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# The Polymerisation of Ethylene on Chromium Oxide Catalysts

## III. An Infrared Study of the Adsorption of Carbon Monoxide on Active Catalyst

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Supported chromium (VI) oxide which has been pretreated with either ethylene or carbon monoxide at 300°C is active for both the polymerisation of ethylene and the adsorption of carbon monoxide. The reversible adsorption of carbon monoxide at ca. 50°C has been studied using infrared spectroscopy. Correlations between the capacity of the catalyst for the adsorption of carbon monoxide and the rate of polymerisation have shown that carbon monoxide is adsorbed on sites which are catalytically active. Catalyst which has been reduced in carbon monoxide develops a higher capacity for adsorption of carbon monoxide and gives higher rates of polymerisation than catalyst reduced in ethylene. Adsorbed carbon monoxide poisons the polymerisation reaction, but evacuation at 50°C results in a complete recovery of catalyst activity. Partial restoration of the polymerisation activity is also effected by displacement of carbon monoxide from some of the active sites when ethylene is contacted with the poisoned catalyst at 50°C. The modes of adsorption of carbon monoxide on the catalysts and the nature of the polymerisation sites are discussed.

## INTRODUCTION

In a previous study of ethylene polymerisation on a chromium trioxide catalyst (*1, 2*), comparison was made between polymerisation activity and the nature of adsorbed species present, as indicated by infrared absorption spectroscopy. The catalysts used were activated for polymerisation by reduction in ethylene. The work has now been extended using carbon monoxide as the activating agent. Clark *et al.* (*3, 4*) have shown that catalysts treated with carbon monoxide at 250°C possess a similar activity for ethylene polymerisation to those treated with ethylene at 150°C. Similar effects have been noted for carbon monoxide reductions at 300°C (*5, 6*), 425°C (*7*) and 400°C (*8*). Zakharov *et al.* (*5*) suggested that the enhanced activity of catalyst which has been reduced in carbon monoxide may be due either to an increase in the number of centres of propagation, or to an increase in the activity of the existing sites. They showed that the latter effect was the predominant one, and concluded that carbon monoxide interacts with propagation centres and causes an increase in their activity. Hogan (*7*) found that some chemisorption of carbon monoxide occurred when catalysts had been activated, and the formation of surface carboxylate species by adsorption of carbon monoxide was observed by Clark *et al.* (*4*) for those catalysts which had high polymerisation activity.

Carbon monoxide adsorption on oxide surfaces has been investigated using infrared spectroscopy (*9, 10*), and it has been suggested that there is a correlation between the vibration frequencies and the electronic structure of adsorbed CO species. In particular, spectroscopic data are available for the molecule interacting with chromia (*12, 13*), chromia–alumina (*14*), and chromia–silica (*15*). The present paper reports an infrared investigation of the interaction of carbon monoxide with Phillips catalysts, activated with either ethylene or carbon monoxide, together with measurements of rates of ethylene polymerisation on the same catalyst samples. The study was undertaken as an attempt to characterise the nature of the active centres in the polymerisation reaction.

## EXPERIMENTAL

The chromium oxide catalyst and the ethylene were identical samples to those used before (*1, 2*). Carbon monoxide (British Oxygen grade X) was used without further purification.

The apparatus and methods used to measure spectra and rates of polymerisation have been given elsewhere (*2*). The samples used in this study were exclusively of the self-supporting type, containing 200 mg catalyst, pressed at 98 MN $m^{-2}$.

Following calcination in a stream (50 $cm^3$ $min^{-1}$) of oxygen (20%) and nitrogen (80%) at 460°C for 16 hr and evacuation at 300°C, to a final pressure of $<2 \times 10^{-3}$ N $m^{-2}$, the catalyst discs were activated at 300°C in either ethylene (initial pressure 4 kN $m^{-2}$) or carbon monoxide (initial pressure 2.8 kN $m^{-2}$). The oxygen and nitrogen used in the calcination were purified and dried by passage over activated charcoal and 4 Å molecular sieve. The volume of the reaction system was the same as that used earlier (*2*), and thus a pressure of 4 kN $m^{-2}$ corresponded to 1000 $\mu$mole gas. Activation was carried out for between 15 min and 24 hr for ethylene, and for 5–60 min for carbon monoxide. After activation in ethylene, the sample was evacuated at 300°C for 30 min to a final pressure of $<2 \times 10^{-3}$ N $m^{-2}$, and then cooled to the temperature of the infrared beam (ca. 50°C). In the case of samples treated with carbon monoxide, cooling to 50°C took place in the presence of the gas phase, prior to evacuation for 60 min at this lower temperature. Carbon monoxide was introduced to the samples at 50°C, initially at a pressure of $<10$ N $m^{-2}$, and the infrared spectrum of the adsorbed species recorded. Adsorption isotherms were determined by measuring the spectra in the presence of increasing gas phase pressures of carbon monoxide, up to 13 kN $m^{-2}$. That part of the absorbance in the region of the bands associated with the presence of adsorbed carbon monoxide which was due to absorption by the gas phase was subtracted from the total value obtained. This procedure became increasingly important for pressures of carbon monoxide $>2$ kN $m^{-2}$. The samples were then evacuated at 50°C for 60 min to $<2 \times 10^{-3}$ N $m^{-2}$ pressure. Ethylene (initial pressure, unless stated otherwise ca. 1 kN $m^{-2}$) was admitted and the rate of polymerisation measured (*2*) by recording the rate of increase of absorption bands associated with the growing polymer chains.

In another series of experiments, the above procedure was followed for carbon monoxide activation, but the ethylene polymerisation was performed in the presence of preadsorbed carbon monoxide. Ethylene was admitted at an initial pressure of 100 N $m^{-2}$.

## RESULTS

### (*a*) *Activation in Ethylene at 300°C*

After reduction in ethylene, the catalyst samples were yellow-green to green, depending upon the length of treatment, showing that reduction of some Cr(VI) to Cr(III) had occurred. The infrared spectra of adsorbed ethylene were identical to those found earlier (*2*) for pressed discs of catalysts. Adsorption of carbon monoxide at 50°C gave rise to two bands at 2202 and 2189 $cm^{-1}$ (Fig. 1). Both bands increased in intensity with increasing gas phase pressure, the latter band moving steadily to 2184 $cm^{-1}$. The band at 2202 $cm^{-1}$ was much weaker than that at 2189 $cm^{-1}$ for all surface coverages. No bands due to adsorbed carbon monoxide were observed below 2000 $cm^{-1}$. The adsorption of carbon monoxide produced no changes in the absorption bands in the region 2800–3000 $cm^{-1}$ due to adsorbed ethylene. Adsorption isotherms were recorded for four times of contact between ethylene and

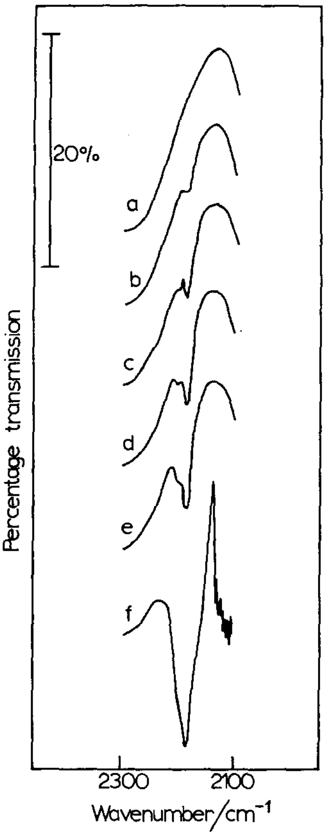


FIG. 1. Adsorption of carbon monoxide at ca. 50°C on catalyst which had been reduced in ethylene for 23 hr at 300°C. Equilibrium pressures (kN m$^{-2}$) of carbon monoxide were (a) 0, (b) 0.02, (c) 0.11, (d) 0.44, (e) 1.02, (f) 13.3. Percentage transmission values at 2300 cm$^{-1}$ were 78%.

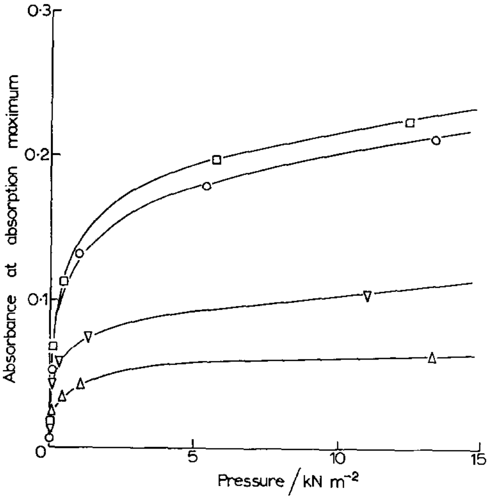


FIG. 2. Isotherms at 50°C for the adsorption of carbon monoxide on catalyst which had been reduced in ethylene at 300°C for ○ 15 min, □ 30 min, ▽ 2 hr, △ 23 hr.

catalyst at 300°C (Fig. 2). The adsorption of carbon monoxide was reversible, all absorption bands disappearing within 5 min of evacuating the samples at 50°C. Rates of ethylene polymerisation were measured after each of the isotherms had been determined and the carbon monoxide removed. The first order rate constants $k_1$, defined and measured as before (*2*), are given in Table 1. In the kinetic investigations described in this paper, first order loss of ethylene was always observed, and the constant $k$ (Ref. *2*, Eq. 1) was found to have a value of 290 N m$^{-2}$. The slight difference between this value and that of 230 N m$^{-2}$ found in the earlier work arises because, in the current investigations, pressed discs of catalyst were used, whereas experiments were previously performed with loosely packed powder. The difference in geometry in the two cases is reflected in a slightly different value of $k$. The absorbance of the band at 2189 cm$^{-1}$ due to adsorbed carbon monoxide at surface coverages tending to unity is also given in Table 1. The capacities of the discs for the adsorption of carbon monoxide at

TABLE 1

FIRST ORDER RATE CONSTANTS FOR ETHYLENE POLYMERISATION AND MAXIMUM ABSORBANCES AS A FUNCTION OF TIME OF PRETREATMENT[a]

| Preatment time | $10^4 k_1$(sec$^{-1}$) | $A_{max}$[b] |
|---|---|---|
| 15 min | 2.9 | 0.22 |
| 30 min | 2.9 | 0.24 |
| 2 hr | 0.9 | 0.11 |
| 23 hr | 1.2 | 0.07 |

[a] Conditions: temperature, 50°C; and maximum absorbances, 2184–2189 cm$^{-1}$, for carbon monoxide adsorption. Contact (pretreatment) between ethylene and catalyst at 300°C.

[b] From the shape of the isotherms it is very difficult to decide upon the exact $A_{max}$ value. No clear plateau value is reached, with the possible exception of the 23 hr experiment. The values given relate to the value of the absorbance at a pressure of 15 kN m$^{-2}$.

50°C changed with pretreatment time in the same manner as the rate of ethylene polymerisation, also at 50°C.

### (*b*) *Activation in Carbon Monoxide at 300°C*

Carbon monoxide, adsorbed on samples which had been reduced in carbon monoxide, gave two overlapping narrow absorption bands with maxima at 2189 and 2184 $cm^{-1}$. The high frequency band appeared at low coverages, the second band increasing in intensity as more carbon monoxide was adsorbed. This latter band was dominant at high coverages on those samples which had been contacted with carbon monoxide at 300°C for times of 5–15 min. It remained as a small shoulder for those samples which had undergone longer periods of pretreatment (30–60 min). The best resolution of the two bands was observed for catalyst which had been calcined in air at 800°C prior to reduction in carbon monoxide at 300°C and adsorption of carbon monoxide at 50°C (Fig. 3). The spectral isotherms obtained by consideration of the total intensity of the two bands for a series of discs pretreated with carbon monoxide for various times at 300°C were similar to those obtained on ethylene treated samples, although the overall capacity for carbon monoxide adsorption was greater. The samples also showed a clearer upper limit to the quantity of adsorbed material in the pressure range studied (up to 13 kN $m^{-2}$). The capacity for adsorption ($A_{max}$, Table 2) increased with increasing time of contact with carbon monoxide at 300°C. This increase was paralleled by an increase in the rate of ethylene polymerisation at 50°C (Table 2). The correlation between rate of polymerisation and the capacity for carbon monoxide adsorption is shown in Fig. 4. Although reduction of the catalyst took place during the pre-

TABLE 2

FIRST ORDER RATE CONSTANTS FOR ETHYLENE POLYMERISATION AND MAXIMUM ABSORBANCES DUE TO ADSORBED CARBON MONOXIDE AS A FUNCTION OF TIME OF PRETREATMENT WITH CATALYST[a]

| Pretreatment time (min) | $10^3\, k_1(sec^{-1})$ | $A_{max}$ for CO adsorption |
|---|---|---|
| 5 | 2.38 | 0.08 |
| 5 | 2.61 | 0.15 |
| 10 | 2.78 | 0.23 |
| 20 | 3.19 | 0.23 |
| 30 | 4.35 | 0.51 |
| 60 | 5.02 | 0.63 |

[a] Conditions: ethylene polymerisation and adsorption of CO at 50°C. Catalyst and carbon monoxide in contact at 300°C during pretreatment.

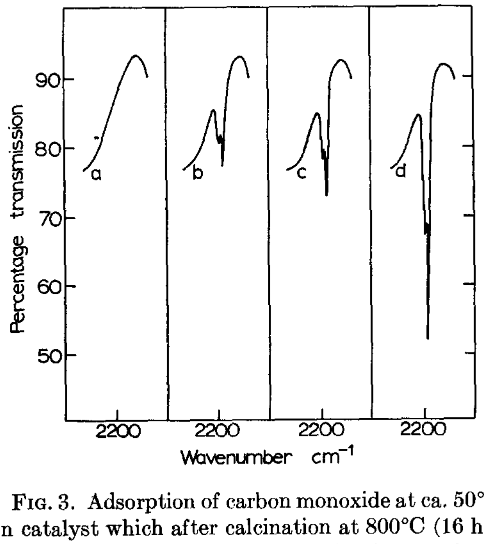


FIG. 3. Adsorption of carbon monoxide at ca. 50°C on catalyst which after calcination at 800°C (16 hr) had been reduced in carbon monoxide for 30 min at 300°C. (a) Background spectrum; (b), (c), and (d) increasing coverage of carbon monoxide.

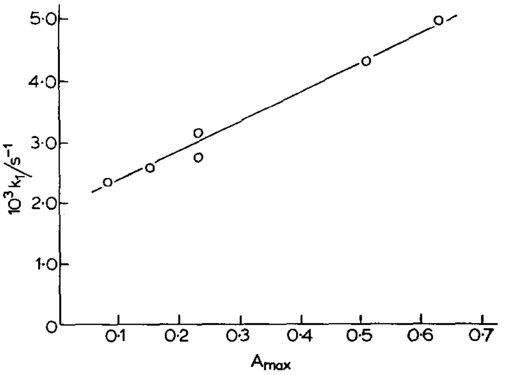


FIG. 4. Correlation between the first order rate constants for ethylene polymerisation and the capacity of the catalyst for the adsorption of carbon monoxide for samples which had been reduced in carbon monoxide at 300°C for various times.

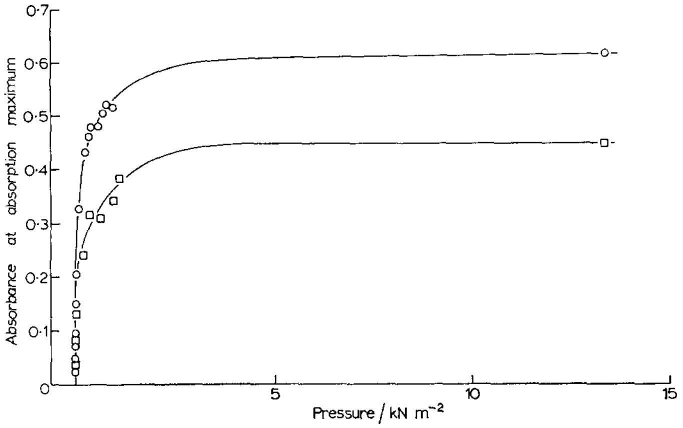


FIG. 5. ○ Isotherm at 50°C for the adsorption of carbon monoxide on catalyst which had been reduced in carbon monoxide at 300°C for 1 hr.

□ Corresponding isotherm after polymerisation of a small amount of ethylene at 50°C.

treatment with carbon monoxide at 300°C (as evidenced by the production of carbon dioxide in the gas phase) the samples were still yellow in colour, in contrast with those reduced in ethylene which were yellow-green or green. The maximum rate constant per gram of catalyst for ethylene polymerisation on discs reduced with carbon monoxide was $k_g = 2.5 \times 10^{-2}$ sec$^{-1}$ g$^{-1}$. That for samples activated in ethylene was $k_g = 1.5 \times 10^{-3}$ sec$^{-1}$ g$^{-1}$. Thus discs treated with carbon monoxide were ca. 17 times more active than those treated with ethylene at the same temperature of 300°C. Mass spectroscopic examination of the gas phase after carbon monoxide treatment at 300°C showed that 0.76 ± 0.07 moles $CO_2$/mole $CrO_3$ reduced had been produced for the sample showing maximum polymerisation rate.

Isotherms for carbon monoxide adsorption were measured before and after a small quantity of polymer had been produced on the surface by contact of the active catalyst with ethylene at 50°C. The results are shown in Fig. 5. The presence of polymer on the catalyst reduced the amount of carbon monoxide which was adsorbed.

Freshly calcined and evacuated samples which had not previously been contacted with either carbon monoxide or ethylene at 300°C gave no absorption bands on exposure to carbon monoxide at 50°C. Even after standing for 24 hr in the presence of gas phase pressures of up to 13 kN m$^{-2}$, no adsorption took place. The catalyst support was also shown not to give rise to absorption bands when treated with carbon monoxide at 50°C, following a 300°C pretreatment with ethylene or carbon monoxide. Thus carbon monoxide adsorbs only on the chromia portion of the catalyst after suitable high temperature activation.

### (c) *Rate of Polymerisation of Ethylene in the Presence of Adsorbed Carbon Monoxide*

A disc of catalyst was exposed to carbon monoxide at 300°C, cooled to 50°C, and then outgassed at this lower temperature. On admitting ethylene, polymerisation occurred immediately with no detectable induction period. If, however, some carbon monoxide was preadsorbed on the disc, an induction period occurred and the subsequent rate of polymerisation was slower than in the absence of carbon monoxide. Moreover, during the induction period, some desorption of carbon monoxide took place, leaving a residual quantity which remained constant during polymerisation. (Fig. 6). This behaviour was investigated for a series of discs on which varying amounts of adsorbed carbon monoxide were

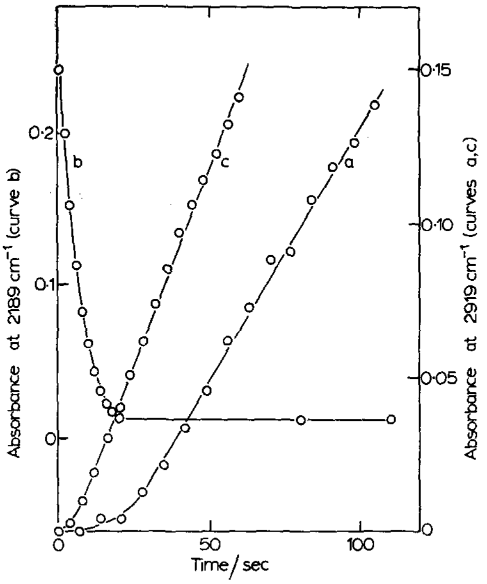


FIG. 6. Curves (a) and (b) represent the appearance of polymer (measured by the intensity of the infrared band at 2919 cm$^{-1}$) (2) in the presence of preadsorbed carbon monoxide and the desorption of carbon monoxide on the introduction of ethylene in two identical experiments. Curve (c) represents the appearance of polymer in the absence of preadsorbed carbon monoxide. Catalyst samples had been reduced in carbon monoxide at 300°C for 1 hr.

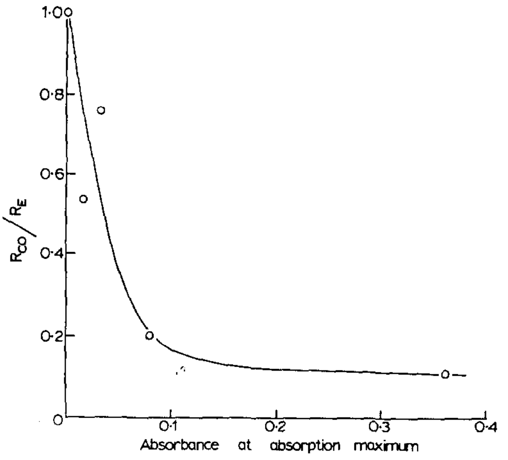


FIG. 7. Dependence of the rate of polymerisation on the residual amount of carbon monoxide adsorbed during the polymerisation reaction (see text for details).

present during polymerisation. All samples had been activated in carbon monoxide (300°C, 60 min) and ethylene was admitted at 50°C at an initial pressure of 100 N m$^{-2}$. Ethylene was admitted from a cold trap whose volume was less than 0.3% of the dead space of the infrared cell. The ethylene was measured from a dosing system of known volume and condensed in the trap (liquid nitrogen) prior to polymerisation. After isolating the dosing system the trap was warmed to room temperature, and then opened to the sample in the cell. Thus an accurately known quantity of ethylene was admitted to the cell with only a very slight change in cell volume and hence pressure of carbon monoxide gas. After allowing sufficient polymerisation to occur for rate measurements to be made, the cell was evacuated for 60 min with the sample at 50°C. Ethylene was then readmitted to the catalyst at the same initial pressure as before and the rate of polymerisation measured again. In all cases this rate was faster than the rate recorded in the presence of carbon monoxide. The results are presented in Fig. 7 and Table 3.

The choice of a particular value of the initial pressure of ethylene used in these experiments was not arbitrary. From earlier experiments it was found that the admission of ethylene at a pressure of 30 kN m$^{-2}$ to a disc on which carbon monoxide had been preabsorbed resulted in complete removal of the latter and polymerisation took place rapidly. In contrast, admission of ethylene at lower pressures (ca. 10–50 N m$^{-2}$) did not cause either any reduction in the intensity of infrared bands due to adsorbed carbon monoxide or any polymerisation to occur. Thus the value of 100 N m$^{-2}$ was chosen as a satisfactory minimum for partial removal of the carbon monoxide and the concomitant production of polymerisation centres.

## DISCUSSION

The positions of the absorption bands at 2202 and 2189–2184 cm$^{-1}$ due to carbon monoxide adsorbed on catalyst pretreated with ethylene at 300°C are very close to that found for gaseous carbon monoxide. Vibrational frequencies for CO and $CO^+$ evaluated *(9)* from data given by Herzberg *(16)* would lead to infrared bands at

TABLE 3

Comparison of the Rates of Polymerisation of Ethylene in the Presence and Absence of Adsorbed Carbon Monoxide[a]

| Pressure of CO during preadsorption (N $m^{-2}$) | $A_{CO}(t = 0)$[b] | $A_{CO}(t = t)$ | $R_{CO}[10^3 k_1 (sec^{-1})]$ | $R_E[10^3 k'_1 (sec^{-1})]$ | $k_1/k'_1$ |
|---|---|---|---|---|---|
| 0 | 0 | 0 | — | 5.02 | 1.00 |
| 26.7 | 0.21 | 0.027 | 3.92 | 5.80 | 0.68 |
| 27.9 | 0.24 | 0.014 | 3.28 | 5.80 | 0.57 |
| 97.1 | 0.31 | 0.08 | 0.93 | 4.58 | 0.20 |
| 545 | 0.52 | 0.37 | 0.67 | 6.12 | 0.11 |

[a] Polymerisation of ethylene at 50°C.

[b] $R_{CO}$, presence of adsorbed carbon monoxide; $R_E$, absence of adsorbed carbon monoxide; (t = 0) denotes absorbance at ca. 2189 $cm^{-1}$ before the admission of ethylene; (t = t) indicates the absorbance due to adsorbed carbon monoxide during the polymerisation of ethylene.

2143 and 2184 $cm^{-1}$ for CO and $CO^+$, respectively. Gardner and Petrucci (*17*) have calculated that $CO^{2+}$ should give an infrared band at 2205 $cm^{-1}$, and have presented (*11*) a relationship between the frequency of vibration of adsorbed carbon monoxide and the number of valence electrons present in each CO unit. The change in vibrational frequency on ionizing the neutral (gas phase) molecule is attributable to the removal of electrons from the weakly antibonding lone pair orbital of the carbon atom. Studies of the adsorption of carbon monoxide on oxides indicate that absorption bands in the range ca. 2170–2210 $cm^{-1}$ are due to carbon monoxide weakly bonded to surface cations or held at these sites by dipolar forces. These conclusions are supported by the results of Angell and Schaffer (*18*) which showed that the adsorption of carbon monoxide on cation-exchanged zeolites was dependent upon the nature of the cations and on their percentage exchange. The reversibility of the isotherms (Fig. 2) for carbon monoxide adsorption at 50°C on chromium oxide samples which had been reduced in ethylene at 300°C and the observation that preadsorbed ethyl groups (*2*) are unaffected by the adsorption of carbon monoxide, show that weakly electron attracting centres are present in catalyst pretreated with ethylene at 300°C. This pretreatment leads to catalysts with high activity for the polymerisation of ethylene (*1, 2*). The results in Table 1 suggest that there is a relationship between the polymerisation activity of the catalyst samples and their capacity for adsorption of carbon monoxide. The sites available for the adsorption of carbon monoxide are therefore probably also the active sites for ethylene polymerisation. This conclusion is consistent with the results for carbon monoxide adsorption on catalyst which had been reduced in carbon monoxide at 300°C.

The bands at 2184 and 2189 $cm^{-1}$ due to carbon monoxide adsorbed on catalyst which had been reduced in carbon monoxide at 300°C are similar to those obtained for samples reduced in ethylene. Pretreatment with either ethylene or carbon monoxide leads to similar adsorption sites in the catalyst surface. However, reduction in carbon monoxide enables a clear distinction to be drawn between bands at 2184 and 2189 $cm^{-1}$ which arise from carbon monoxide adsorbed on two types of weakly electron attracting sites. The band observed at 2202 $cm^{-1}$ for ethylene activated samples is not seen when carbon monoxide is used for the pretreatment. Samples activated in ethylene were yellow-green to green in colour, whereas those activated in carbon monoxide were yellow. The 2202 $cm^{-1}$ band is probably due to the presence of $Cr^{3+}$ ions in the catalyst surface. A band near 2200 $cm^{-1}$ has been reported when carbon monoxide adsorbs on alumina (*14*) or silica (*15*) supported chromium(III) oxide. Clark *et al.* (*4*) observed infrared bands at 2220 and 2190 $cm^{-1}$ when carbon monoxide was adsorbed on silica–alumina supported chromium(VI) oxide which had been reduced in carbon monoxide. The more intense 2190 $cm^{-1}$ band is in accord with that at 2189 $cm^{-1}$ observed in the present work. The absence of the 2220 $cm^{-1}$ band here may arise because of differences in the two studies between either the oxide supports, or the extent to which the catalyst was reduced. Krauss (*22*) has attributed a band at ca. 2185 $cm^{-1}$ to carbon monoxide complexed in the catalyst.

When silica-supported chromium(VI) oxide has been partially reduced in carbon monoxide, there is an increase in the activity of the catalyst for ethylene polymerisation. The maximum catalytic activity observed was ca. 17 times greater than for discs pretreated with ethylene at the same temperature of 300°C. The capacity for carbon monoxide adsorption also changed in the same sense. Samples treated with carbon monoxide at 300°C adsorbed up to ca. 2½ times more carbon monoxide than ethylene activated catalysts (cf. Tables 1 and 2). The relationship between polymerisation activity and capacity for the adsorption of carbon monoxide (Fig. 4) suggest that there are sites which possess high catalytic activity but adsorb little or no carbon monoxide and sites which are both catalytically active and adsorb appreciable quantities of carbon monoxide. The results reflect the heterogeneity of the surface sites both for ethylene polymerisation and carbon monoxide adsorption.

Clark *et al.* (*4*) observed infrared bands ascribed to surface carboxylate ions at 1415 and 1590 $cm^{-1}$ after treatment of chromium(VI) oxide supported on silica–alumina with carbon monoxide at 250°C. The enhanced activity of the catalyst for the polymerization of ethylene was associated with the presence of carboxylate ions. In the present study no infrared bands due to carboxylate species were observed for catalyst which had been activated in carbon monoxide at 300°C, although bands have been observed for catalyst which was treated with ethylene at 300°C (*2*). The higher activity (Tables 1 and 2) of catalyst which had been activated in carbon monoxide cannot be associated with the presence of carboxylate ions in the oxide surface.

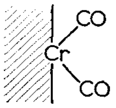
Ermakov *et al.* (*6*) found by iodometric analysis that contact between supported chromium(VI) oxide and carbon monoxide at 200°C resulted in the complete reduction of chromium ions to oxidation states of 3+ or less. It was suggested that either $Cr^{3+}$ or $Cr^{2+}$ ions were involved in the propagation centres for the polymerization reaction. A similar conclusion was reached by Krauss and Stach (*20, 21*) who showed for catalyst which had been reduced in carbon monoxide that the polymerization activity was a linear function of the concentration of $Cr^{2+}$ ions in the surface. The latter was monitored by measurement of the intensity of the visible band at 725 nm which gives rise to the blue color associated with Cr(II) atoms. In the present work measurement of the quantity of carbon dioxide produced during reduction of catalyst in carbon monoxide at 300°C enabled the average oxidation state of the chromium ions to be evaluated. The stoichiometry of the reduction process is given by

$$2Cr^{6+} + 3O^{2-} + 3CO \rightarrow 2Cr^{3+} + 3CO_2$$

The molar ratio of carbon dioxide formed to chromium(VI) oxide in the unreduced catalyst was 0.76 ± 0.07 for the most active catalyst prepared (Table 2) by reduction (for 60 min) in carbon monoxide at 300°C. Thus the average oxidation state of the chromium ions in the active catalyst was 4.5 ± 0.2, a figure which is similar to those deduced for active catalysts which had been reduced in ethylene at 300°C (*2*). Reduction in either ethylene or carbon monoxide led to catalyst for which the active sites in the polymerization of ethylene are chromium ions probably in the 5+ (but also possibly in the 4+) oxidation state. This conclusion is apparently inconsistent with the suggestion by Krauss and Stach

(*20–22*) that $Cr^{2+}$ ions are the active polymerization sites. However, in the present work, the blue color which is characteristic of $Cr^{2+}$ ions was never observed. For catalyst which had been reduced in ethylene, the absence of the blue color supports the comment by Krauss and Stach (*20*) that the formation of Cr(II) is precluded by the presence of water as an oxidation product of the reduction process. The formation of water promotes the reduction of higher oxidation states of chromium to the +3 oxidation state (*7b, 19*) and also makes the $Cr^{3+}$ ions resistant to further reduction. The polymerization activity of catalyst which had been reduced in ethylene showed a maximum for reduction times which were considerably less than the time required to reduce all the Cr(VI) atoms to Cr(III) (*1, 2*). This has been taken before (*2*) as strong evidence that the active sites in the catalyst surface are chromium atoms in an oxidation state higher than +3. In the present study of catalyst which had been activated in carbon monoxide at 300°C, the absence of any blue ($Cr^{2+}$) or even green ($Cr^{3+}$) colour in the active catalyst samples and the average oxidation state of 4.5 for the chromium atoms in the most active catalyst suggest that the activity is also associated with an oxidation state of chromium higher than 3+. The samples prepared by Krauss and Stach (*20, 21*) which contained $Cr^{2+}$ ions and were catalytically active had undergone considerably more reduction than the samples studied here. The results of the separate studies may not therefore be necessarily inconsistent but may indicate that both $Cr^{5+}$ and $Cr^{2+}$ ions are capable of acting as sites for the polymerization of ethylene.

The greater capacity for carbon monoxide adsorption found for samples treated with carbon monoxide rather than with ethylene is in part due to the presence of a greater number of sites which are active for ethylene polymerization and available for the adsorption of carbon monoxide. However, a quantitative comparison of the rates of polymerization suggests that the average activity of sites produced during carbon monoxide pretreatment is higher. It has been proposed before that this is the dominant factor (*5*). The increased capacity for carbon monoxide adsorption may arise because there are two possible positions for a CO unit to adsorb at each active site produced by carbon monoxide activation (*7*). Ethylene pretreatment produces some sites to which ethyl groups are attached, and only one "free" position per site remains (*2*). Thus formulae I and II represent the adsorption of carbon monoxide on sites produced by activation of the catalyst by reduction in carbon monoxide and in ethylene, respectively. The appearance in some experiments of two clearly defined infrared bands at 2184 and 2189 $cm^{-1}$ may be associated with the possibility of two adsorption positions per active site for catalysts which have been reduced in carbon monoxide. This possibility also exists, but to a lesser extent, for catalyst which has been activated in ethylene at 300°C followed by evacuation at 300°C. The evacuation removes adsorbed ethyl groups from some of the sites (*1, 2*) which are therefore available for the adsorption of two carbon monoxide molecules.



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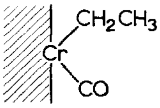
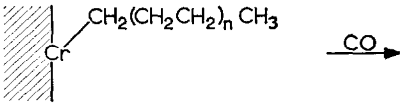
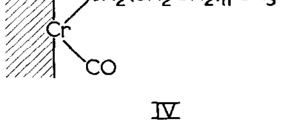


II

The capacity for the adsorption of carbon monoxide on catalysts which have been reduced in carbon monoxide is decreased by the build up of polyethylene on the catalyst surface. Sites from which polymer has not desorbed (III) (*7*) will adsorb only one carbon monoxide molecule per site (IV) compared with two molecules



III



IV

per site (I) before polymerization. The results in Fig. 5 show that build up of polymer caused a ca. 27% decrease in the amount of carbon monoxide which could be adsorbed. A 50% decrease would not be expected, because polymer will desorb from some sites leaving two positions vacant for the adsorption of carbon monoxide. However, the present results are evidence that the sites on which carbon monoxide adsorbs are also active for the polymerization of ethylene. The results (Fig. 6) for the polymerization of ethylene in the presence of adsorbed carbon monoxide confirm this conclusion.

The desorption of carbon monoxide (Fig. 6) on the addition of ethylene shows that ethylene is more strongly adsorbed than carbon monoxide. The decrease in the intensities of infrared bands due to adsorbed carbon monoxide is accompanied by an increase in the rate of polymerization of ethylene. The correlation between the increase in rate and the desorption of carbon monoxide is confirmed by the absence of an induction period for polymerization runs carried out in the absence of adsorbed carbon monoxide (Fig. 6). The correlation (Fig. 7) between the rate of polymerization and the amount of carbon monoxide which remains adsorbed during polymerization indicates that the majority of the catalytically active sites are poisoned by only a small fraction of the total amount of carbon monoxide which the surface is capable of adsorbing. This is consistent with the conclusion deduced from other results (Fig. 4) that the distribution of active sites in the surface is heterogeneous. The few sites upon which carbon monoxide is most strongly adsorbed are also those which are catalytically most active. At low coverages carbon monoxide is adsorbed on these sites and their catalytic activity is lost. At high coverages of carbon monoxide the polymerization activity is low and only decreases slowly as the coverage of carbon monoxide increases. There are sites in the surface which are able to adsorb carbon monoxide but only exhibit a low activity for the polymerisation of ethylene. These sites are far more numerous than those of high catalytic activity.

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## REFERENCES

1. ELEY, D. D., ROCHESTER, C. H., AND SCURRELL, M. S., *Proc. Roy. Soc. A* **329,** 361 (1972).
2. ELEY, D. D., ROCHESTER, C. H., AND SCURRELL, M. S., *Proc. Roy. Soc. A* **329,** 375 (1972).
3. CLARK, A., "Addition and Condensation Polymerisation Processes," Paper 91, p. 387. 155th meeting of the American Chemical Society, 1968.
4. CLARK, A., FINCH, J. N., AND ASHE, B. H., *in* "Proc. Int. Congr. Catal. 3rd, Amsterdam," (W. M. H. Sachtler, G. C. A. Schuit, and P. Zweitering, Eds.), p. 1010. Interscience, 1965.
5. ZAKHAROV, V. A., ERMAKOV, Y. I., AND KUSHNAREVA, E. G., *Kinet. Katal.* **8,** 1183 (1967).
6. ERMAKOV, Y. I., ZAKHAROV, V. A., AND KUSHNAREVA, E. G., *J. Polym. Sci. A* **9,** 771 (1971).
7. HOGAN, J. P. (a) *American Chemical Society Polymer Reprints.* **10,** 240 (1969); (b) *J. Polym. Sci.* **8,** 2637 (1970).
8. HILL, T., *Discuss. Faraday Soc.* **41,** 314 (1966).
9. LITTLE, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, London, 1966.
10. HAIR, M. L., "Infrared Spectroscopy in Surface Chemistry." Marcel Dekker, New York, 1967.
11. GARDNER, R. A., AND PETRUCCI, R. H., *J. Phys. Chem.* **67,** 1376 (1963).
12. DAVYDOV, A. A., SHCHEKOCHIKHIN, Y. M., AND KEIER, N. P., *Kinet. Katal.* **10,** 1103 (1969).
13. ZECCHINA, A., COLUCCIA, S., GUGLIELMINOTTI, E., AND GHIOTTI, G., *J. Phys. Chem.* **75,** 2774 (1971).
14. LITTLE, L. H., AND AMBERG, C. H., *Can. J. Chem.* **40,** 1997 (1962).
15. BORELLO, E., ZECCHINA, A., MORTERRA, C., AND GHIOTTI, G., *J. Phys. Chem.* **73,** 1286 (1969).
16. HERZBERG, G., "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," p. 522. Van Nostrand Reinhold, New York, 1950.

17. Gardner, R. A., and Petrucci, R. H., *18th Congr. Int. Union Pure and Appl. Chem.*, Montreal, Paper B1-30 (1961).
18. Angell, C. L., and Schaffer, P. C., *J. Phys. Chem.* **70**, 1413 (1966).
19. Matsumoto, A., Tanaka, H., and Goto, N., *Bull. Chem. Soc. Jap.* **38**, 1857 (1965).
20. Krauss, H. L., and Stach, H., *Inorg. Nucl. Chem. Letters* **4**, 393 (1968).
21. Krauss, H. L., and Stach, H., *Z. Anorg. Allg. Chem.* **366**, 280 (1969).
22. Krauss, H. L., *Proc. Fifth Int. Congr. Catal.*, Palm Beach, Paper 8. North-Holland Publishing Co. (1972).