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Hydrogenation of Olefins and Polymerization of Ethene over Chromium Oxide/Silica Catalysts

V. *In Situ* Infrared Measurements and Investigation of the Polymer

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The mechanism of the polymerization of ethene over chromium oxide/silica catalysts was investigated by *in situ* infrared measurements of the catalyst after D_2 activation, CO adsorption, or polymerization of ethene. After D_2 treatment a broad band at 2550–2760 cm^{-1} showed the presence of OD groups, caused by a spillover of deuterons via chromium ions toward the silica surface. After polymerization on such a catalyst an indication was obtained for the presence of CD bonds, while after polymerization on a normally reduced catalyst (CO, 470°C) the absorption band of a CH_3 group was observed. Both facts as well as results presented earlier point to an initiation reaction of ethene with H (or D) atoms from the silica surface and a Cr^{2+} ion to form an ethyl group bonded to a chromium ion. Propagation then proceeds by *cis* insertion of $\sigma\pi$-adsorbed monomer. Evidence for this was obtained from the CO adsorption experiments. The produced polymer was isolated from the catalyst and its molecular weight was determined. From these measurements a number of active sites of 0.3% of all chromium atoms could be deduced. Such a small number would not have allowed an observation by ir of CH_3 groups. The discrepancy was explained by taking into account the porous structure of the catalyst; only polymer chains at the outer ends of the pores can grow to full extent while chains located at the interior part will soon become inaccessible for ethene molecules because the pores become clogged by the polymer formed at their outer ends.

INTRODUCTION

In the first paper of this series (*1*) experiments were discussed to elucidate the structure of a catalyst CrO_x/SiO_2 somewhat similar to that used for the polymerization of olefins; a model was proposed to account for the experimental results. In a subsequent paper (*2*) the results of a kinetic study of the polymerization reaction were presented. A major feature of the conclusions derived from these and similar studies on the hydrogenation of olefins on the same catalyst (*3, 4*) was the recognition of the important role of protons on the silica support (silanol groups) in influencing the valency of the chromium cations, bivalent or trivalent, and with it the type of catalytic activity, polymerization or hydrogenation, a point that seems to have escaped the attention of many authors earlier engaged in similar studies. As regards the polymerization activity of the catalyst, it appears to go through a maximum determined by the Cr^{2+}/Cr^{3+} ratio. Since the presence of the silanol groups was found to lead to slow oxidation of Cr^{2+} to Cr^{3+} this could either mean that the active site is a combination of Cr^{2+} + Cr^{3+} or that it is a combination of

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$Cr^{2+} + H^+$. In the present paper results of experiments will be presented designed to allow a decision as to which of the two models is the most realistic. They consist of *in situ* infrared measurements before and during the reaction. In addition, studies as to the molecular weight and structure of the polymers formed were found to allow a quantitative estimate of the number of active sites present on the catalyst surface.

Our investigations were terminated in 1974 and the results were published in the Ph.D. thesis of one of the authors (*5*); a summary of the reaction model was given in 1975 (*6*). Owing to external circumstances the full publication of the results was delayed considerably: our first paper therefore carried only the literature references up to 1974, viz., Borello and others (*7–14*), Eley *et al.* (*15, 16*), and Krauss and Stach (*17*). In later years Zecchina *et al.* (*18–21*) published a series of most interesting papers on the spectroscopy of the catalyst while more recently (*22*) they gave a new model for the propagation of the polymerization chain reaction. In the following we shall compare their results and models with ours.

EXPERIMENTAL

Catalyst preparation. The preparation of the catalyst is described elsewhere (*1*), including a description of the calcination and the reduction with CO. *In situ* infrared measurements were performed on catalysts containing 1.7 or 4.3 wt% Cr and the preparation of relatively large amounts of polymer was carried out with catalysts containing 1.35, 1.4, or 1.8 wt% Cr.

The support was Davison silica gel grade 12, surface area 600 m^2/g, pore volume 0.4 cm^3/g. It should be emphasized that this support probably differs considerably from those used in industrial operation, having a considerably greater surface area and a much smaller pore volume.

Infrared measurements. The apparatus is shown schematically in Figs. 1 and 2. A thin disk (6.16 cm^2, thickness 0.1 mm) was pressed of 100 mg powdered, calcined catalyst (1.7 or 4.3 wt% Cr) at 290 mPa; this disk was placed in the sample holder (Fig. 2). The catalyst disk could then be heated in the infrared cell either in a static atmosphere or in a gas stream. The heating was performed by means of a variable spot heater (a halogen bulb placed in a parabolic reflector) and the temperature was measured with a thermocouple, placed at about 2 mm from the catalyst disk. In this way a temperature of 500°C could be reached, but only when we used the glass infrared cell shown in Fig. 2.

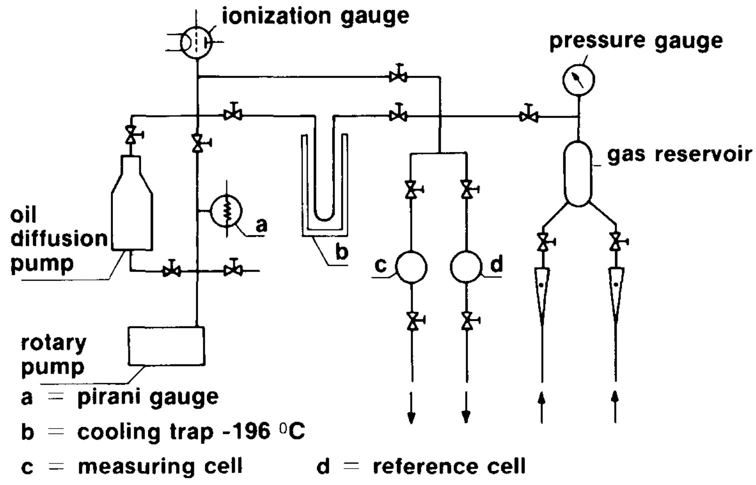

FIG. 1. Apparatus for *in situ* infrared measurements.

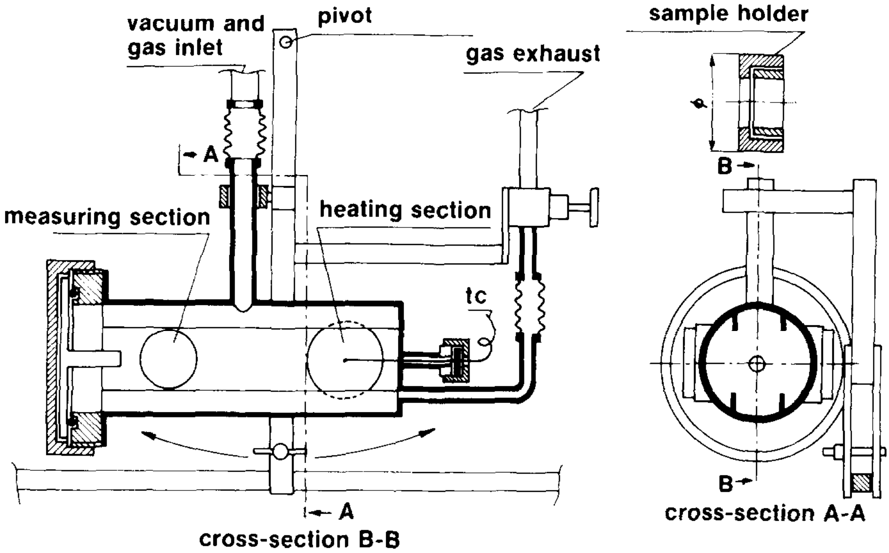

FIG. 2. Glass cell for *in situ* infrared measurements.

In this cell the disk was heated in one part of the cell after which the sample holder was rolled to the part where the infrared measurements were performed. In some cases a stainless-steel cell was used (described in Ref. (*23*)), in which the disk remained at the sample place during heating and infrared measurements. Due to the geometry of this cell it was impossible to heat the catalyst higher than 380°C.

The system could be evacuated to 10 Pa and various gases (e.g., H_2, D_2, CO, C_2H_4) could be admitted up to pressures of 100 kPa. A reference cell was used to compensate for the infrared spectrum of the gas and both cells were sealed with KBr windows (the heating part of the glass cell was sealed with quartz windows). In the glass cell the light path was 5 cm, in the steel cell it was 11 cm. Infrared absorption was measured with a Grubb-Parsons type MK-3 spectrometer (400–8500 cm^{-1}) and registered logarithmically. The effective surface area of the infrared bundle was about 1 cm^2.

The catalyst was dried at 470°C *in vacuo* or in a helium stream during 15 hr and this process was monitored via the intensity of the OH absorption band at about 3500 cm^{-1}. Reduction was carried out with CO at 380°C (steel cell) or at 470°C (glass cell); hereafter the adsorption of various gases or polymerization of ethene was performed.

Investigation of the polymer. Polymer samples were prepared at 0 or at 95°C by using the dynamic method described earlier (*2*), the amount of polymer was determined by weighing the reactor before and after polymerization. The catalyst (about 13 g) with polymer (about 2 g) was then treated with a mixture of 250 cm^3 methanol and 35 cm^3 HCl during a time, further indicated as reflux time. Nitrogen was bubbled through the liquid to prevent boiling retardation and polymer oxidation. After the refluxing 150 cm^3 decalin (predistilled) was added and the methanol was removed by distillation. There remained a green suspension of catalyst in water together with a solution of polyethene in decalin. The solution was decanted and the polymer was coagulated by pouring the solution into 1.5 dm^3 methanol. The polymer was filtered and dried at 80°C *in vacuo*. By a subsequent similar procedure some more polymer could be recovered from the catalyst suspension. In this way we finally arrived at a recovery of maximally 78% of the produced polymer. The procedure of refluxing in methanol/HCl was found to be necessary, because a simple treatment of the catalyst with various organic solvents proved to be ineffective in recovering the polymer.

Various properties of the recovered polymer were determined. Molecular weight was measured by viscosimetry of polymer solutions (which gives a measure of the viscosity-averaged molecular weight) and in some cases by osmometry (which gives the number-averaged molecular weight). The number of olefinic double bonds was measured with ir, and by means of a specific reaction. The number of side branches (methyl groups) was measured by ir or with Differential Scanning Calorimetry (DSC), a technique related to DTA. The ir and DSC also provided information on the degree of crystallinity of the polymer. The osmometric and DSC measurements were performed at the Central Laboratory of DSM.

Molecular weight measurements. The polymer was dissolved in decalin, the decalin being pretreated before use with concentrated sulfuric acid, washed with distilled water, dried and finally distilled. Samples with different polymer concentrations were obtained by dilution of the original solution. Viscosities of the solutions were measured at 135 ± 0.5°C in a "suspended level" viscosimeter developed at the Central Laboratory of DSM (Fig. 3); the intrinsic viscosity $[\eta]$ was determined by extrapolation to a polymer concentration of zero. The osmotic pressure of a solution of the polymer in trichlorobenzene was measured at 114°C in a block osmometer with cellulose membranes. Again solutions with different polymer concentrations were investigated and the number-averaged molecular weight (M_n) was determined from a plot of $\frac{\Pi}{RTC}$ against the concentration C according to:

$$\frac{\Pi}{RTC} = \frac{1}{M_n} + A_2C$$

in which

Π = osmotic pressure
R = gas constant
T = temperature
A_2 = second virial coefficient (i.e., a constant).

Determining the number of double bonds. With infrared absorption it is in principle possible to determine the number of double bonds from the bands related to the olefinic C–H out of plane vibrations. Some of the molar extinction coefficients are given in Table 1 and with this and the measured intensity of the respective absorption bands the number of the various olefinic bonds can be calculated according to Lambert–Beers law. Since the concentration is then found in moles per cubic decimeter, this number must be multiplicated by $14/d_p$ (d_p = density of the polymer ≈ 0.95 g/cm^3) in order to obtain the number of olefinic bonds per 1000 C atoms. The light path through the sample (the thickness of the disk) was 0.06 mm. It should be mentioned that the *cis* double bonds cannot be measured by this method because of the presence of strong absorption bands at 720

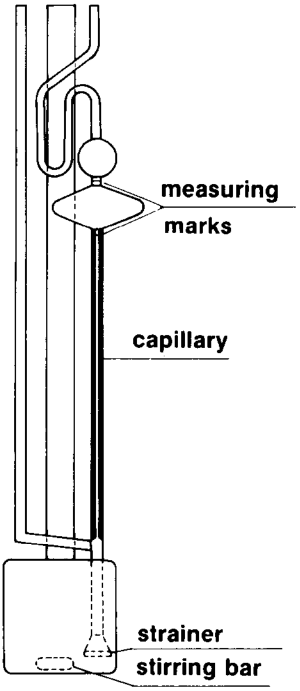

FIG. 3. Suspended level viscosimeter (developed by Central Laboratory, DSM).

TABLE 1

The Olefinic Out of Plane Vibration

Type of double bond	Wave-number (cm^{-1})	ε (dm^2/mol)
Vinyl $R_1CH{=}CH_2$	1005–982	
	915–905	1550
cis-$R_1CH{=}CHR_2$	730–675	850
trans-$R_1CH{=}CHR_2$	980–960	1390
Vinylidene $R_1R_2C{=}CH_2$	895–885	1590
Trisubstituted $R_1R_2C{=}CHR_3$	840–810	

and 731 cm^{-1} due to the CH_2 rocking mode of long chains.

Another technique used for measuring the number of double bonds is based on the reaction of these bonds with toluene in the presence of $AlCl_3/HCl$ at 90°C.[4] The product of this reaction needs careful drying to remove all toluene, after which the intensity can be determined of the infrared absorption band at 1600 cm^{-1}, caused by the skeletal vibration of the aromatic nucleus. The molar extinction coefficient of this band is 290 dm^2/mol.

Other, normally applicable techniques for determining the number of double bonds were unsuccessful because of practical problems (uv, bromine number, coulometry) or were not sensitive enough (NMR).

Determining the number of side branches. From the intensity E of the infrared absorption band at 1365 cm^{-1} (deformational mode of CH_3) the number of methyl groups in the polymer can be calculated with:

$$CH_3/100\ C = \frac{2.70 \times 10^{-2}\ E}{l}$$

in which l is the thickness of the sample disk (0.06 mm) (*24*). This equation is stated to be approximately correct for solid polymers, but is not particularly accurate.

Another potentially useful technique is Differential Scanning Calorimetry, a technique which resembles DTA in that the sample and a reference material are both heated at a constant heating rate. In contrast to DTA, the amount of power supplied to the sample holder at phase transition is changed in such a way that the temperature difference between sample and reference remains zero, which enables a quantitative measurement of transition energies. The number of side branches and end groups A per 100 C atoms is found from the lowering of the melting point of the polymer according to

$$A = 13.1 - 0.097T_m$$

in which T_m is the temperature at which the last remaining crystals are melting. By comparing the measured melting energy with the known melting heat of pure crystalline polyethene (293 J/g) the percentage crystallinity can be found.

An indication for crystallinity is also obtained from the splitting of certain infrared absorption bands of the polymer, viz., the bands at 1460 and 720 cm^{-1}.

Since the polymer is recovered from a decalin solution, the percentage crystallinity gives no information on the polymer as formed; for this reason no data are given here.

RESULTS

In Situ Infrared Absorption after Adsorption of CO

According to our experience interaction of CO with a catalyst previously activated by a CO reduction at room temperature usually did not lead to the formation of new bands. If, however, the catalyst directly after reduction was cooled to room temperature in the presence of CO a band system could be observed at room temperature that is situated near 2200 cm^{-1} and another around 2300 cm^{-1}. The second system appeared connected with the presence of CO_2 presumably formed during the reduction. The 2200 cm^{-1} system could be eliminated

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[4] This method was developed by P. Piet of the Polymer Department of the Technical University, Eindhoven.

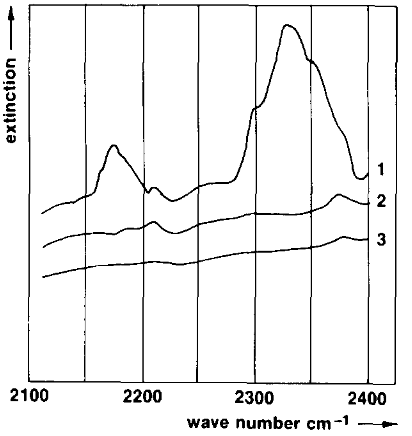


FIG. 4. Infrared spectra after reduction with CO (10.7 kPa); (1) after cooling to room temperature, (2) pressure decreased to 13.3 Pa, (3) pressure decreased to 0.13 Pa.

by evacuation at room temperature: if hereafter CO was reintroduced the band usually did not reappear except under certain circumstances that will be reported later on.

The 2200-cm^{-1} system consists of at least four bands, viz., 2176 ± 1, 2185 ± 1 (the strongest single band), 2195 ± 1, and 2203 ± 2 (the weakest) cm^{-1} (Fig. 4). Careful evacuation showed the 2176- and 2195-cm^{-1} bands to disappear first while the band at 2203 cm^{-1} proved the most resistant to evacuation. If the activation procedure, directly followed by infrared inspection and evacuation, was repeated various times in succession no CO adsorption at room temperature could be observed any more. However, reoxidation of the sample followed by reduction again restored the original situation, i.e., CO adsorption became again observable; this shows that the phenomenon has no connection with the surface structure of the catalyst but is entirely due to the state of reduction of the catalyst. Zecchina *et al.* (*18, 19*) report similar although not entirely equal observations. According to their description the bands can also be formed at room temperature and the system consists of a triplet at 2181, 2186, and 2191 cm^{-1} of which the 2186-cm^{-1} band is strongly pressure dependent and the 2181- and 2191-cm^{-1} bands are more resistant to evacuation. Integration of the band intensities leads Zecchina *et al.* to a value of 1 CO per 1 Cr, in agreement with our earlier reported data (*1*). Zecchina *et al.* also described a second band system that became observable at low temperature (−80°C): it was quite complicated with all bands below 2160 cm^{-1} down to 2135 cm^{-1}.

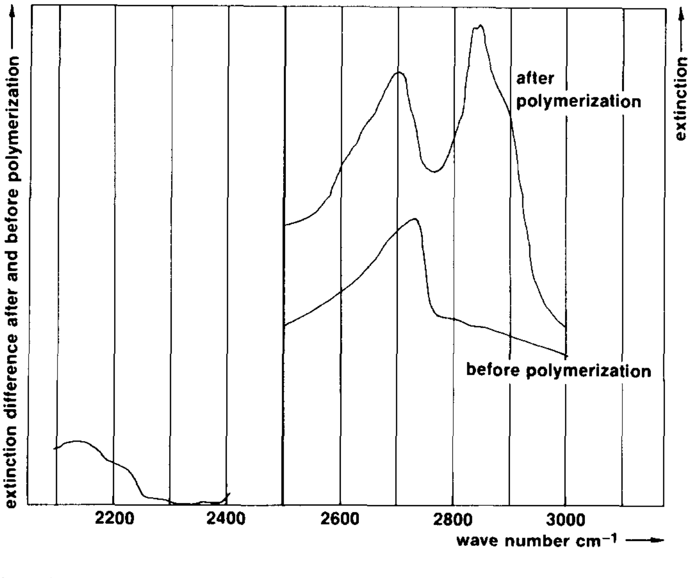


FIG. 5. Infrared spectra before and after polymerization of ethene on a deuterated catalyst.

They reported also that prolonged heat treatment caused the 2200-cm^{-1} band system to decrease and that reoxidation–reduction restored the original situation.

In Situ Infrared Spectra after Treatment with D_2

Treating a CO-reduced catalyst with D_2 at 200°C (15 hr) results in the formation of a broad absorption band at 2550–2760 cm^{-1} (Fig. 5); its intensity was hardly influenced by evacuation at room temperature. This band is very probably caused by OD groups at the silica surface; its broadness points to an appreciable interaction between the various OD groups. The exchange of the OH groups at the surface with gaseous D_2 can be explained by assuming a reductive adsorption of D_2 on Cr^{3+}, followed by a spillover of deuterons to the silica surface and of protons to Cr^{2+} (see also Ref. (*4*)).

In Situ Infrared Spectra after Contact with Ethene

The polymerization of ethene can be monitored by its infrared absorption bands. It is our experience that a reduced sample is only active for polymerization if after CO adsorption the earlier mentioned bands in the range 2175–2205 cm^{-1} are present in the spectrum (Zecchina *et al.* (*18*) confirm this and operate with the integrated intensity of the ir bands between 2150 and 2250 cm^{-1} as a suitable parameter for activity).

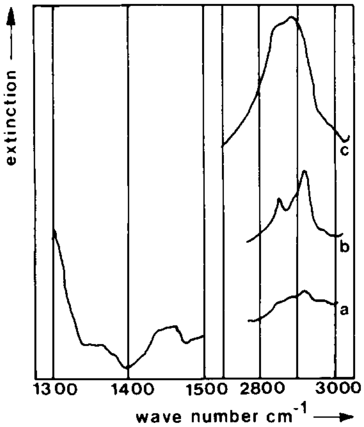


FIG. 6. Infrared spectra after polymerization of ethene; (a) 21 min at 13.3 kPa, (b) 40 min at 33.3 kPa, and (c) 65 min at 13.3 kPa.

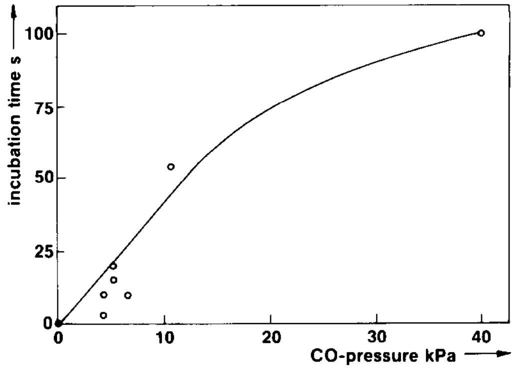


FIG. 7. Incubation time for polymerization after CO adsorption (polymerization at different ethene pressures).

After CO was removed by evacuation and ethene was introduced ir absorption bands developed at 1340–1390 (weak), 1425–1475, 2833 ± 7, 2904 ± 8, and 2960 ± 10 cm^{-1} (Fig. 6). They increased in intensity with the time of exposure to ethene. On evacuation the bands remained of constant intensity so their presence was clearly connected with the presence of polyethene. The band at 2960 cm^{-1} can be assigned to the asymmetrical stretching mode of a CH_3 group. The band at 2904 cm^{-1} is typically connected with CH_2 groups and its growth can be used to monitor the polymer growth. The intensity of the 2960-cm^{-1} band became relatively smaller compared to that of the 2904-cm^{-1} band at increasing intensity of the latter. Using the 2904-cm^{-1} band as a probe for the activity some interesting observations could be made.

When CO was not removed before the introduction of ethene it was found that on introducing ethene the CO absorption band at 2175–2205 cm^{-1} decreased immediately but polymer bands became detectable only after some time had elapsed. This time lapse will be called incubation time; it increased with increasing CO pressure (Fig. 7). In fact, when the CO pressure was higher than the C_2H_4 pressure no polymerization took place at all. If the cell was evacuated after some polymer had formed and CO was readmitted to the catalyst at room temperature, the absorption band at 2185 cm^{-1} was observed although somewhat less intense than prior to the polymerization. As mentioned earlier, this was contrary to what was observed for a fresh catalyst. Readmitting ethene to this system caused the CO band to disappear while at the same time the polymer band at 2904 cm^{-1} increased in intensity. In this case no incubation time was observed.

Apparently, ethene is capable of removing CO from the active site thereby restoring catalytic activity. This phenomenon was earlier observed in dynamic experiments after purging with helium (*2*). After some polymerization has occurred, however, intermediate dosages of CO fail to inhibit subsequent polymerization although CO is adsorbed (as evidenced by the appearance of the 2185-cm^{-1} band) and expelled by ethene.

If ethene was admitted to a D_2-treated catalyst, all absorption bands related to polyethene chains were immediately observed, except for the band at 2960 cm^{-1} (due to CH_3 groups). The OD absorption band was found to have shifted by an amount of 30 cm^{-1} toward lower frequencies (Fig. 5). Differential spectra show a broad band around 2140 cm^{-1}, which is at a position where one might expect the CD vibration to become observable; normally no absorption is observed in this part of the spectrum when C_2H_4 is present.

The lowering of the frequency of the OD absorption band is indicative for the presence of polymer chains, which perturb the OD groups (*15*). A similar effect has been observed after adsorption of CH_4 on silica (*25*). Most important, however, are the results that point to the presence of CD absorption bands after polymerization over a D_2-treated catalyst and those that indicate the presence of CH_3 groups after a normal polymerization experiment.

Molecular Weight Measurements

The results of the viscosity measurements are shown in Fig. 8 and in Table 2. In a few cases also the number-averaged molecular weight M_n was determined and these results are also included in Table 2, which furthermore contains information about each experiment. Figure 8 shows a somewhat unexpected phenomenon: after long reflux times (e.g., more than 70 hr) the molecular weight of the recovered polymer was found to be appreciably smaller than after shorter reflux times. This effect was confirmed by the M_n measurements and was most probably due to cracking of the polymer during the interaction with methanol/HCl. The cracking might be initiated by small amounts of oxygen in the nitrogen stream, used to stir the solution. Judging from the curves in Fig. 8 cracking was only occurring after some time had elapsed and this points to the presence of a limited amount of a substance that was consuming oxygen. This substance could very well be the reduced chromium atoms of the catalyst and in that case also some other results shown in Table 2 can be explained. If a catalyst covered with polymer was exposed for some days to the air, prior to refluxing in methanol/HCl, the recovered polymer had small molecular weights, even after short reflux times. In this case all chromium atoms would have been oxidized when refluxing was started, so now cracking could take place immediately after introducing nitrogen.

Therefore, we conclude, that on a catalyst, containing 1.43 wt% Cr, a polymer is formed with $M_n = 142{,}000$ at 0°C and with $M_n = 15{,}400$ at 95°C.

Number of Double Bonds

The number of the various types of double bonds that could be detected with infrared absorption measurements are given in Table 3, which also includes the result of the alkylation method. The results of the infrared method may be somewhat low be-

TABLE 2

Molecular Weight Measurements

No.	Cr (wt%)	Polymerization temperature (°C)	Amount of polymer formed (g)	Reflux time (h)	$[\eta]$ (cm^3/cg)	M_n
1	1.79	0	1.81	50	3.05	
2	1.79	0	1.90	75	0.58	
3	1.79	0	1.72	95	2.58	
4	1.79	0	1.81	125	0.67	
5	1.79	0	1.99	145	0.46	14,000
6	1.79	0	1.84	170	0.39	30,000
7	1.79	0	2.06	170	0.72	15,000
8	1.43	0	1.34	7	2.18	142,000
9	1.43	0	1.46	25	2.27	
10	1.43	0	1.47	40	2.27	
11	1.43	0	1.41	70	2.18	
12	1.43	0	1.62	116	0.48	
13	1.43	0	1.38	145	0.84	
14	1.43	0	1.45	170	0.52	
15	1.43	95	0.98	7	0.57	15,400
16	1.43	95	0.90	20	0.65	
17	1.43	95	1.01	40	0.58	
18	1.43	95	1.19	70	0.82	
19	1.43	95	1.01	95	0.35	
20	1.35	0	1.43	7	4.2	
21	1.35	0	1.47	7[a]	0.34	
22	1.35	0	1.37	7[a]	0.40	22,400

[a] Exposed to air for some days before HCl/CH$_3$OH treatment.

cause, as already mentioned, *cis* double bonds cannot be detected in this way. The result of the alkylation method, on the other hand, may be somewhat high, because of the presence of some residual free toluene. When these facts are taken into account, it can be inferred that both methods agree to a considerable extent by giving a number of about one double bond per chain. It is also remarkable that after a short reflux time (sample 8) only vinyl-type double bonds are observed. Apparently some isomerization is taking place during refluxing, which is understandable since refluxing was performed in an acid medium. Therefore it can be concluded that the recovered polymer molecules originally contain one vinyl group per molecule.

TABLE 3

Number of Double Bonds in the Polymer

No.	M_n	C_{vinyl} per 1000 C	C_{trans} per 1000 C	$C_{vinylidene}$ per 1000 C	C_{total} per 1000 C	C_{total} per chain
8	142,000	0.13	—	—	0.13	1.31
6	30,000	0.14	0.29	—	0.43	0.92
7	15,000	—	0.54	0.40	0.94	1.01
5	14,000				1.85	1.85[a]

[a] Alkylation method.

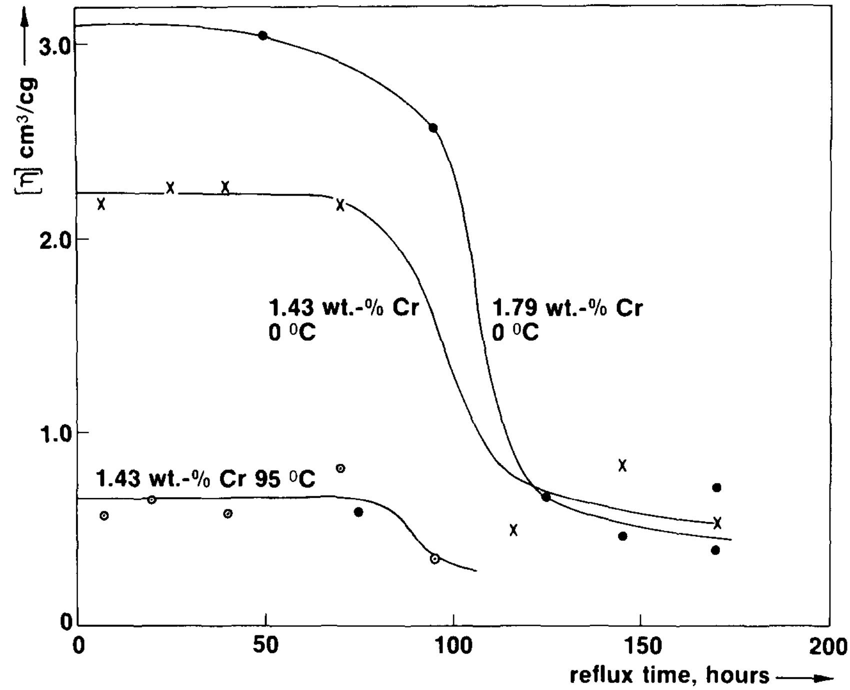


FIG. 8. Intrinsic viscosity of polymer as a function of the reflux time (in HCl/CH_3OH).

Number of Side Chains and End Groups

Most accurate results are obtained with DSC and these results are given in Table 4, in which A is the number of side branches and end groups per 100 C atoms. In this table also M_n is given, when measured and in those cases also the total number of side branches and end groups per polymer molecule was calculated. From this table it can be seen that the number of side branches and end groups ranges up to 1 per 100 C atoms, or to about 10 per chain, which means that the polymer chain is only slightly branched. The infrared results agree very well with these numbers, so it can be concluded that the detected side branches and end groups are mostly methyl groups.

TABLE 4

Results of DSC Measurements

No.	Cr (wt%)	Polymerization temperature (°C)	Reflux time (h)	T_m (°C)	A
7	1.79	0	170	131	0.4
8	1.43	0	7	138	0.1
15	1.43	95	7	128	0.7
20	1.35	0	7	139.5	—
21	1.35	0	7[a]	129	0.6
22	1.35	0	7[a]	128.5	0.6
23	1.35	95	7	125	1.0
24	1.35	95	7	127	0.8
25	1.35	95	7	127	0.8

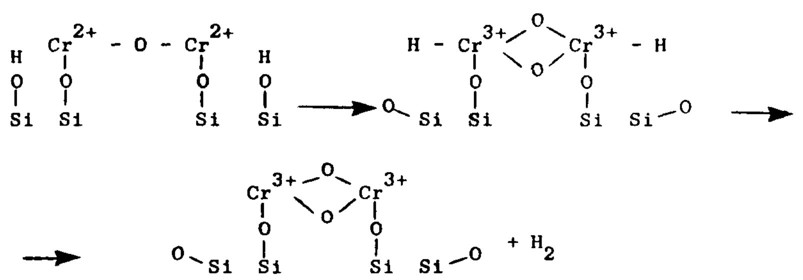
[a] Exposed to air for some days before HCl/CH_3OH treatment.

DISCUSSION

In our earlier papers (*1–4*) we developed models for the surface of our CrO_x/SiO_2 catalyst and for the mechanisms of the reactions occurring on this surface. The present report will deal mostly with the mechanistic models. In order to understand these well it will be helpful to begin with a description of the surface.

We start from Peri's model of a silica surface (*26*) and from McDaniel's estimates for the silanol occupation as a function of the temperature (*27*). For a catalyst with 1.7 wt% Cr on a surface of 600 m^2/g there are 0.33 Cr atoms/nm^2 occupying 0.33 potential silanol sites, assuming Cr being present as pairs. Since Peri estimates the maximum number of silanol groups to be 4.5 per nm^2 there are still 4.15 potential sites left. McDaniel estimates that after a calcination at 500°C one of these will still contain a silanol groups, while calcination at 700°C will reduce this number to 0.5. Consequently, after calcination at 500°C each Cr will on the average have one silanol neighbor and calcination at 700°C will still result in half the Cr atoms having a silanol neighbor.

The Cr atoms on our catalyst are most probably present as pairs. This follows from the observed Weiss constant of −135 K (*1*), which points to antiferromagnetic interactions. This picture is consistent with the fact that these catalyst readily produce H–D exchange and it explains also the earlier described intermediate reoxidation of reduced Cr by hydroxyl groups (*1*) as shown in:

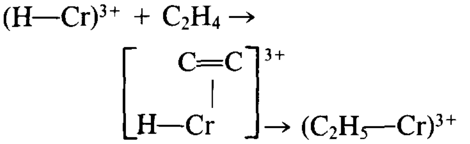


(1)

Krauss (*28*) on the other hand observed low Weiss constants for his catalysts and he did not notice any intermediate reoxidation by hydroxyl groups. Apparently his catalysts did not contain many binary complexes presumably because the Cr content was much smaller than on our catalysts. They were, however, very active for polymerization, so therefore Cr pairs appear not to be essential for this reaction.

The presence of many Cr_2 complexes on our catalysts may give rise to appreciable deviations from the homogeneous OH distribution so far assumed to exist. Prolonged reduction by CO leads to a gradual removal of OH groups by the mechanism illustrated in Eq. 1. This means that after CO reduction there will not be many hydroxyl groups present close to the Cr pairs. Pretreatments at high temperatures in inert gases will probably restore the random distribution through hydroxyl migration. As shown earlier (*2*) these pretreatments also largely influenced polymerization and for that reason it was postulated that an active polymerization site consists of a Cr^{2+} cation with a silanol group in its immediate surroundings. We now propose the following model for the initiation reaction:

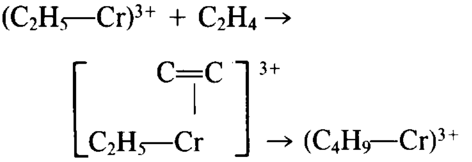
$$OH^- + Cr^{2+} \rightleftarrows O^{2-} + (H{-}Cr)^{3+} \quad (2)$$



$$(H{-}Cr)^{3+} + C_2H_4 \rightarrow \begin{bmatrix} & C{=}C \\ & | \\ H{-} & Cr \end{bmatrix}^{3+} \rightarrow (C_2H_5{-}Cr)^{3+} \quad (3)$$

Ethene adsorbs via $\sigma\pi$-backbonding on the active Cr species and combines with the hydroxyl to form an ethyl group connected with the Cr ion.

Subsequent propagation can be described similar to the accepted Ziegler–Natta mechanism.



$$(C_2H_5\text{—}Cr)^{3+} + C_2H_4 \rightarrow \left[\begin{array}{c} C{=}C \\ | \\ C_2H_5\text{—}Cr \end{array}\right]^{3+} \rightarrow (C_4H_9\text{—}Cr)^{3+} \quad (4)$$

The olefin is adsorbed via $\sigma\pi$-backbonding on an empty ligand site and following the *cis*-insertion mechanism first proposed by Arlman and Cossee (*29*), is subsequently inserted between radical and cation.

The object of the *in situ* infrared experiments was to study and identify the reaction intermediates in the very early stages of the reaction. In this way we might be able to observe the CH_3 groups before they were overgrown by CH_2 groups. As shown in Fig. 6 we did indeed observe a band at 2960 cm^{-1} where one expects a band due to C_{prim}–H. After more prolonged polymerization this band was overgrown by the 2904-cm^{-1} band, caused by CH_2 groups, thereby indicating that the 2960-cm^{-1} band is involved in the initiation reaction but not in the propagation. Eley and co-workers (*15*) earlier observed the same band but they considered it as derived from the cracking of ethene used to reduce their catalyst. However, since we performed the reduction with CO this does not explain its existence in our case.

If the catalyst after reduction was treated with D_2 we obtained strong and broad bands at positions expected for O–D stretchings (such as 2730 cm^{-1}) confirming that the surface was partially deuterated, probably by a mechanism which is the reverse of Eq. 1. No band at 2960 cm^{-1} was observed when polymerization was started. On the other hand differential infrared spectra before and after polymerization showed the presence of a weak and very broad band at 2140 cm^{-1} where one expects the C–D stretching; this band was not found for catalysts not pretreated by D_2. Hogan (*30*) also mentions the presence of C–D stretchings when D_2 was added during polymerization. His explanation was that, on termination, a polymer molecule splits off a hydride ion, the remaining Cr–H being especially vulnerable to H–D exchange. However, we observed the band already in the very early stages of polymerization when termination could be hardly operative.

At first glance it might look strange that a partial deuteration of the surface (the OH stretching band was still rather strong) would cause the complete disappearance of the 2960-cm^{-1} band. However, deuteration will have taken place via the chromium ions, which means that these ions will be surrounded by OD groups, the more remote silanol groups still being OH. Therefore it is understandable that no polymer molecule can start with a CH_3 group, at least when the active site is represented as proposed.

From molecular weight measurements of the recovered polymer it can be deduced that at 0°C maximally about 0.3% of all chromium ions present were active and at 95°C this number is 1.75%. An estimate of the number of CH_3 groups from the band intensity and an assumed extinction coefficient of 2000 dm^2/mol learned that at least 3% of the Cr ions were carrying a CH_3 group which at first sight points to an inconsistency in our model. However, by taking into account our catalyst pore structure this discrepancy can be easily explained. From pore volume and surface area we estimate that our catalyst samples had pores with an average diameter of 2.4 nm, which is indeed a very narrow pore. When we assume a random distribution of Cr ions and of active sites over the total pore volume it becomes clear that polymerization can start at all sites, but very soon chain growth in the pores will become inhibited by clogging of the pore mouth with polymer. Therefore the polymer molecules that are recovered will have originated at the pore ends and at the surface of the catalyst particles. The number of chains that were started will have been much larger thus explaining their ir observability. Two observations are supporting this picture. First we noticed that at certain conditions catalyst particles tended to stick together on polymerization and second, as was earlier reported (*2*), on raising the chromium content of the catalyst we observed that polymerization became more concentrated on the outer part of the catalyst particles. This picture also explains why we observed the 2960-cm^{-1} band, while most other workers did not. Our catalyst, although very poor as producer of polyethene, had the merit of magnifying the initiation reaction.

It is interesting to compare our results with those of Beck and Lunsford (*31*). They find that on a catalyst with 0.45 wt% Cr a polymer is obtained with a molecular weight of 6000. From the amount of polymer (0.5 g/g cat) they conclude that all chromium ions are active. Assuming their catalyst had a pore volume of 1 cm^3/g (they give no data on this point) it can be calculated that all polymer molecules with molecular weight 6000 can easily grow in the pores. Therefore the main difference between their results and ours can be ascribed to a difference in pore structure, their catalyst being much more open. Finally, it is noteworthy to point at the difference in polymerization rates between the Beck and Lunsford catalyst and ours. At 24°C we find 81 mg ethene g cat^{-1} min^{-1} at 7 kPa, while Beck and Lunsford find 0.72 mg ethene g cat^{-1} min^{-1} at 40 kPa.

Lebenstorf and Larson (*32*) recently showed that homogeneous catalysts resembling the Phillips and Union Carbide (chromocene/SiO_2) catalysts do not polymerize ethene. They ascribe this to the fact that the homogeneous catalyst is a complex with only one Cr atom. However, catalysts synthesized by Krauss (*28*) contain mostly mononuclear complexes and nevertheless were quite active. We believe that the homogeneous catalyst lacked activity because no hydrogen atoms were available to initiate the polymerization.

Our next point of discussion concerns the propagation step. It is directly connected with the adsorption of ethene and CO and therefore a discussion of the spectroscopy of these adsorptions is highly relevant. The spectroscopy of adsorbed CO was studied in great detail by Borello and others (*7–14*) and Zecchina and co-workers (*18–21*) and it also played an important part in our work. The bands observed by Zecchina and by our group are very similar although not entirely equal. They consist of a set of closely spaced bands in the range 2170–2205 cm^{-1}. There is agreement in that the bands belong to a type of CO adsorption with a stoichiometry of Cr/CO = 1/1. If the catalyst is reduced several times in succession the ir bands are not observed anymore and both groups agree in that the intensity of the 2170- to 2205-cm^{-1} system is a good measure for polymerization activity; a catalyst that showed no ir bands after CO adsorption was not active for polymerization. Where the two groups disagree is in the details of the adsorption and in the assignments of the bands. We found that the bands were only observed when the sample was cooled in CO from the activation temperature to room temperature; if the system was subsequently evacuated the bands disappeared and often did not return after readmittance of CO. However, when the system was allowed to form some polymer and then to adsorb CO, formation of the 2185-cm^{-1} band could be observed as a reversible phenomenon. Neither Zecchina nor Eley (*15, 16*), who also observed the CO band system, mention similar difficulties with reversibility. The individual bands in the system are two strong bands at 2185 and 2203 cm^{-1} and two weak bands at 2176 and 2195 cm^{-1}. The latter are easily removed by evacuation while the stronger bands are more resistant.

We now assign the bands as follows. The strongest band at 2185 cm^{-1} is connected with CO adsorbed on a Cr^{3+} cation; this band is also observed on α-chromia (*11*). The bands at 2176 and 2195 cm^{-1} are assigned to the symmetric and asymmetric stretching mode, respectively, of Cr^{3+} (CO_2) and the band at 2203 cm^{-1} should belong to CO adsorbed on a $(X\text{–}Cr)^{3+}$ species where X is H or C_nH_{2n+1}. These assignments are based on the fact that the wave numbers are all higher than that of the free CO molecule, indicating that the CO molecule acts as a donor ligand; the electrons donated are those of the slightly antibonding "lone pair" at the carbon atom. When we assume that no CO is adsorbed on Cr^{2+} it becomes clear why no ir bands are observed after prolonged reduction, since in that case only Cr^{2+} ions will have been present without any silanol groups in their immediate vicinity. As CO adsorption only takes place on Cr ions that were situated close to silanol groups (Cr^{3+}, $(X\text{–}Cr)^{3+}$) also the correlation between ir activity and polymerization activity becomes obvious, bearing in mind our polymerization model. The assignments of the ir bands seem to contradict the observed overall stoichiometry of CO/Cr = 0.97 (*1*). However, this ratio was measured by pulsing CO at 0°C over a catalyst that was reduced just up to the point where the reduction of Cr^{6+} was completed and at this point the intermediate reoxidation of Cr^{2+} ions by hydroxyl groups (Eq. 1) is still readily taking place. Therefore, that catalyst will have contained only a small amount of Cr^{2+} ions. Also by using a technique, in which CO pulses are followed by periods with no CO in the gas phase, the complexes with two CO molecules per Cr ion will probably not have been present.

Only one thing remains unexplained in this respect, namely, the apparent activated adsorption of CO. As already mentioned we were unable to observe ir absorption of adsorbed CO when CO was admitted to the catalyst at room temperature. Since all other investigators do not seem to have observed such an effect and since the same effect also occurred on CO_2 adsorption (not reported), we believe that this phenomenon is an artifact, probably caused by our experimental procedure. The exact nature of it, however, remains unknown.

The results obtained when ethene is admitted to a CO-poisoned catalyst can now be explained as follows. On admittance of ethene the intensity of the 2185-cm^{-1} CO band decreases immediately, but only after some time has elapsed (depending on the ratio of the ethene pressure and the CO pressure) the typical polymer band at 2904 cm^{-1} develops. It should be remembered that the behavior of the various bands was investigated by tuning the spectrometer at 2185 or 2904 cm^{-1}, respectively, and monitoring the extinction at that frequency. The fast disappearance of the 2185-cm^{-1} band does not mean that CO is desorbed that fast, but it probably merely reflects a shift of the band to lower frequencies, because of the electron donating effect of the coadsorbed ethene molecule. This effect, however, will also weaken the Cr–CO band, so the CO molecule will finally desorb, thereby rendering the site active for polymerization. Whether polymerization will occur will depend on the ethene pressure relative to the CO pressure, as is observed. The disappearance of the 2185-cm^{-1} band after adsorption of ethene implies that ethene is also adsorbed on sites that are not active for polymerization. We have not observed ir absorption bands of adsorbed ethene molecules, but it is reported that such bands are often very weak (C═C) (*33*) or located at the same wavelength as for gaseous C_2H_4 (C—H) (*34*).

When some polymerization has taken place, CO can still adsorb on the Cr ions, as is evidenced by the appearance of the 2185-cm^{-1} band. Admittance of ethene in this situation again causes the 2185-cm^{-1} band to disappear fast (again due to the electron donating effect) but now the polymer band at 2904 cm^{-1} continues to grow immediately. This implies that CO adsorption inhibits initiation but not propagation. We assume that the adsorbed CO has stabilized the $(H\text{–}Cr)^{3+}$ complex, probably by inducing a more negative charge on the hydrogen atom. Adsorption of an ethene molecule on a $(H\text{–}Cr)^{3+}\text{–}CO$ species therefore will not immediately result in the formation of an ethyl group. The CO molecule will have to desorb first, due to the electron donating effect of the ethene molecule, and only then initiation can take place according to Eq. 3.

Last point of discussion is the termination reaction. In an earlier paper (*2*) we discussed the kinetics of polymerization and then suggested that the observed maximal polymerization rate at 310 K could be explained in two ways. One explanation involved different values for polymerization enthalpy and entropy as compared with the values of the crystalline polymer, due to steric hindrance in the narrow pores. In this picture the polymer molecule remained attached to the chromium ion and termination would not occur on our catalyst. Supporting this could be the fact that we only succeeded in removing the polymer from the catalyst with a boiling solution of HCl in methanol and not with normal polymer solvents. The second explanation for the kinetic results involved a termination reaction according to

$$(C_nH_{2n+1}\text{–Cr})^{3+} + O^{2-} \rightleftarrows C_nH_{2n} + OH^- + Cr^{2+} \quad (5)$$

This reaction then would have to be endothermic with a reaction enthalpy of 68 kJ/mol. This explanation is supported by the structure of the recovered polymer as observed by ir spectroscopy: there was approximately one double bond per polymer molecule, this double bond being a vinyl bond.

We now believe that, although steric hindrance still might play a role, a termination reaction as depicted in Eq. 5 really occurs. The endothermic character of the termination explains why termination is faster and polymer weights are smaller at higher temperatures. The necessity of using HCl/methanol to remove the polymer from the catalyst then does not result from a necessary fission of the Cr–C bond, because that would most probably lead to a saturated or an alcoholic termination of the polymer. It appears that the acid solution, rather than attacking the Cr–polymer bond hydrolyzes Si–O–Si bonds. One could model the catalyst support structure as particles (called secondary particles) consisting of a packing of small spheres (primary particles) with an average diameter of 2.4 nm. These primary particles are bonded to each other by Si–O–Si bonds. Therefore hydrolyzing these bonds will disintegrate the secondary particles thereby freeing the polymer.

CONCLUSIONS

Our final conclusion is that the active site is formed from a Cr^{2+} cation and a proton from a neighboring silanol group. Together with an olefin molecule they form a complex that shows a marked similarity with the Ziegler–Natta site in having a metal–alkyl bond next to a ligand vacancy. The active site is an intermediate in an oxidation process of Cr^{2+} to Cr^{3+} by interaction with two silanol groups either simultaneously or in quick succession. It is therefore necessary to dehydrate the silica surface to a certain extent in order to obtain active catalysts. The often observed small numbers of active sites (10^{16}–$10^{17}/m^2$ as observed in our case) are probably partly connected herewith. Another factor influencing the number of actual polymerization sites is the geometry of the carrier. On many active sites polymerization will start but only on the sites that are located at the outer ends of the pores polymerization can continue until large size molecules are formed. The sites at the interior of the catalyst will soon become inaccessible for ethene because of the blocking of the pores by these polymer molecules.

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