



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Support for the metallacyclic structure has recently been obtained from reactions between organometallic chromium complexes and ethylene where five membered metallacyles are formed (13). The metallacyclic species may propagate as such and termination may occur by hydrogen transfer from one of the β-methylene groups to the opposite α-carbon, thus forming linear polymer chains with one methyl and one vinyl end group as expected. For the allylic species, ethylene, insertions may occur either on the Cr–H bond or on the Cr–allyl bond with the allyl ligand bonded in a monohapto fashion.

In the present work we have used diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to study the prereduced catalyst in granular form. We found this method to give excellent signal-to-noise ratio in the ν(C–H) region, together with much easier sample preparation as compared to transmission methods. The drawbacks are that quantitative measurements are difficult to perform, and low signal-to-noise ratio in the (C=C) stretch and (C–H) deformation regions may be obtained. However, the latter problem is reduced by diluting the catalyst in an inert material with low absorbance in the actual frequency region.

By using the DRIFTS technique, we have studied the coordination of ethylene and the very early stages of polymerisation on the reduced Phillips catalyst. This catalyst contains, due to its heterogeneity, chromium sites with different degrees of interaction with the silica surface. Only a minor part of the chromium sites are active for polymerisation. The major challenge is therefore to be able to distinguish between the action of the few active sites from the behavior of the majority of inactive species.

2. EXPERIMENTAL

The supported catalyst was prepared by impregnation of an aqueous solution of CrO_3 on silica (EP10 from Crosfield Chemicals) by the incipient wetness method. The amount of CrO_3 used was chosen to give 1.0 wt% Cr on the dry catalyst. After impregnation, the catalyst was dried at 80°C for 16 h, then activated in a flow of dry air at 800°C at fluidizing conditions for 16 h, cooled to 350°C in dry, oxygen-free nitrogen, and finally reduced by 15% CO in nitrogen at 350°C for 3.5 h. The catalyst was then stored under argon atmosphere in a glovebox.

The DRIFT spectra were recorded with a resolution of 4 cm^{-1} on an Perkin Elmer 2000 FTIR instrument. A MCT detector was used, and each spectrum was averaged over 32 scans. The PE2000 instrument is fitted with a Harrick DRA (diffuse reflectance accessory) equipped with a Harrick HVC chamber.

The catalyst was loaded into the DRIFTS cell under argon atmosphere in a glovebox. The sealed cell was then mounted in the IR spectrometer for data acquisition. The mirrors on the DRA normally had to be tuned slightly in order to get maximum energy throughput to the MCT detector. In some experiments, the catalyst was mixed with a certain amount of dried CaF_2. In this way increased signal to noise ratio in the region 1300–2000 cm^{-1} was obtained. We found that the catalyst behavior in ethylene polymerisation was not changed by the presence of CaF_2.

The cell was linked to an argon line where other gases such as ethylene, CO, and isobutene could be admitted by using a syringe. An argon flow of 50 ml/min was steadily flushed through the cell, and typically 0.10 ml of gaseous reactant could be injected into this flow. Argon (99.999% from AGA), ethylene (polymerisation grade from Borealis AS), isobutene (>99% from Fluka), and carbon monoxide (99.97% from Hydro gas) were used without further purification.

In DRIFTS spectra recorded on silica or on the Cr(II)/SiO_2 catalyst prepared by the method described above, a region with low absorbance was observed around 900 cm^{-1}.

If the Cr(II)/SiO_2 catalyst was exposed to oxygen, a strong band at ca 905 cm^{-1} appeared. This band is assigned to the Cr=O stretching band of Cr(VI) (14, 15). The total time of each DRIFTS experiment in the present work was between 10 and 25 min. During this period we observed no formation of a Cr=O stretch band. Only after several hours on stream, a band at 905 cm^{-1} appears, indicating partly oxidation of the sample.

The setup in which the gas flow just passes through the cell was used. In this case only a fraction of the injected gas comes in contact with the catalyst sample. The rest of the gas just passes through the cell without getting in contact with the catalyst. Alternatively, a setup in which the gas passes through the catalyst sample and thereby allowing a better contact between gas and catalyst can be used. The former setup was preferred, since similar spectra were obtained when using the two setups, but the rate of the reactions were easier to control with the former.

In order to study the polymer produced during the DRIFTS experiments, parallel polymerisation experiments were carried out in closed bottles of 36 ml with 1.0 g of dry catalyst under argon atmosphere. Ethylene was introduced in molar ratios of 0.5, 1.0, and 3.0 of total chromium content. After a few minutes stirring at room temperature, no hydrocarbons could be detected in the gas phase by GC. After hydrolysing these samples by adding excess water, the hydrocarbon content in the gas phase was >99.8% ethylene. Only traces of other organic species could be detected. DRIFT spectra of the these catalyst samples were recorded, before they were digested in an excess solution of hydrofluoric acid at room temperature. From the samples with ratios 1.0 and 3.0, some polymer particles could be collected from the surface of the resulting greenish, but clear solution. These polymer particles were washed in water, dried, and pressed with KBr for IR-transmission studies. In the experiment with ethylene to chromium in ratio 0.5, no polymer particles could be collected.

Possible finely dispersed oligomers were extracted from the HF solutions with dichlorometane. After about 1 h mixing, the HF/water part was removed, and KBr powder was added to the dichloromethane extract. The dichloromethane solvent was removed by heating at 30°C over 12 h and the remaining solid was pressed into pellets for IR-transmission study. These pellets were almost completely free of organic species.

3. RESULTS AND DISCUSSION

In the following sections the results from DRIFTS experiments in which different probe molecules such as ethylene, isobutene, and carbon monoxide have been added to the prereduced Cr(II)/SiO_2 catalyst. All spectra have been ratioed to the IR spectra recorded of the catalyst before admitting the gas samples, if not otherwise stated.

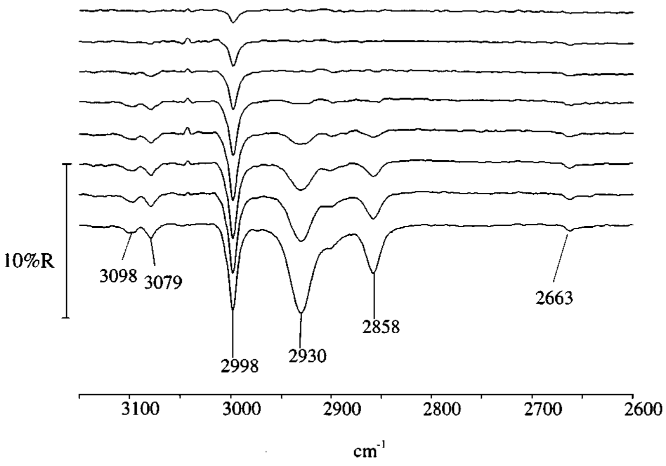


FIG. 1. DRIFT spectra in the ν(C–H) region of early stages in ethylene polymerisation on the Cr(II)/SiO_2 catalyst at room temperature. The baseline of the spectra in the sequence have been shifted vertically for clarity.

Reaction with Ethylene at Ambient Temperature

Gaseous ethylene has, due to its D_{2h} symmetry, two C–H stretch modes which are IR-active. After π-coordination, the symmetry is reduced and the ethylene fragment may have four active ν(C–H) bands in the infrared spectrum. Figure 1 shows the spectra recorded after each of eight equal, sequential injections of ethylene. Each spectrum is recorded when steady state is achieved about 3 min after the ethylene injection. After the four first injections a strong band at 2998 cm^{-1} and three bands of lower intensity at 3098, 3079, and 2663 cm^{-1} are observed. The band at 2998 cm^{-1}, previously also observed by other groups (8, 16, 17), is assigned to ν_s(C–H) of ethylene π-bonded to chromium. We assign the two bands at 3079 and ca 3098 cm^{-1}, previously not reported, to ν_{as}(C–H) of the same species. These assignments are based on work with ethylene complexes of late transition metals (18, 19).

A weak band around 2660 cm^{-1} has in a previous investigation been assigned to a methyl group in chromium–ethylidene species (8). However, the intensity of the band at 2663 cm^{-1} observed in the present work correlates strongly with the intensities of the modes assigned to coordinated ethylene. In addition, the band is observed before any methylene bands are detected, and the intensity seems to remain constant during polymerisation. No evidence of ν(C–H) of a Cr=CH–R group (band observed at 3016 cm^{-1} in Ref. (8)) can be observed in the present study. We therefore suggest that the mode at 2663 cm^{-1} is an overtone or combination band of CH_2 deformation modes of coordinated ethylene (20).

Because the ethylene is passed through the cell and only a part of the gas comes in contact with the catalyst sample, and, since information is mostly obtained from the upper part of the sample when using DRIFTS (21), we are not able to measure the ratio between coordinated ethylene and total chromium content. The concentration of coordinated ethylene has by other groups been estimated to be around 50% (17) and 40% (8) of total chromium content, based on the assumption that one ethylene molecule coordinates to each chromium atom.

After the fourth injection of ethylene two new bands at 2930 and 2858 cm^{-1} appear, which are assigned to methylene groups of polyethylene. These two bands increase steadily with each ethylene injection while the intensities of the other bands in this region stay constant. As observed by others, no end groups such as methyl or vinyl are observed in this early stages of polymerisation (9, 16, 17, 22). The weak band at approximately 2900 cm^{-1} is most probably a splitting of the methylene bands due to crystallisation of the polymer, as observed by Krimm and co-workers (23) for crystalline $C_{36}H_{74}$.

To increase the signal-to-noise ratio in the region 1300–1700 cm^{-1}, the catalyst was diluted with equal amounts (by weight) of dried CaF_2 powder. Spectra of this sample after different ethylene injections are illustrated in Fig. 2. The band at 1448 cm^{-1} and the weak band near 1584 cm^{-1} can be assigned to $\delta_{as}(CH_2)$ and $\nu(C{=}C)$ of π-coordinated ethylene (8). At more advanced stages of polymerisation the bending modes of methylene groups are observed at 1471 cm^{-1}, together with a shoulder at about 1463 cm^{-1}. The band at 1471 cm^{-1} is unique for the crystalline phase of linear hydrocarbon chains of polyethylene (24).

Figure 3 shows spectra recorded every 20 s after an injection of ethylene, before steady state is achieved. The amount of ethylene injected in this experiment was about 10 times the volume of each injected volume of Fig. 1. A short time after the large ethylene injection, a new band appears at 3004 cm^{-1}, and at the same time the band at 3079 cm^{-1} is broadened and shifted to higher frequency. At increasing time the intensities of the bands at 2931 and 2859 cm^{-1} increase, while the band at 3004 cm^{-1} decreases. No gaseous ethylene (observed at 2987 cm^{-1}) is detected after the very first spectrum.

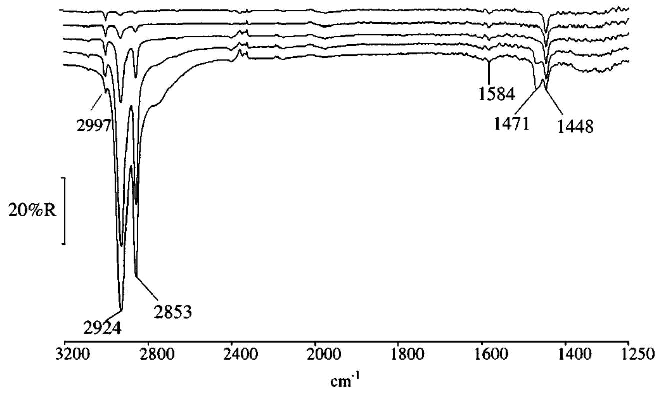


FIG. 2. DRIFT spectra of early and more advanced stages of ethylene polymerisation on the Cr(II)/SiO_2 catalyst at room temperature. The catalyst is diluted with equal amounts (by weight) of CaF_2. The baseline of the spectra in the sequence have been shifted vertically for clarity.

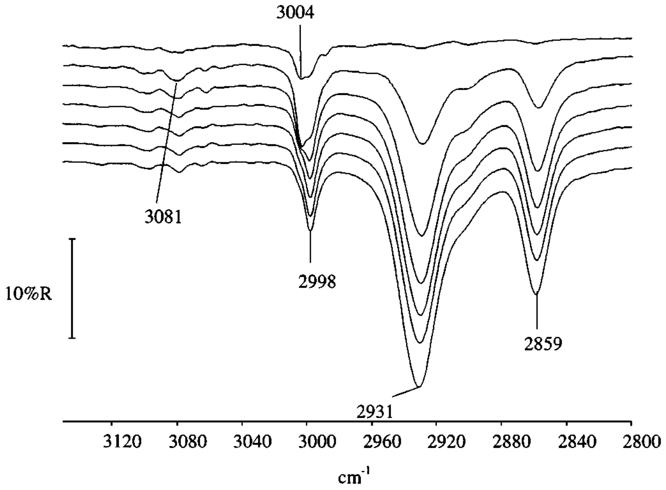


FIG. 3. DRIFT spectra in the ν(C–H) region on the Cr(II)/SiO_2 catalyst recorded every 20 s after one "large" ethylene injection. The baseline of the spectra in the sequence have been shifted vertically for clarity.

We assign the mode at 3004 cm^{-1} to ν(C–H) of coordinated ethylene that is weakly bonded to chromium sites. The simultaneous growth of the methylene bands when the band at 3004 cm^{-1} decreases suggests that the "transient" ethylene is in a resting position before it is incorporated into the polymer chain. DFT modeling of the $Cp_2Zr^+R(C_2H_4)$ catalyst indicates that ethylene forms a "stable" π-complex before it inserts into the Zr–C bond (25). The "transient" ethylene species can then either be coordinated to active sites, or it can be loosely bonded to inactive site. For the latter possibility, ethylene can be released and incorporated into polymer chains on polymerisation active sites nearby. It should be noted that the mode at 2998 cm^{-1} seems to be unaffected by the transient ethylene present.

At more advanced stages of polymerisation, a broad band at ca 2760 cm^{-1} appears (see Fig. 2). This band has by other groups been assigned to the ν(C–H) of a carbene group in an agostic interaction with chromium (9) and also to methylene groups directly bonded to polymerisation active sites (16). In a study with sulphated TiO_2, Al-Mashta *et al.* attributed a band in this region to the interaction between C–H bonds on the polymer chain with Ti^{4+} surface sites (26). We support this latter assignment, since a broad band at ca 2760 cm^{-1} is observed only at more advanced stages of polymerisation (see Figs. 2 and 4). Support for this assignment is obtained by adding saturated hydrocarbons to the Cr(II)/SiO_2 catalyst. Figure 4 shows the spectrum of the Cr(II)/SiO_2 catalyst containing a small amount of pentane, together with a spectrum recorded after several injections of ethylene. The similarity of the two spectra in the region

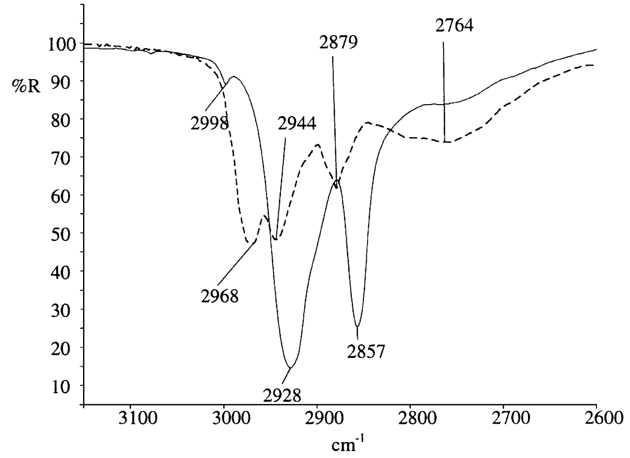


FIG. 4. Full line: DRIFT spectrum recorded at advanced stage in ethylene polymerisation on the Cr(II)/SiO_2 catalyst. Dashed line: DRIFT spectrum of the Cr(II)/SiO_2 catalyst, previously suspended in pentane and partly dried under reduced pressure. The background is a spectrum of a dry sample, unexposed to ethylene.

between 2700 and 2800 cm^{-1} show that this broad band may well be due to solvation of the highly unsaturated chromium ions by the aliphatic hydrocarbon present. In both cases this band disappears upon addition of air or moisture.

As also noticed in previous work with the Cr(II)/SiO_2 catalyst, no end groups are observed at the early stage of the polymerisation at ambient temperature (9, 16, 17, 22). This may be interpreted in different ways. First, the lack of vinyl and methyl fragments can be used as valuable information when speculating about the mechanism for initiation. The formation of alkyl chains where both ends are attached to surface chromium atoms have therefore been suggested (22, 27). On the other hand, the lack of observable end groups may also be the consequence of a low number of active sites present. With very few sites at the experimental conditions used, the number of end groups can be below the detection limit of the experiment.

If a metallacyclic structure is present, end groups should most probably be detectable after termination. Termination can be induced either by adding water or HCl after the initial stages of polymerisation, i.e. when the first traces of methylene groups are detected. When adding HCl or argon saturated with water, the bands assigned to coordinated ethylene quickly disappear, and only the methylene modes from the polymer remain. However, no methyl nor vinyl groups are detected. This indicates that the number of active sites and thus of end groups is below the detection limit of the DRIFTS experiment.

In order to measure the molecular weight of the polymer produced during the DRIFTS experiments, parallel experiments were performed in sealed bottles. As described in the Experimental part, three catalyst samples were reacted with ethylene in ethylene to chromium ratios of 0.5, 1.0, and 3.0, respectively. The samples were subsequently terminated with water. DRIFT spectra of these samples were recorded, and all showed modes assigned to methylene groups but no end groups were observed. For the sample with the lowest ethylene to chromium ratio, the methylene bands are very weak. This is reasonable because most of the ethylene remains just coordinated to chromium sites and is released when water is added. The spectra of the samples with ethylene to chromium ratios of 1.0 and 3.0 both show strong methylene bands.

The catalyst samples containing a small amount of polymer were treated with a water solution of hydrofluoric acid in order to remove all silica. After this treatment, polymer particles could be collected from the surface of the solution as small light green particles for the two samples with highest ethylene to chromium ratios. The green color most likely arises from the Cr^{3+} present. IR analysis of this polymer (pressed with KBr into pellets) showed no detectable amount of methyl groups at 1378 cm^{-1}. However, a very weak band at 908 cm^{-1} was observed, which is assigned to terminal vinyl groups. Splitting of the methylene deformation band due to crystalline hydrocarbon chains (24) indicates that the molecular weight of the alkyl chains formed is high. This splitting is observed at ethylene to chromium ratios as low as 1.0. The polymer samples were also analysed by GPC, and the results are presented in Table 1.

The same molecular weight is obtained for the polymer produced with one injection of ethylene added and with three times more ethylene added in three separate injections. If one large dose of ethylene is added, the molecular weight is higher. The results indicate that one active site makes only one polymer chain when ethylene is present and that termination only takes place in the periods with no gas phase ethylene. The most probable termination mechanism at these conditions is spontaneous β-hydrogen transfer to chromium.

From the measured M_n of 25,000 at an ethylene to chromium ratio of 1.0, one can estimate the concentration of active sites to be about 0.1% of the total chromium content, assuming that one active site is responsible only for one polymer chain. The low number of active sites may be a

TABLE 1

Results from GPC Analysis of the Polymer Obtained at Early Polymerisation Levels

Ethylene/Cr ratio	M_n	M_w
1 : 1	25,000	205,000
3 : 1[a]	30,000	195,000
3 : 1[b]	>50,000	>305,000

[a] Three separate doses of ethylene added.

[b] All ethylene added in one dose. Only a fraction of the polymer was soluble in 1,2-dichlorobenzene at 150°C, indicating that the "real" molecular weight is much larger.

consequence of the special conditions used in the present study: ambient temperature; low ethylene pressure (maximum 120 mbar partial pressure of ethylene at the beginning of each injection, decreasing with reaction time); and no fragmentation of the silica support. The latter may lead to exposure of more active sites. The polymerisation reaction may also be diffusion controlled; ethylene reacts mainly on the outer sphere of each silica particle, and diffusion of ethylene into smaller pores may be hindered by polyethylene already formed on the outer surface.

Typically, between 1 and 10% of total chromium content have been suggested to be active for polymerisation under realistic conditions, depending on the total chromium content and the method used for active site determination (1, 28). By using labeled methanol as a quenching agent, Yermakov and Zakharov (29) have determined the number of active centers at relative low polymerisation rates to about 0.2% of total chromium content.

The present results may explain the absence of end groups in the DRIFT spectra presented in Figs. 1 and 2 above. Even at the very early stages of polymerisation, the concentration of end groups are probably below the detection limit. We can, therefore, not draw any conclusions concerning the mechanism for the initiation step for the catalyst.

Reaction with Ethylene at 100°C

When producing polyethylene with the Phillips catalyst in industrial processes, the temperature used is normally in the range 90 to 110°C. For this catalyst the temperature of polymerisation is the parameter that has the greatest influence on the molecular weight of the polymer produced. To get a better understanding of how the catalyst works at realistic temperatures we have carried out DRIFTS analyses at 100°C.

Figure 5 shows the DRIFT spectra recorded at 100°C with the $Cr(II)/SiO_2$ catalyst after each of a number of ethylene injections. Methyl groups are now readily observed at 2969 and 2884 cm^{-1}, assigned to $\nu_{as}(C{-}H)$ and $\nu_s(C{-}H)$, respectively. No peaks stemming from unsaturated end groups are observed. A similar polymerisation was also carried out in a closed bottle at 100°C as described in the experimental part and in the previous section. IR spectra of the polymer isolated after removal of the silica by HF showed only a moderate increase in vinyl content as compared to the analogous experiment at room temperature.

However, a significant amount of methyl was observed in this polymer, the amount of methyl being about 10 times higher than the amount of vinyl. We observe no methyl side groups on the polymer formed in closed bottles at 100°C (30).

These observations show that the methyl groups observed in the DRIFT spectra cannot only be due to the presence of end groups of growing alkyl chains. To explain the growth in the methyl band intensities with additional injections of ethylene, chain branching has to be considered as well. The side groups are most probably formed by incorporation of 1-olefins formed on some sites at low ethylene pressure. Termination by β-hydrogen transfer to chromium will be favored in the period just before an ethylene injection when the partial pressure of ethylene in the cell is close to zero. The 1-olefins produced will be incorporated in the polymer chains and thus lead to highly branched polyethylene.

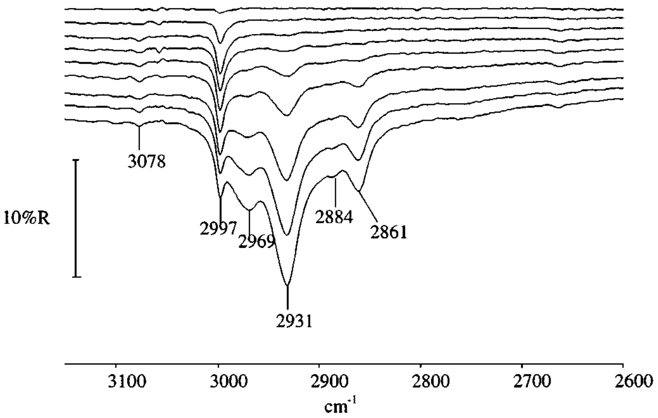
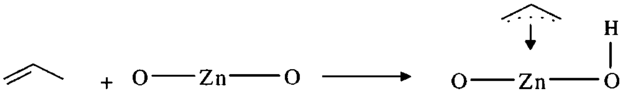


FIG. 5. DRIFT spectra in the ν(C−H) region at early stages in ethylene polymerisation on the $Cr(II)/SiO_2$ catalyst at 100°C. The baseline of the spectra in the sequence have been shifted vertically for clarity.

It should be noted that if ethylene is added as one large injection, instead of several small ones, a much lower number of methyl groups are observed. This supports our interpretation. Rebenstorf (16, 27) also observed formation of methyl groups when polymerising ethylene with the prereduced Phillips catalyst at temperatures above 150°C. These modes were not observed at lower temperatures (below 100°C). He attributed the changes in performance to different polymerisation mechanisms at the different temperatures.

Reaction with Isobutene

Formation of π-allyls when adding olefins (propylene or higher) to TiO_2 and ZnO have been reported (26, 31). Dent and Kokes (31) studied the interaction of propylene on dehydrated zinc oxide and found that this chemisorption is dissociative. Formation of O−H groups was confirmed spectroscopically, and the remaining hydrocarbon species was shown to be allylic species in a trihapto bonding mode:



TiO_2 (26) is active for polymerisation of isobutene, but along with the polymer formed, 2-methylallyl species were observed. In contrast, formation of allylic species after adsorption of olefins on the Cr(II)/SiO_2 catalyst at room temperature has not been confirmed. However, it is well known that the reaction of trisallyl chromium on dehydrated silica gives an active polymerisation catalyst (32), for which one or two of the original allyls ligands remain attached to chromium (33). The asymmetric (C$\overset{...}{=}$C$\overset{...}{=}$C) stretching mode of coordinated allyls on a chromium/silica surface has been assigned to a band at approximately 1520 cm^{-1} (34), in agreement with the observations for π-allyls on TiO_2 and ZnO (26, 31).

To study the interaction of olefins with the Cr(II)/SiO_2 catalyst, propene, higher 1-olefins, and α,ω-dienes are not suitable because polymerisation occurs and partly mask possible surface complexes formed. On the other hand, olefins with an internal double bond and sterically hindered olefins are inert with respect to polymerisation (35). Due to this, we have studied the interaction between isobutene and the Cr(II)/SiO_2 catalyst. A DRIFT spectrum of the catalyst saturated with isobutene is shown in Fig. 6. As expected, isobutene coordinates to the Cr(II)/SiO_2 catalyst at room temperature as ethylene does, but no polymerisation is observed. A similar spectrum is obtained if isobutene is admitted to the catalyst heated to 100°C. The spectra indicates that isobutene is nondissociatively adsorbed on the chromium catalyst. The strong band at 1605 cm^{-1} is assigned to the C=C stretch of coordinated isobutene, the weak mode at 3071 cm^{-1} and the somewhat stronger band at 3001 cm^{-1} can be ascribed to the $=CH_2$ asymmetric and symmetric stretches, respectively. The geminal pair of methyl groups will couple, which results in splitting of the CH stretch and deformation modes of the methyl groups (36).

When adding humid argon, all bands shown in Fig. 6 disappear. GC analysis confirms that isobutene is the sole species released upon hydrolysis.

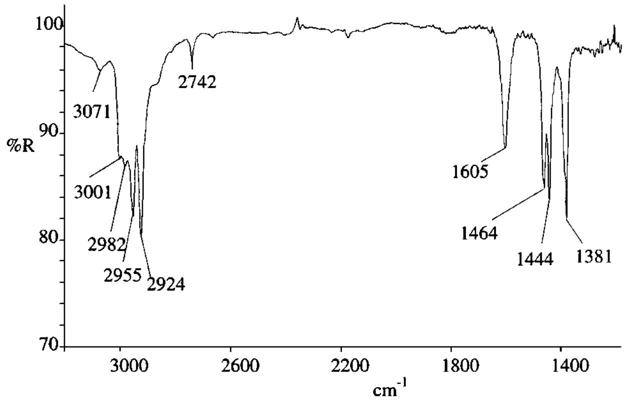


FIG. 6. DRIFT spectrum of Cr(II)/SiO_2 (mixed with equal amounts of CaF_2) after exposure to 1.5 ml of isobutene in the argon flow through the DRIFT cell. The gaseous isobutene has been removed by flushing with argon through the cell for some minutes.

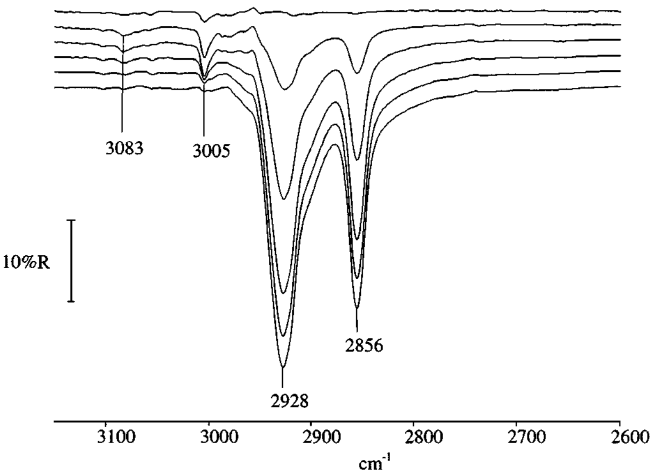


FIG. 7. Polymerisation on the Cr(II)/SiO_2 catalyst, which previously has been saturated with isobutene. The DRIFT spectra are recorded every 20 s after one "large" ethylene injection. The background is the spectrum shown in Fig. 6. The baseline of the spectra in the sequence have been shifted vertically for clarity.

When ethylene is introduced to a catalyst sample, which first is exposed to excess amounts of isobutene and then flushed with argon, polymerisation starts immediately, as indicated by growing methylene bands. No coordinated ethylene is observed when steady state conditions have been reached. During ethylene polymerisation, the band at 1605 cm^{-1} stays unaffected, showing that coordinated isobutene is not replaced by ethylene. Figure 7 shows spectra recorded every 20 s after one "large" ethylene injection. As observed for the ethylene only case (see Fig. 3), a transient ethylene species is observed at 3005 cm^{-1}. Further, a weak band following the same intensity change with time is observed at 3083 cm^{-1}. This band is not so clearly observed in Fig. 3 due to the overlapping modes of the primary ethylene. This band is assigned the ν_{as}(C–H) stretch of the transient ethylene. It is reasonable to assume that isobutene plays the same role as the first batches of ethylene injected in the catalyst in the ethylene only case. As observed for the ethylene only case, the peaks assigned to the stable π-coordinated olefin are not changed by the presence of the transient ethylene species. This may indicate that the two different π-coordinated ligands are bonded to different chromium sites.

Reaction with CO and Isobutene or Ethylene

Infrared spectra recorded for CO adsorbed on the reduced Phillips catalyst have been discussed in a large number of publications in order to distinguish between chromium ions with different degrees of unsaturation (5, 9, 22, 37, 38) and between Cr(II) or Cr(III) (39, 40). With the catalyst preparation used in the present work, it is proposed that at least three kinds of Cr(II) species exist (9), which

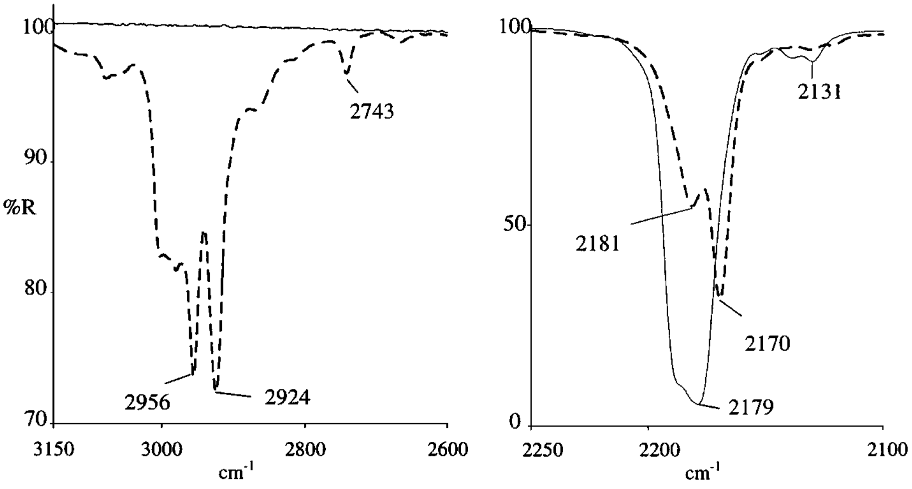


FIG. 8. Full line: DRIFT spectrum of the Cr(II)/SiO_2 catalyst after saturation with CO at ambient temperature. Dashed line: DRIFT spectrum of the same sample after subsequent exposure to excess amounts of isobutene.

interact differently with either siloxane bridges or silanol groups.

In the present work, different experiments involving CO and olefins have been performed at ambient temperature. In one experiment a catalyst sample was saturated with isobutene, then flushed with argon before CO was admitted. No shift in the band frequencies and only a weak reduction in intensities were observed for the bands assigned to coordinated isobutene; i.e., coordinated isobutene was not replaced by CO. Carbonyl bands appear at 2170 and 2181 cm^{-1}, shifted about 10 cm^{-1} to lower wavenumbers than the typical carbonyl stretches on a Cr(II)/SiO_2 catalyst without isobutene. Unlike carbonyl bands of the latter catalyst, the intensities of the 2170 and 2181 cm^{-1} bands quickly reduce when flushing with argon. We assign these bands to CO weakly adsorbed on sites already containing (one or two) coordinated isobutene ligands.

In the reverse experiment (isobutene added to a CO saturated sample), a large intensity decrease of the carbonyl triplet is observed when isobutene is admitted; however, the ease of removal is dependent on the CO coverage. At high CO coverage (see Fig. 8), CO is not replaced completely by isobutene and carbonyl bands at 2170 and 2181 cm^{-1} remain. If the catalyst is only partly covered with CO before isobutene exposure, CO can be removed completely.

Some groups (9, 16, 41) have studied the interaction of CO with samples precontacted with enough ethylene such that polymerisation has started. Carbonyl bands at lower frequencies than observed on samples without ethylene pretreatment has been ascribed to CO coordinated to sites

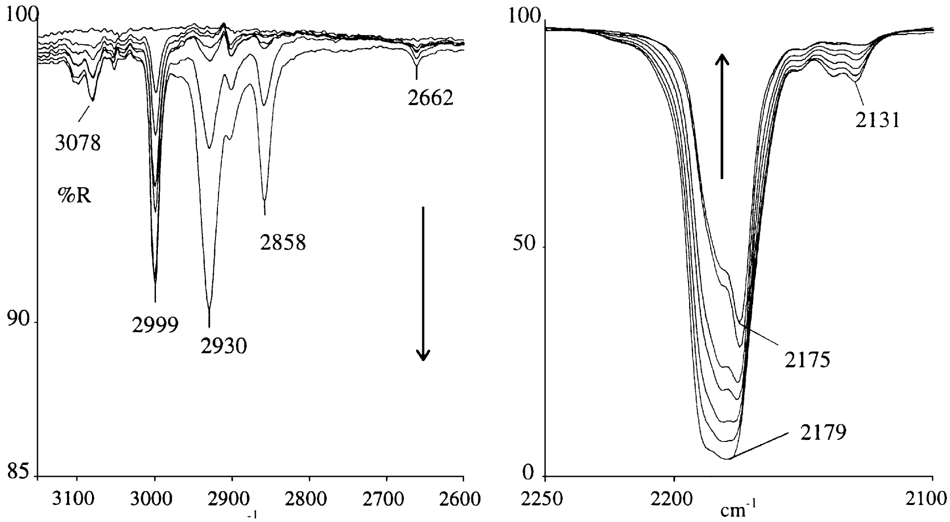


FIG. 9. The development during sequential injections of ethylene on the Cr(II)/SiO_2 catalyst observed by DRIFTS. The sample has prior to ethylene addition been saturated with CO at RT. The arrows indicate in which direction the development proceeds.

containing polymer chains. On a catalyst sample containing coordinated ethylene and some polymer, we observe labile carbonyl bands at 2175 and 2181 cm^{-1} after introducing CO, in accordance with the previously reported results. Coordinated ethylene is not removed, but a shift in the symmetric C–H stretch band at 2998 cm^{-1} upwards to about 3000 cm^{-1} is observed when CO is admitted.

If the catalyst first is saturated with CO before ethylene is admitted, the strong triplet of CO bands reduces into a sharp mode at 2175 cm^{-1} (see Fig. 9), somewhat higher than when isobutene is used. Also, a shoulder at higher frequency is observed. The intensity of the ethylene band (at 2998 cm^{-1}) increases and reaches about the same intensity as without pretreatment with CO. Growing methylene bands show that polymerisation takes place, but the rate of polymerisation is much slower than on samples without CO pretreatment. If the catalyst is only partly covered with CO before ethylene exposure, the adsorbed CO is nearly completely removed after a few doses of ethylene. In this case the polymerisation is as rapid as without CO at all. These results agrees with earlier work by Groeneveld *et al.* (42), who found that feeding ethylene to a catalyst partly covered with CO led to removal of CO, thereby restoring the catalytic activity.

The similarity in the spectra obtained with the nonpolymerising isobutene and with ethylene makes us conclude that the shift in carbonyl band position observed for the latter is not due to coordination of CO to active polymerising sites, but rather to chromium sites already keeping at least one π-bonded ethylene (or isobutene). This is also more reasonable when taking the amount of active sites into consideration.

4. CONCLUSIONS

DRIFTS gives excellent signal-to-noise ratio in the region from 4000 to 2000 cm^{-1}. The ease of sample preparation makes the method well suited for studying highly sensitive catalysts such as the prereduced $\mathrm{Cr(II)/SiO_2}$ polymerisation catalyst. From the present investigation some new observations have been made.

At ambient temperature, ethylene coordination is observed, and a number of new assignments for the π-ethylene-chromium species have been done. No peaks that can be assigned to chromium-carbene fragments are observed. In accordance with observations by other groups, no bands that can be assigned to methyl groups are observed at these conditions. However, GPC measurements of the molecular weight of the polyethylene produced at the same conditions as used in the DRIFTS experiments, with ethylene to chromium ratios of 1.0 and 3.0, show that only 0.1% of the chromium is active. This result suggests that the lack of observable methyl end groups or other fragments that can give information about the mechanisms for initiation of the polymerisation, can be due to the low number of active species present.

A "transient" band at 3004 cm^{-1} is assigned to an ethylene coordinated to chromium in a labile position before it is incorporated into the polyethylene chain. This position could either be on active chromium sites, or on inactive sites close to an active chromium site. No gaseous ethylene is observed in the period when the intensity of the "transient" band decreases and the intensities of the methylene bands of the polymer chain increase.

When the DRIFTS experiments are carried out at 100°C, bands stemming from methyl groups are readily observed. The intensity of these bands are strongly dependent on the way ethylene is introduced. It is concluded that the main portion of the methyl observed is due to the short chain branches formed. The short chain branches are formed by incorporation of low molecular weight α-olefins produced at these conditions with low partial pressure, or total absence, of ethylene which will favor chain termination by spontaneous β-hydride transfer to chromium. The α-olefins formed are later incorporated into polymer chains.

Experiments with the nonpolymerising isobutene show that isobutene coordinates in a similar manner as ethylene does. However, coordinated isobutene does not block for polymerisation. A similar transient ethylene species is observed for the catalysts saturated with isobutene. Experiments in which sequences of carbon monoxide and either ethylene or isobutene is added were used to assign certain carbonyl bands to chromium sites bonded both to carbon monoxide and to the olefin.

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