

# On the Role of Surface Hydroxyls during the Cr/SiO<sub>2</sub>-Catalyzed Polymerization of Ethylene

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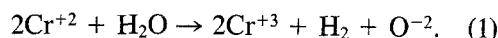
The onset of polymerization of ethylene over a 0.5% chromium supported on silica catalyst was studied using a diffraction-type IR spectrophotometer. Detailed investigations emphasizing the hydroxyl region of the IR spectrum suggested the importance of silanol groups in the processes of reaction initiation, termination, and catalyst deactivation. The formation of chromium-bound hydroxyls and their role in catalyst deactivation were suggested. © 1990 Academic Press, Inc.

## INTRODUCTION

The interactions occurring between molecules of polyethylene and silica-supported chromium catalysts may be classified as being chemical or physical in nature. Both types of interactions are influenced by the procedures used in reducing/activating the Cr catalyst and by the state of the silica surface. They are also very much related to the presence of various hydroxyls on the catalyst surface, as will be shown in this study.

Silanol groups are involved in the anchoring of chromium to silica via Si-O-Cr linkages. Reversely, the hydrolysis of such linkages is favoured when water has not been effectively removed from the reaction system (1). Accordingly, the degree of dehydroxylation of the support, the temperature, and the atmosphere of pretreatment may affect the formation of stable chromium surface structures (2). Water molecules evolved during reduction/activation can adsorb to form silanols, adjacent to the reduced chromium sites. The interactions between these latter two surface entities

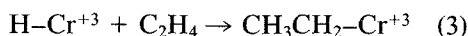
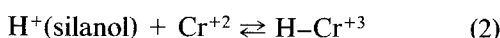
not only may result in a decrease in the coordination unsaturation of chromium sites but also may oxidize the chromium (3-7) as per the surface reaction,



McDaniel (8) found that by increasing calcination temperatures to 925°C, the more advanced degree of dehydroxylation increased the rate of chain initiations per site and, correspondingly, lowered the average molecular weight of the polymer. This commercially significant relationship apparently depends on the population of surface hydroxyls coordinating the active chromium centers on the silica surface.

Myers and Lunsford (9) found that increasing the activation temperature from 400 to 900°C resulted in a tenfold increase in activity with no more than a twofold increase in the number of active sites. They attributed these effects to the enhancement of coordinative unsaturation of Cr (III) sites.

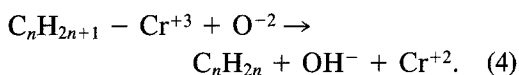
Groeneveld *et al.* (6, 10) suggest direct involvement of silanols during the adsorption of the initial ethylene molecule upon the chromium site as follows:



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and also in a termination step,



Eley *et al.* (11) found the deuteroyl groups on silica interacted physically with growing polymer. It is well known that water vapour behaves as an effective inhibitor of ethylene polymerization resulting in deactivation of the catalyst (12, 13). Such evidence as the above clearly demonstrates that the silanol groups are directly involved in the preparation of the catalyst, in its activation, and during the polymerization of ethylene. For this reason, this study focuses on the IR spectral character exhibited in the hydroxyl band region and the correlation of these changes in activity of Cr/SiO<sub>2</sub> catalyst during the course of polymerization of ethylene.

Recently, Ghiotti *et al.* (14) have advanced a mechanism for ethylene polymerization, involving a metallacyclobutane intermediate, based on IR measurements during the early stages of polymerization ( $P(\text{C}_2\text{H}_4) = 2 \text{ kPa}$  and several minutes contact time). They observed a broad band about  $2750 \text{ cm}^{-1}$  and assigned it to the interaction between the vinylic C–H group and the Cr ion. This complex appeared and disappeared reversibly upon CO adsorption and desorption. Their mechanism did not predict the formation of terminal groups (such as methyl or vinyl groups) and it assumes that cyclic polymer chains continuously grow permanently attached to one or two chromium sites. Without a termination step, and assuming one chromium site per chain, the number of polyethylene chains should correspond to the number of active chromium sites and their molecular weight should be proportional to the time of polymerization.

At present, the mechanism proposed by Ghiotti *et al.* (14) appears to be somewhat limited in predicting the phenomena encountered during ethylene polymerization.

## EXPERIMENTS

### 1. Materials

To ensure adequate transparency in the IR beam, Cr/SiO<sub>2</sub> catalysts were prepared with 0.5 wt% Cr, a Cr content lower than those in commercial catalysts. The catalysts were prepared by impregnating silica (Cab-O-Sil M-5) using aqueous solutions of Cr<sub>2</sub>O<sub>3</sub> or Cr(NO<sub>3</sub>)<sub>3</sub> (purchased from Fisher), followed by drying at 105°C, and calcination at 550°C for 16 h. For IR transmission measurements, the silica (or catalyst) powder was compressed (hydraulic pressure at 280 MPa) into thin wafers (about 12 mg/cm<sup>2</sup>), placed in the IR cell, activated by heating in dry oxygen (550–850°C) for 2 to 15 h, evacuated, and then reduced with CO (300 to 500°C) or ethylene (200 to 400°C). The surface area (BET, liquid N<sub>2</sub>), about 165 m<sup>2</sup> g<sup>-1</sup>, was not affected seriously by the activation–reduction procedure. The pore size distribution for compressed wafers exhibited the features expected for a densely packed structure, with pores in the range 2–10 nm, of average radius 6 nm. The average pore volume was 0.53 cm<sup>3</sup> g<sup>-1</sup>.

To examine possible interaction between catalyst powder and polyethylene, layered wafers were prepared by compressing catalyst powder sandwiched between two thin layers of commercial packaging film (1.2 mg cm<sup>-2</sup>).

Deuteroylation experiments used 99.7% D<sub>2</sub>O vapour (AECL) or deuterium gas (99.5%, Matheson). Deuteroyl–hydroxyl exchange generally reached 50 to 100%. Ethylene gas (99.5% min, Matheson) was used without further purification.

### 2. IR Measurements

A modified Kiselev-type IR cell (15) was used to study the polymerization of ethylene at 25 to 200°C and ethylene pressures ranging from 13 Pa to roughly 300 kPa. The IR spectra were recorded at room temperature using a Perkin–Elmer Model 580B infrared spectrophotometer with data station.

IR absorption spectra were also recorded during the adsorption of various saturated and unsaturated hydrocarbons (Poly Sci Corp., analytical standards).

## RESULTS AND INTERPRETATION

### 1. Adsorption of Ethylene (Reversible)

The catalyst was pretreated with  $O_2$  at  $550^\circ C$ , cooled to  $25^\circ C$ , and evacuated to  $10^{-3}$  Pa. Ethylene was introduced to the IR cell containing the oxidized catalyst, enabling IR spectra to be recorded within several minutes after initial contact. The series of spectra shown in Fig. 1 are plotted as differences in absorbance, i.e., ordinate = [absorbance observed at  $P(C_2H_4)$ ] less [absorbance observed from oxidized catalyst *in vacuo*]. The gradual increase in ethylene pressure from 6 to 118 kPa resulted in a correspondingly diminishing "free hydroxyl" band at  $3748\text{ cm}^{-1}$ , accompanied by the appearance and growth of a new band at about  $3635\text{ cm}^{-1}$ . The disappearance of one hydroxyl band accompanied by the appearance of a new hydroxyl band appear to be related. The difference between these two band frequencies ( $\text{cm}^{-1}$ ) will be called a "shift." The shift in this free hydroxyl band measured about  $113\text{ cm}^{-1}$ . The displacement of hydroxyl bands is pressure-dependent and fully reversible. After a short evacuation period, the free hydroxyl band was fully restored and the corresponding new hydroxyl band disappeared.

After repeating these experiments with deuterioxylated catalyst, an analogous  $77\text{ cm}^{-1}$  shift was observed from  $1762$  to  $2685\text{ cm}^{-1}$ . Ethylene contacting the oxidized catalyst at ambient temperature did not reduce the supported chromium, exhibiting behavior practically identical to ethylene adsorption on silica.

### 2. Interactions between Growing Polymer and Catalyst

The catalytic polymerization of ethylene on  $Cr/SiO_2$  catalyst at about  $25^\circ C$  was recorded with complete spectral scans at suc-

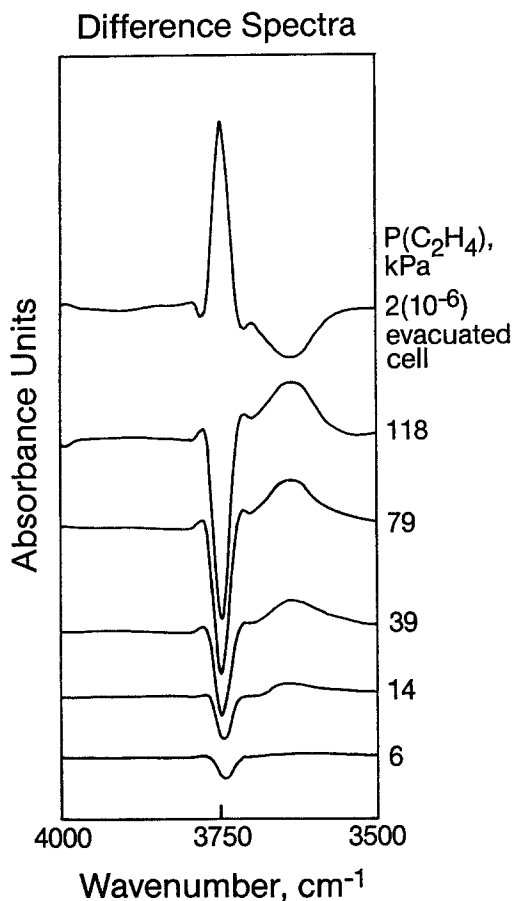


FIG. 1. Difference spectra for ethylene adsorption on oxidized 0.5%  $Cr/SiO_2$  catalyst at  $25^\circ C$ . Ordinate values = [absorbance at  $P(C_2H_4)$ ] - [absorbance for oxidized catalyst *in vacuo*].

cessively advancing levels of polymerization as shown in Fig. 2. The changes are characterized broadly by the increasing CH stretching band intensities,  $2800\text{--}3000\text{ cm}^{-1}$ , and CH bending band intensities,  $1400\text{--}1500\text{ cm}^{-1}$ , accompanied by the spectral changes in the fundamental hydroxyl region. The free hydroxyl band at  $3748\text{ cm}^{-1}$  continually diminishes with polymerization whereas a new band develops at about  $3696\text{ cm}^{-1}$  (shift of  $52\text{ cm}^{-1}$ ). The magnitude of this hydroxyl displacement appears to relate to the temperature of catalyst dehydroxylation rather than to the degree of polymerization. At an advanced

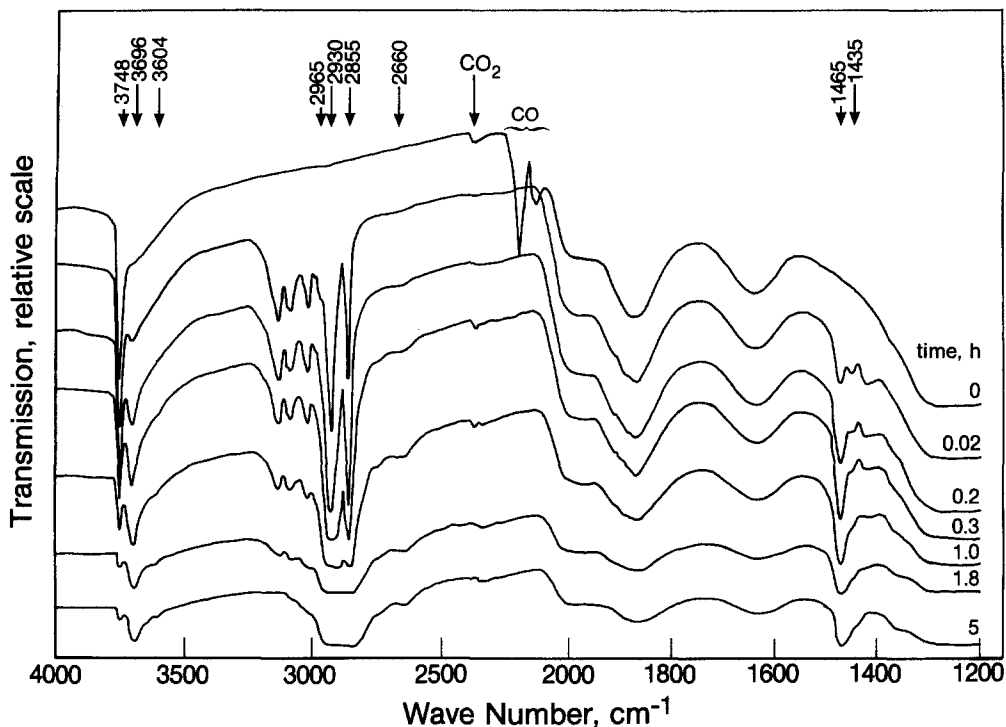


FIG. 2. IR spectra at increasing extents of polymerization on 0.5% Cr/SiO<sub>2</sub> at 25°C.

polymerization stage, another small absorption band was observed at 3604 cm<sup>-1</sup>.

On deuteroylated catalyst, the changes in the deuteroyl spectral region, 2500–2800 cm<sup>-1</sup>, induced by polymerization of ethylene, paralleled those shown in Fig. 2 for the hydroxyl region. The free deuteroyl band at 2762 cm<sup>-1</sup> decreased with a new band appearing at 2725 cm<sup>-1</sup>, its intensity increasing with extent of polymerization; the shift was 37 cm<sup>-1</sup>. The presence of the deuteroyl band equivalent to the small hydroxyl band at 3604 cm<sup>-1</sup>, expected at about 2630 cm<sup>-1</sup>, was difficult to confirm because of interfering absorption bands from the polymer formed on the surface of the wafer.

Quantitative measurements of the IR band intensities were correlated with ethylene consumption as shown in Fig. 3. Even though the advanced stages of polymerization resulted in considerable loss of wafer

transparency in the IR beam, some good correlations resulted during the onset of polymerization (relatively slow polymerization rates at 25°C and  $P(\text{C}_2\text{H}_4)$  of 80 Pa). The total mass of polymer equaled about 1% of the initial catalyst mass. Figure 3 shows essentially linear functions especially for the 2854-cm<sup>-1</sup> CH band. Both the disappearing (3748-cm<sup>-1</sup>) and appearing (3696-cm<sup>-1</sup>) hydroxyl bands exhibit direct proportionality to the extent of polymerization.

At the start of polymerization, the free hydroxyl (3748 cm<sup>-1</sup>) intensity shows a near-instantaneous partial disappearance, frequently observed during such experiments. This drop ranged from 0.1 to 15% of the total population of free hydroxyls and was affected by the mode of catalyst activation/reduction employed. This experimental behaviour may be attributed to immediate ethylene consumption by the active

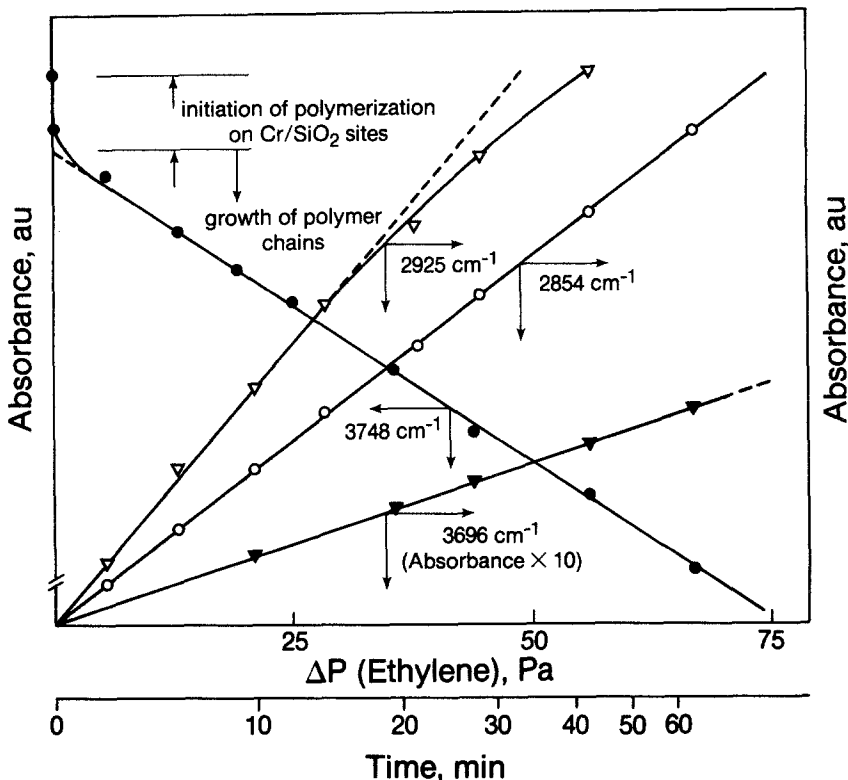


FIG. 3. Correlations between absorbance of IR bands and ethylene polymerized (based upon data from Fig. 2).

chromium sites initially present on the surface of  $\text{Cr/SiO}_2$ . (Experiments at low initial values of  $P(\text{C}_2\text{H}_4)$  generally indicated that the greater the initial  $P(\text{C}_2\text{H}_4)$ , the more active the catalyst involved).

### 3. Hydroxyl Band Changes during the Start of Polymerization

To isolate the various processes (ethylene adsorption, catalyst reduction, reaction initiation, and propagation) which more or less overlap, the following procedure was adopted. The catalyst wafer was evacuated and oxidized with  $\text{O}_2$  at  $550^\circ\text{C}$ , cooled to  $25^\circ\text{C}$ , and reevacuated. In Fig. 4, spectrum 1 represents ethylene adsorption at 100 kPa and  $25^\circ\text{C}$  (see also corresponding spectra on Fig. 1). Because  $\text{CrO}_3$  does not reduce at  $25^\circ\text{C}$ , the wafer was heated to  $200^\circ\text{C}$ , and spectra 2 and 3 were recorded after 0.02

and 0.2 h, respectively. Between spectra 1 and 2, water is evolved during catalyst reduction, and between spectra 2 and 3 one sees the effect of ethylene polymerization.

The interactions between polyethylene and the  $\text{Cr/SiO}_2$  surface can also be generated by heating catalyst powder sandwiched and then compressed between layers of thin polyethylene film. Such interactions were only observed after evacuation above  $105^\circ\text{C}$  and they parallel those seen in Fig. 2. The shift of the free hydroxyl band from  $3748$  to  $3696\text{ cm}^{-1}$ ,  $51\text{ cm}^{-1}$ , reproduces that during polymerization. In the temperature range  $105$  to  $300^\circ\text{C}$ , the free hydroxyl population decreases and above  $300^\circ\text{C}$  the process reverses because the polyethylene film starts to decompose (disappearance of CH bands in the region,  $2800$ – $3000\text{ cm}^{-1}$ ).

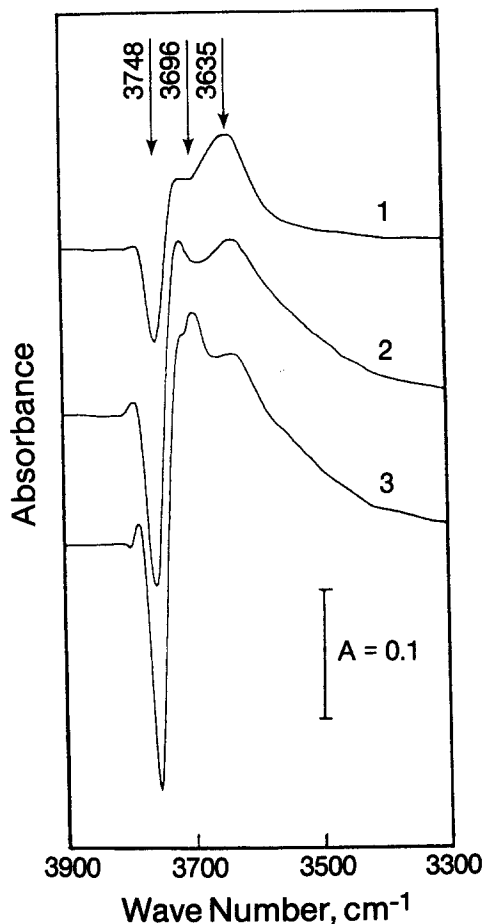


FIG. 4. Difference spectra recorded during onset of polymerization of ethylene: (1) adsorption of ethylene at 100 kPa, 25°C; (2) heating at 200°C for 0.02 h; (3) heating at 200°C for 0.2 h. Ordinate values = [absorbance of resulting spectra] - [absorbance of reference spectra for oxidized catalyst ( $O_2$  at 550°C) *in vacuo*].

#### 4. Adsorption of Hydrocarbons on $Cr/SiO_2$ Catalyst

To study the interactions between polymer chains and the catalyst surface in the hydroxyl region, some IR measurements taken during adsorption of various hydrocarbons were recorded. Figures 5 and 6 depict the spectra taken for various saturated and unsaturated hydrocarbons, respectively, and also list the difference (in  $cm^{-1}$ ) between that of the free hydroxyl band ( $3784\text{ cm}^{-1}$ ) and the band which appears af-

ter adsorption of the hydrocarbon. Methylene hydrogens in the saturated hydrocarbon molecules are likely to hydrogen-bond with free hydroxyls during adsorption because the  $3784\text{-cm}^{-1}$  band intensity decreases and new perturbed hydroxyl bands appear. The magnitude of the free hydroxyl band shift increases with increasing hydrocarbon chain length, the larger shifts approaching that observed for polyethylene ( $52\text{ cm}^{-1}$ ). The hydrocarbon adsorption becomes less reversible the longer the hydrocarbon molecule.

Although for a given saturated hydrocarbon the degree of interaction with the free hydroxyls depends upon the pressure of the hydrocarbon adsorbate present, the amount of adsorbate does not affect the resulting hydroxyl shift significantly ( $\pm 1\text{ cm}^{-1}$ ).

The unsaturated hydrocarbon molecules tested (see Fig. 6) contained a single dou-

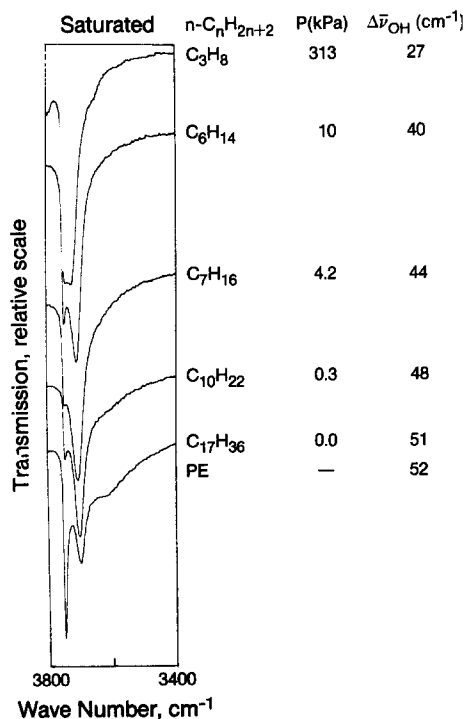


FIG. 5. IR spectra in hydroxyl region after adsorption of saturated hydrocarbons on 0.5%  $Cr/SiO_2$  at 25°C.

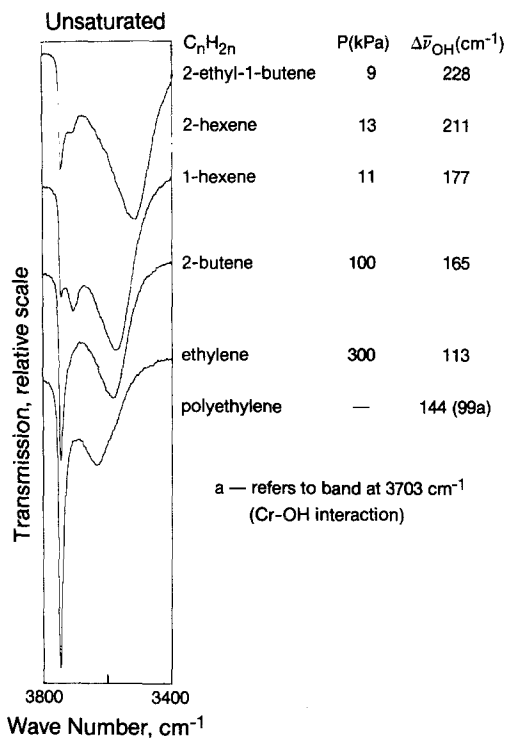


FIG. 6. IR spectra in hydroxyl region after adsorption of unsaturated hydrocarbon molecules on 0.5% Cr/SiO<sub>2</sub> at 25°C.

ble-bond and their interaction with free hydroxyls on the catalyst surface resulted in a much larger shift ranging from 113 to 228  $\text{cm}^{-1}$  in contrast to those for saturated hydrocarbons, 27 to 52  $\text{cm}^{-1}$ . The extent of the shift depended on the number of carbon atoms in the unsaturated molecule; the more central the latter's position, the larger the induced shift.

The magnitude of the free hydroxyl band shift also depended upon the adsorbate pressure, e.g., for 2-butene, the shift increased by 25  $\text{cm}^{-1}$  when  $P(C_4H_8)$  was 115 kPa. The adsorption of alkenes containing methyl and methylene groups also created a small hydroxyl band at about 3708  $\text{cm}^{-1}$ . The shift of 40  $\text{cm}^{-1}$  suggests that both vinyl and alkyl groups are influential during the adsorption of alkenes at relatively high pressure.

### 5. Adsorption of Water on Cr/SiO<sub>2</sub>

Figure 7 shows difference spectra determined for various pretreatments of the 0.5% Cr/SiO<sub>2</sub> catalyst followed by adsorption of water vapour. The water vapour was introduced in amounts corresponding to 0.22 to 0.30 molecules of H<sub>2</sub>O per square

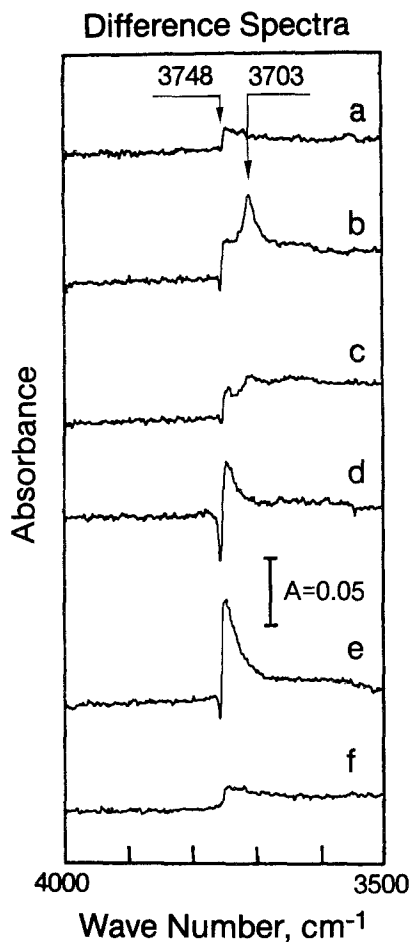


FIG. 7. Difference spectra for adsorption of water vapour after different pretreatments on 0.5% Cr/SiO<sub>2</sub> catalyst; all samples were first evacuated (0.01 Pa) and calcined for 15 h (0.5–0.9 kPa) while at 850°C: (a) cooled to 25°C and evacuated; (b) cooled to 400°C, reduced with CO (7.8 kPa) for 0.5 h, then as per (a); (c) evacuated at 850°C for 15 h before cooling; (d) cooled to 300°C, evacuated, reduced with ethylene (80 Pa, 6 min), then as per (a); (e) cooled to 500°C, evacuated, reduced with H<sub>2</sub>, then as per (a); (f) treatment as per (a) with silica alone. Ordinate values = [absorbance, water added] – [absorbance after pretreatment].

nanometer of catalyst surface, amounts in excess of that required for complete hydroxylation of the chromium content of the catalyst. Spectra d and e show that water is formed *in situ* during the reduction of the catalyst by ethylene or hydrogen. Cases a and f compare water adsorption on the catalyst and the support, respectively. The most important features presented in Fig. 7 were:

(i) the appearance of a  $3703\text{-cm}^{-1}$  band after reduction by CO at  $400^\circ\text{C}$  followed by evacuation at the same temperature (spectrum b) and also after evacuation of the oxidized catalyst at  $850^\circ\text{C}$  (spectrum c). It is possible that high-temperature evacuation results in the reductive decomposition of anchored  $\text{CrO}_3$  forming  $\text{O}_2$  and  $\text{Cr}^{+2}$ .

(ii) the water formed *in situ* during reduction by either ethylene or hydrogen (spectra d and e) alters the IR hydroxyl region essentially identically. Reduction by ethylene reduces the intensity of the  $3749\text{-cm}^{-1}$  band even more so.

(iii) after the  $850^\circ\text{C}$  treatment both the oxidized catalyst and the support display little adsorption capacity for water at  $25^\circ\text{C}$  (spectra a and f).

Further experiments with addition of water ( $0.06$  to  $0.5$   $\text{H}_2\text{O}$  molecules/ $\text{nm}^{-2}$ ) to the CO-reduced catalyst ( $400^\circ\text{C}$ ,  $8$  kPa,  $15$  min) result in the appearance and intensification of the  $3703\text{-cm}^{-1}$  band. At higher water levels ( $266$  Pa,  $15$  min), the hydrogen bonding of the excess water essentially masks the  $3703\text{-cm}^{-1}$  band.

The stability of the  $3703\text{-cm}^{-1}$  band while being heated ( $25$  to  $200^\circ\text{C}$ ) under vacuum was also examined. With increasing temperature, the  $3703\text{-cm}^{-1}$  band gradually disappeared, vanishing at  $200^\circ\text{C}$ . Rather surprisingly, readmission of water at  $25^\circ\text{C}$  nearly restored the original band at  $3703\text{ cm}^{-1}$ .

The influence of water formed *in situ* during hydrogen reduction of the catalyst was studied at reduction temperatures ranging from  $200$  to  $600^\circ\text{C}$ . The reduction starts

about  $300^\circ\text{C}$  and seems to be completed by  $600^\circ\text{C}$ . This water formed as the reduction production increases the intensity of the  $3748\text{ cm}^{-1}$  free hydroxyl band but with significant tailing toward higher frequencies (perturbed hydroxyl bands). The broad adsorption at about  $3500\text{ cm}^{-1}$  and the appearance of a band at about  $1625\text{ cm}^{-1}$  (not shown here) confirms the view that water is also adsorbed without dissociation on the support surface.

## DISCUSSION

In the course of ethylene polymerization on  $\text{Cr}/\text{SiO}_2$ , adsorption of ethylene molecules occurs either on the silica surface or on reduced chromium sites. The former is pressure-dependent and fully reversible whereas the latter must be dissociative and accompanied by reduction of Cr sites, which then catalyze the polymerization of ethylene.

### 1. Adsorption of Ethylene on Silica

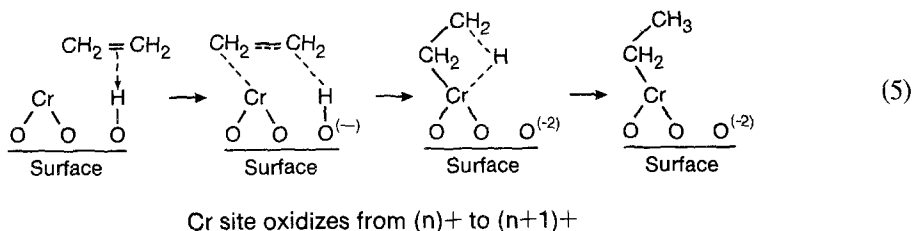
Adsorption of ethylene is accompanied by a shift,  $113\text{ cm}^{-1}$ , of free silanols from the  $3748\text{-cm}^{-1}$  band to the  $3635\text{-cm}^{-1}$  band, detectable when  $P(\text{C}_2\text{H}_4)$  exceeded  $1$  kPa. This shift agrees with that observed by Little and Mathieu for ethylene adsorbing on porous glass (16). The equivalent displacement for silica deuterioxylys,  $2762 - 2685 = 77\text{ cm}^{-1}$ , is about the value to be expected. The ethylene-silica interaction probably involves hydrogen bonding between  $\pi$ -electrons of the ethylene molecule and weakly protonated hydrogen atoms in the silanol groups. Since essentially identical behaviour was observed on either the silica or the oxidized  $\text{Cr}/\text{SiO}_2$  catalyst, chromium trioxide virtually is not involved at ambient temperature. Under industrial reaction conditions, where  $P(\text{C}_2\text{H}_4)$  may reach  $1$  MPa, it is very likely that the bulk of the silanol population has interacted with ethylene and thus provides a "reservoir" of ethylene molecules available to the chromium propagation centers.



## 2. Chemisorption of Ethylene on Cr Sites

The chemisorption of ethylene on reduced chromium sites is likely to involve  $\pi$ -

electrons of ethylene forming a  $\sigma$ -bond between the chromium atom and the ethyl group as shown in reaction 5,



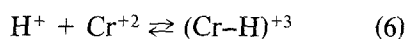
Reaction (5) proposes that a hydrogen atom must be supplied to form an ethyl group when initiating polymerization. The source of the hydrogen has not been resolved unequivocally in the literature. Eley *et al.* (11) proposed the source to be the self-dehydrogenation of another adsorbed ethylene molecule. Groeneveld *et al.* (6) proposed that silanols, vicinal to the chromium site, provided a source of hydrogen atoms (somewhat as depicted in reaction 5). They observed a deuterium-carbon band in the evolved polymer (small IR band at  $2150\text{ cm}^{-1}$ ) during the initial polymerization on deuterioxyated Cr/SiO<sub>2</sub>. In our study, the  $2150\text{-cm}^{-1}$  C-D band could not be observed during polymerization, but some alternative evidence supporting vicinal silanols as the source of hydrogen was obtained.

The immediate decrease in free hydroxyl band intensity ( $3748\text{ cm}^{-1}$ ) shown in Fig. 3 cannot be attributed to adsorption of ethylene upon silica. Experimentally, the physical interaction between free silanols and ethylene was only observed when  $P(\text{C}_2\text{H}_4)$  exceeded  $1000\text{ Pa}$ ; whereas, the quantitative contribution of free silanols during the start of polymerization was within the range 0.1 to 15% of the total population of silanols. The magnitude of this contribution was dependent upon the state of the catalyst surface after the activation-reduction procedure.

The reduction of the oxidized chromium catalyst with ethylene ( $300^\circ\text{C}$ ,  $10\text{ Pa}$ ), fol-

lowed by chemisorption of ethylene upon the reduced chromium sites, influenced the IR hydroxyl bands (see spectrum d of Fig. 7). Even though adsorption of water produced during the reduction obscured the spectra, a significant drop in the intensity of free silanols ( $3748\text{ cm}^{-1}$ ) can be observed, presumably coincidental with the same silanol involvement shown in Fig. 3.

Our view, reaction 5, and that expressed by Groeneveld *et al.* differ. Our work suggests that proton migration is caused by ethylene adsorption whereas they assumed the equilibrium



existed *a priori* to ethylene adsorption. If one ignores the possible coordination influence of the oxygen anion formed, the repulsive force between the proton and the positively charged chromium atom should render their scheme, reaction 6, unlikely. Only when the electron density in the chromium sphere increases because of the adsorption of ethylene (from intermediate donor electron bond between *P*-electrons of ethylene and the empty *d*-orbital of the chromium atom) can the proton migration become favoured. Reaction 5 was presented in accord with these views.

## 3. Polymer-Catalyst Interactions during Polymerization

A molecule of polyethylene may be represented as a very long molecular chain

with vinyl and methyl groups at opposite ends. Because of the relatively few vinyl groups in the polymer, the saturated character of the polymer should influence the possible interactions between the molecular chain and the catalyst surface.

During polymerization, the free hydroxyl shift is not dependent upon the extent of polymerization or the ethylene pressure and, unlike that for silica or the oxidized catalyst, becomes irreversible. At well-advanced polymerization, the entire population of silanols becomes involved in some interaction with polyethylene (the free hydroxyl or deuterioxyl IR bands vanish entirely when extensive polymer covers the surface).

The polymerization of ethylene on deuterioxylated Cr/SiO<sub>2</sub> resulted in the shift 2762–2725 cm<sup>-1</sup>, or 37 cm<sup>-1</sup>, compared to earlier values of 30 cm<sup>-1</sup> (1, 6). The latter references compared their deuterioxyl shifts to the hydroxyl shift of 32 cm<sup>-1</sup> reported by McDonald (17) for methane adsorption on silica at -196°C, thus implying similar interactions for both physically adsorbed methane and polyethylene with the catalyst surface. However, such a comparison between magnitudes of deuterioxyl and hydroxyl shifts is inappropriate, the theoretical ratio of hydroxyl to deuterioxyl shifts being 1.37 (18). Our experimental value, 52/37 = 1.41, represents good agreement with the theoretical value.

Figure 3 shows sequential changes in the intensities of the CH<sub>2</sub> stretching bands and the free and perturbed hydroxyl bands to be directly proportional to the amount of polymer formed. The linear decrease in free hydroxyls accompanied by a linear increase in perturbed hydroxyls suggests that the growing polymer chains are interacting with the silanols and are oriented somewhat parallel to the surface with multiple attractive physical bonds.

Figure 5 showed that adsorption of several saturated hydrocarbons on the catalyst resulted in hydroxyl shifts from 27 to 50 cm<sup>-1</sup>, in contrast to 52 cm<sup>-1</sup> for polyethyl-

ene. The larger shifts observed with saturated hydrocarbons of higher molecular weight suggests strengthening of the hydrogen bond-surface interaction, the result of many such adsorptive bonds acting on the same molecule with parallel orientation to the surface.

Referring to McDaniels observations (2, 8), about the influence of calcination temperature upon catalytic activity and average molecular weight, some discussion based upon the view described herein has already been presented (19).

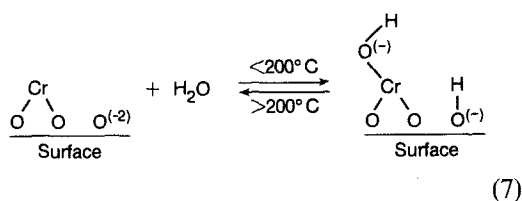
#### 4. Adsorption of Water on Cr/SiO<sub>2</sub>

The population of silanol groups on silica and Cr/SiO<sub>2</sub> result in hydrophilic surfaces. Water may adsorb on silica either dissociatively or molecularly. Less is known about adsorption on supported chromium sites, the focus of this section. The adsorption of water effectively deactivates the chromium active sites during the polymerization of ethylene (3, 7).

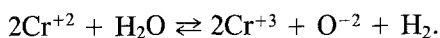
Figure 7 showed that heating of the catalyst above 850°C renders the surface more hydrophobic at ambient temperature. The adsorption of water upon either oxidized catalyst or silica showed little difference, implying that chromium trioxide does not adsorb water. The hydrolysis of Si-O-Cr linkages *in situ* during reduction of the catalyst by either H<sub>2</sub> or ethylene created similar changes in the IR hydroxyl region (see Fig. 7).

The most significant effect was observed after the CO reduction of the catalyst or after high-temperature (850°C) vacuum treatment (Figs. 6b and 6c) when a new band at 3703 cm<sup>-1</sup> appeared. This band was easily masked by the silanol bands resulting from adsorption of water upon silica. It is stable after evacuation at 25°C but gradually disappears with prolonged heating, ultimately vanishing at 200°C. Readmission of water vapor at 25°C restores this band, suggesting that the 3703 cm<sup>-1</sup> originates from stretching vibrations of hydroxyls bound via their oxygen atoms to surface chro-

mium atoms. Zecchina *et al.* (20) observed that adsorption of water on  $\text{Cr}_2\text{O}_3$  generated some rather broad peaks in the region 3800 to 3000  $\text{cm}^{-1}$  which were assigned to stretching hydroxyls originating from dissociation of water. A band at 3700  $\text{cm}^{-1}$  was attributed to a hydroxyl bound to  $\text{Cr}_2\text{O}_3$ . After reduction by CO, one expects Cr (II) sites on the support surface (21). Heterolytic adsorption of water on single Cr (II) sites may be represented as follows:



Hydroxylation of the reduced catalyst at elevated temperatures should favour oxidative adsorption of water (3-6) according to

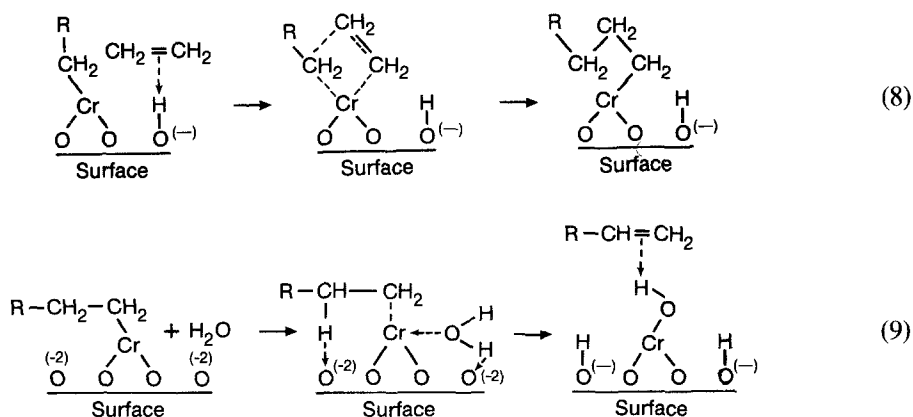


As a result, during reduction by either  $\text{H}_2$  or  $\text{C}_2\text{H}_4$  above 200°C, it is unlikely that hy-

droxyls will be observed as intermediate species.

At advanced stages of ethylene polymerization, a small hydroxyl band at about 3604  $\text{cm}^{-1}$  was often observed (seen faintly in Fig. 2). This band was assigned to hydroxyls which are covalently bonded to chromium sites (3703  $\text{cm}^{-1}$ ) and which interact with the olefinic end of the polymer molecule (3604  $\text{cm}^{-1}$ ). The resulting shift of 99  $\text{cm}^{-1}$  is comparable to those observed for adsorption of unsaturated hydrocarbons (Fig. 6) and to published data (22). This 3604- $\text{cm}^{-1}$  band is always present in commercial PE films (18). During vacuum decomposition of polyethylene-coated Cr/SiO<sub>2</sub> above 300°C, the formation of olefinic character in this region of the IR spectrum was observed (19).

From these interpretations, a mechanism is suggested for initiation involving deprotonation (reaction (5)), propagation not involving deprotonation (reaction (8)) and final termination by water molecules (reaction (9)).



This mechanism assumes that  $\beta$ -elimination of the hydrogen atom occurs normally, followed by proton migration to the silica oxygen anion (6). The heterolytic adsorption of water thus results in the formation of one chromium-bonded hydroxyl and two silanols. These vicinal hydroxyl groups are

involved in coordinative saturation of the chromium site, rendering it catalytically inactive.

The broad band at 2750  $\text{cm}^{-1}$  observed during early polymerization by Ghiotti *et al.* (14) was not seen. The admission of CO at low pressure also did not affect this re-

gion of the spectra. At a more advanced stage of polymerization (about 1% of mass being polymer), a broad band in the region 2800 to 2600  $\text{cm}^{-1}$  appeared, stable to vacuum and CO and O<sub>2</sub> treatments. Further polymerization results in the appearance of at least two overlapping broad bands in this region (see Fig. 2). Although the origin of these broad bands remains unknown, their assignment to an alkylidenic form, a presumed reaction intermediate, appears unlikely.

We observed a CH<sub>3</sub> band at about 2965  $\text{cm}^{-1}$ , the main difficulty with its recognition being the extremely small CH<sub>3</sub>/CH<sub>2</sub> ratio in a typical polymer molecule. Recently, Kraus (23) confirmed both the existence of methyl and vinyl groups in polyethylene molecules on the Cr/SiO<sub>2</sub> surface.

#### CONCLUSIONS

This study of the hydroxyl region of the IR spectrum has introduced additional experimental evidence leading to a more extensive mechanistic model. The model is essentially described in Eqs. (5), (8), and (9), which include the initiation, chain growth, and chain termination deactivation processes. The activation of the Cr/SiO<sub>2</sub> catalyst involves changes in the oxidation states of the chromium site. Additional work, largely based upon temperature-programmed decomposition and reduction, directed at the activation-reduction process will be described subsequently.

The silica hydroxyl groups are involved in interactions with ethylene, water (when formed), and polyethylene. They participate in the three chain reaction steps listed above. The formation of chromium hydroxyls, advanced herein, may be responsible for deactivation of the catalyst.

The dynamics observed for the initial polymerization of ethylene was somewhat limited by the use of a dispersion grating-type of IR spectrophotometer, tracking slowly and monochromatically over the spectral band width. This drawback limited the extent of spectra which could be re-

corded in a finite time and necessitated the use of less active catalysts and reaction conditions favouring slow experimental rates of polymerization. Some of this work will be reexamined, using a faster-scanning FTIR instrument.

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