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Silica-Supported Chromium Catalysts for Ethylene Polymerization

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The initial activity of Cr(III)/SiO_2 catalysts for ethylene polymerization was found to be a strong function of the activation temperature and the metal loading up to a level of 0.1 wt% Cr. Carbon monoxide poisoning of 0.11 wt% Cr(III)/SiO_2 catalysts, activated at 400 and 900°C, indicated that the *active* chromium is only 4 to 7% of the total chromium. Reduction of Cr(III)/SiO_2 with CO at 400°C resulted in a loss in activity at 25°C which was mirrored by an increase in Cr(II) concentration, as determined by chemiluminescence measurements. Increasing the activation temperature from 400 to 900°C resulted in a 10-fold increase in activity with not more than a 2-fold increase in the number of sites. At low temperatures (<50°C) the active site for polymerization is believed to be a surface-isolated Cr(III) ion which is coordinatively unsaturated. Dehydroxylation at elevated temperatures increases the number of coordination sites available for the substrate molecule and the growing polymer chain.

INTRODUCTION

The commercial significance of chromium on silica as a catalyst for the polymerization of ethylene has inspired a large body of research, much of which has been devoted to the characterization of the active site. The identity of the valence state of chromium present in the active site is a subject of controversy. Early researchers in the field recognized that Cr(VI), present in catalysts prepared from chromic acid, was reduced by C_2H_4 to a lower valence prior to the onset of activity (*1*). The easily characterized EPR signal of Cr(V) lead many to believe that this oxidation state was present in the active site (*2*, *3*). Several studies (*2*–*4*) attempted to confirm Cr(V) as the active valence, until Krauss (*5*) discovered that CO effected a "quantitative" reduction of Cr(VI) to Cr(II). The CO-reduced catalysts were found active for ethylene polymerization (*5*), and displayed no induction period on exposure to ethylene. The average oxidation state of chromium was measured by a pulse titration technique, and found to be very close to 2 (*5*). Recent evidence in support of Cr(II) as the active valence was provided by Merryfield *et al.* (*1*), who observed a direct correlation between surface Cr(II), detected by XPS, and the activity of their catalysts.

Based on the observation that catalysts prepared from trivalent chromium salts were active in ethylene polymerization, whereas those catalysts prepared from Cr(II) salts were not, Kazansky and coworkers concluded that Cr(III) was the active valence state (*6*). Additional evidence in support of Cr(III) as the active site was provided by the work of Beck and Lunsford (*7*), who found a direct correlation to exist between the concentration of isolated Cr(III) ions, measured by EPR spectroscopy, and catalytic activity.

One reason for the continuing debate over the identity of the true active valence stems from the inability of many experimental techniques to probe *only* the active chromium. It is generally accepted that the active component represents a small fraction of the total chromium present in these systems (*8*–*10*). Therefore, in order to determine the nature of the active valence one must first have information on the active site density. This provides a basis for interpreting kinetic and spectroscopic evidence in terms of the active chromium species.

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In this paper we present additional evidence to support the role of Cr(III) in the polymerization of ethylene at low temperatures. The contribution made by the silica toward the generation of active catalysts will also be discussed.

EXPERIMENTAL

Materials. $CrCl_3 \cdot 6H_2O$ (Fisher, certified grade) and CrO_3 (MCB Manufacturing) were used in the preparation of the silica-supported chromium catalysts. The support material was a Davison silica gel (952MS) with surface area of 300 m^2g^{-1}. Carbon monoxide and ethylene were supplied by Matheson. Carbon monoxide was ultrahigh purity grade, and was used directly. Ethylene (CP grade) was purified using the freeze-pump technique. Oxygen was obtained from Airco, and was dried over a molecular sieve/$CaCO_3$ column.

Sample preparation. Prior to catalyst preparation the silica was washed with HCl (1 *M*) and deionized H_2O, dried at 110°C, and calcined in air at 500°C for 15 hr. This material gave no background EPR spectrum.

Silica-supported chromium(III) catalysts ($Cr(III)/SiO_2$) containing 0.017, 0.11, 0.49, and 0.99 wt% chromium were prepared by impregnation of the silica gel with aqueous $CrCl_3 \cdot 6H_2O$ solutions. The impregnated gel was dried in air at 100°C for 12 hr. EPR analyses of the air-dried chromium(III) catalysts indicated that no oxidation of chromium had occurred during the drying procedure.

A silica-supported chromium(VI) catalyst ($Cr(VI)/SiO_2$) was prepared by impregnating 20.0 g of silica with a 0.011 *M* chromic acid solution. After drying the impregnated gel at 100°C, the chromium concentration was determined to be 0.29 wt%. Chromium concentrations were determined by standard chemical techniques.

Sample pretreatment. $Cr(III)/SiO_2$ samples, 0.025–0.100 g, were outgassed at 25°C for 12 hr and then heated under vacuum. The first type of heat treatment involved programmed heating (1.5°C min^{-1}) to a final temperature of 400°C. These samples were maintained at 400°C for 5 hr and are denoted as $Cr(III)/SiO_2(400)$. A second vacuum pretreatment, on some samples, involved additional outgassing at 900°C for 2 hr ($Cr(III)/SiO_2(900)$). Unless otherwise indicated, $Cr(III)/SiO_2(400)$ and $Cr(III)/SiO_2(900)$ will denote the activated forms of 0.11 wt% $Cr(III)/SiO_2$.

$Cr(VI)/SiO_2$ samples were activated in a flow of O_2 (5 ml min^{-1}) by heating (7°C min^{-1}) to 850°C and maintained at this temperature for 18 hr. Samples were cooled to room temperature while still in the O_2 stream, and then outgassed for 30 min. Degassing was continued for an additional 30 min at 400°C.

Some samples of each catalyst were reduced with CO at 400°C for various time periods. Following reduction, the samples were outgassed 1 hr at 400°C to remove adsorbed CO and CO_2.

Polymerization. Low-pressure polymerization studies were performed under static, shallow-bed (3–4 mm) conditions. The reaction was followed by monitoring the change in ethylene pressure as a function of time. Polymerization rates were calculated from a natural cubic spline of the experimental data. The slope at time zero is the initial rate.

At low ethylene pressures (50–300 Torr) effective temperature control, during the polymerization reaction, was achieved by precooling the catalyst bed (15–20°C) below the desired reaction temperature. On contact with ethylene the reactor temperature rose rapidly to the level desired. Kinetic measurements at pressures greater than 300 Torr of C_2H_4 were not possible because the exotherms due to ethylene adsorption and polymerization caused uncontrollable heating of the catalyst, rendering kinetic data meaningless.

Chemiluminescence. Luminescence events were recorded using a TRW relay-lense assembly and a photomultiplier in tandem with an oscilloscope. The relay-lense assembly consisted of a sample holder and a lense for focusing the emitted light on the photomultiplier. The chemiluminescence was recorded as an oscilloscope trace which was photographed using ASA 1000 film. Variously treated samples of Cr(III)/SiO_2 and Cr(VI)/SiO_2 were examined for luminescence on exposure to 200 Torr of O_2 (25°C).

RESULTS

Activation Conditions

The pretreatment of Cr/SiO_2 catalysts is a critical aspect in the study of these systems. The temperature of vacuum activation was found to significantly influence the polymerization activity of Cr(III)/SiO_2. Table 1 presents a summary of the activation conditions examined, and polymerization rates measured for these catalysts. Increasing the activation temperature from 400 to 900°C was found to effect a 10-fold change in the initial rate. This increase in rate with activation temperature was expected, in light of results reported by McDaniel and Welch (*11*) and others (*12*), who have attributed this phenomenon to the dehydroxylation of the silica. It has also been proposed that high-temperature treatments may lead to changes in the coordinative environment of the active site (*11, 13*).

The dehydroxylation of silica is largely a kinetic phenomenon at temperatures less than 600°C (*14*). Cr(III)/SiO_2 catalysts activated at 400°C for 12 hr displayed higher polymerization activity than those treated for only 5 hr. The level of activity attained upon conditioning at 900°C, however, did not depend on the length of pretreatment at 400°C.

TABLE 1

Polymerization Rates Obtained for Cr(III)/SiO_2 Activated at Different Temperatures

Catalyst treatment	Polymerization rate[a] (mg C_2H_4 g cat^{-1} min^{-1})
Act. at 400°C (5 hr) *in vacuo*	1.5
Act. at 900°C (2 hr) *in vacuo*	15.3
Act. at 400°C (12 hr) *in vacuo*	4.3

[a] Sample contacted with 300 Torr of C_2H_4 at 25°C.

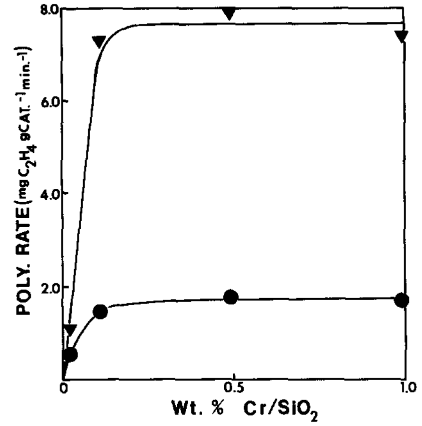


FIG. 1. Polymerization rate as a function of chromium content for Cr(III)/SiO_2(900) (▼), and Cr(III)/SiO_2(400) (●).

Chromium Content

The effect of chromium content on the activity of Cr/SiO_2 catalysts was examined using a series of Cr(III)/SiO_2 (0.01–1.0 wt%) samples. Activation temperatures of both 400°C (Cr(III)/SiO_2(400)) and 900°C (Cr(III)/SiO_2(900)) were used. The polymerization rates measured for Cr(III)/SiO_2 were found to be dependent on metal content up to a loading of 0.1 wt%. In Cr(III)/SiO_2(400) samples which contained <0.1 wt% Cr, the dependence of rate on chromium loading was of a nonintegral order (Fig. 1). Samples of greater than 0.1 wt% Cr revealed a zero-order dependence of polymerization rate on metal loading.

These effects of metal loading were more clearly illustrated in the study of the Cr(III)/SiO_2(900) catalysts. The ethylene polymerization rate was first order in metal loading up to 0.1 wt% (Fig. 1). Increasing the chromium content further (0.1 to 1.0 wt%) resulted in no change in the polymerization rate.

Mass transfer control of a reaction, catalyzed by metals supported on porous solids, can be indicated by the zero-order dependence of rate on metal content (*15*, *16*). The results presented in Fig. 1 were analyzed according to criteria established by Wiesz and Prater (*16*), to determine the significance of pore diffusion as a rate-controlling phenomenon. This analysis indicated that the zero-order dependence of the rate for 0.1 to 1.0 wt% Cr(III)/SiO$_2$ was due solely to the intrinsic kinetics of the reaction.

Polymerization Kinetics

The pressure dependence for ethylene polymerization over Cr(III)/SiO$_2$(900) is shown in Fig. 2. At low pressure (50–100 Torr) the reaction was first order in C_2H_4. As the ethylene pressure was increased (up to 300 Torr), the rates measured were lower than expected for a strictly first-order reaction. The deviation from first-order behavior may have been due to rapid fouling of the support by polymer, such that initial rates could not be correctly determined, or to a change in overall order with respect to C_2H_4. Clark and Bailey (*17*), favor a Langmuir–Hinshelwood mechanism for the polymerization reaction, which correctly predicted the appearance of a rate maximum with increased C_2H_4 pressure. The behavior shown in Fig. 2 was probably a result of the reaction becoming zero order in C_2H_4, due to saturation of the catalyst surface with monomer. Heating effects, however, prevented accurate measurement of the polymerization rate at C_2H_4 pressures above 300 Torr. Therefore, an extended study of the pressure dependence could not be carried out.

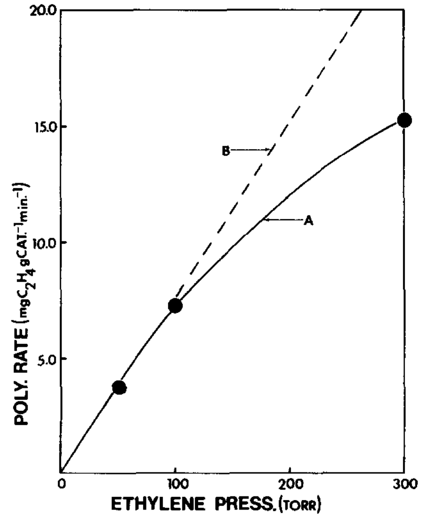


FIG. 2. Polymerization rate as a function of the initial pressure of ethylene for Cr(III)/SiO$_2$(900). (A) Observed behavior, (B) first-order behavior.

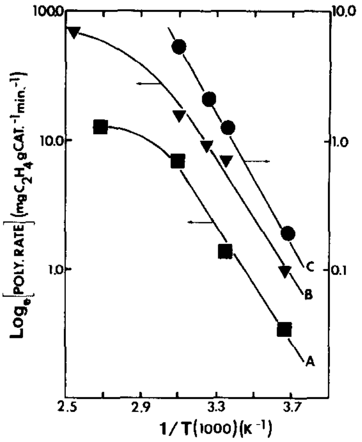


FIG. 3. Arrhenius plots for Cr(III)/SiO$_2$. (A) 0.11 wt% Cr(III)/SiO$_2$(400), (B) 0.11 wt% Cr(III)/SiO$_2$(900), (C) 0.017 wt% Cr(III)/SiO$_2$(900).

The effects of activation temperature and chromium loading were further investigated through examination of the temperature dependence of polymerization. Cr(III)/SiO$_2$ (0.11 wt%) activated at 400°C (Fig. 3A) and 900°C (Fig. 3B) displayed good fits to the Arrhenius equation for temperatures up to 50°C, but at temperatures above 50°C, the dependence became nonlinear. The Arrhenius plot for 0.017 wt% Cr(III)/SiO$_2$(900) is also shown in Fig. 3C.

Activation energies determined, in the temperature range 0 to 50°C (Table 2), for each of the Cr(III) catalysts examined, proved to be identical within experimental error. The results are in agreement with previously reported values, which range between 7 and 14 kcal mole^{-1} (*2, 8*).

Carbon Monoxide Poisoning and the Active Site Concentration

It is important to note that the active chromium responsible for the polymeriza-

TABLE 2

Arrhenius Activation Energies for Ethylene Polymerization with $Cr(III)/SiO_2(400$ and $900)$

Catalyst	E_a[a] (kcal mole^{-1})
0.11 wt% $Cr(III)/SiO_2(400)$	10.4 ± 1
0.11 wt% $Cr(III)/SiO_2(900)$	10.3 ± 1
0.017 wt% $Cr(III)/SiO_2(900)$	11.5 ± 0.5

[a] Obtained in the range 0 to 50°C.

tion activity in Cr/SiO_2 catalysts has long been thought to be only a small fraction of the total amount of chromium present in the catalyst (*8–10*). In the past, the active chromium has been examined by techniques which involved inhibiting, or terminating growth of the polymer during a reaction (*9, 10*). In the present study, small quantities of CO, a known poisoning agent (*9, 18*), were preadsorbed (at 25°C) on catalysts prior to polymerization.

The adsorption of CO (at 25°C) on $Cr(III)/SiO_2(400$ and $900)$ decreased the polymerization activity of these catalysts (Figs. 4A and B). The gradual decay of polymerization activity observed on CO-poisoned catalysts was a consequence of the indiscriminate adsorption of CO on both active and inactive chromium. The CO adsorption probably occurred first on active chromium sites; hence, an initially sharp decrease in the polymerization rate was observed (Fig. 4). An estimate of the active site density was obtained from the abscissa intercept of the line that is tangent to the decay curve at zero CO adsorption. Each mole of CO adsorbed was taken to be equal to 1 mole of active sites, leading to an active site concentration of 8.6×10^{17} sites g cat^{-1} for $Cr(III)/SiO_2(900)$ (Table 3). Samples of $Cr(III)/SiO_2(400)$ which were poisoned by CO revealed an active site concentration of 4.9×10^{17} sites g cat^{-1}. These site concentrations are an upper limit to the actual concentration of active centers, and correspond to 4 and 7% of the total chromium present in the 0.11 wt% $Cr(III)/SiO_2$ catalysts activated at 400 and 900°C, respectively. They are in good agreement with the values reported by Zakharov and Ermakov (1.8×10^{17}–1.5×10^{18} sites g cat^{-1}) (*10*), but are significantly lower than that reported by Hogan (1.5×10^{19} sites g cat^{-1}) (*9*).

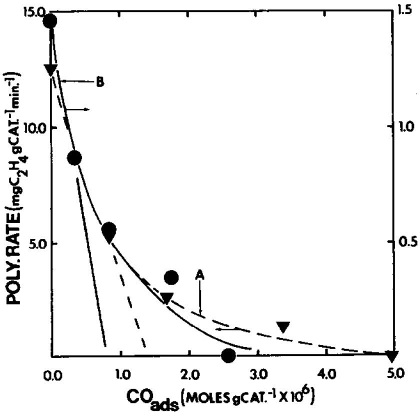


FIG. 4. Polymerization rate as a function of adsorbed CO: (A) 0.11 wt% $Cr(III)/SiO_2(900)$, (B) 0.11 wt% $Cr(III)/SiO_2(400)$. Tangents represent slopes at zero CO adsorption.

CO Treatment and Chemiluminescence

The activity of $(Cr(VI)/SiO_2)$ was examined following calcination of the catalyst in O_2 at 850°C. The unreduced, calcined Cr(VI) catalyst was, as expected, inactive for the polymerization of ethylene at 25°C. Samples of $Cr(VI)/SiO_2$ which were exposed to 600 Torr of C_2H_4 at 160°C, attained a high level of activity ($r_{C_2H_4} = 55$ mg C_2H_4 g cat^{-1} min^{-1}) at that temperature, follow-

TABLE 3

Active Site Concentrations for 0.11 wt% $Cr(III)/SiO_2$

Activation[a] (°C)	Sites g cat^{-1}	Cr[b] (nm^{-2})	%Cr_{ACT}[c]	wt% Cr_{ACT}[d]
400	4.9×10^{17}	0.0016	3.8	0.0041
900	8.6×10^{17}	0.0029	6.9	0.0075

[a] Treatment performed *in vacuo*.
[b] S.A. = 300 m^{2}g^{-1}.
[c] Percentage of total Cr present in the sample which was active.
[d] Weight percent of active Cr.

ing a 30-min induction period. Reduction in CO (400°C for 0–60 min), of the calcined $Cr(VI)/SiO_2$, eliminated the induction period and produced catalysts which displayed polymerization activity at 25°C. The activity of $Cr(VI)/SiO_2$ (T = 25°C, $P_{C_2H_4}$ = 100 Torr) as a function of reduction time is shown in Fig. 5. The maximum rate was attained for samples which had been reduced in CO for 5 min. Further reduction of Cr(VI) catalysts resulted in rapid loss of polymerization activity. Samples treated for 60 min with CO were inactive, indicating a full reduction of Cr(VI) to Cr(II) (*7*).

The adsorption of O_2 (200 Torr, 25°C) on CO-reduced Cr/SiO_2 catalysts was accompanied by a bright red–orange chemiluminescence. The luminescence phenomenon, as observed previously (*5, 9, 19*), is attributed to the adsorption of O_2 on Cr(II), resulting in its oxidation to Cr(VI). The specificity of the chemiluminescence for Cr(II) suggests that a direct correlation exists between the intensity of the luminescence and the relative amount of Cr(II) present in reduced catalyst samples. As expected, the intensity of the chemiluminescence was found to increase as a function of reduction time for samples of $Cr(VI)/SiO_2$ (Fig. 5). From the chemiluminescence data, it was determined that the reduction was quite rapid; samples reduced for 15 min (400°C) displayed 75% of the luminescence obtained for those that were reduced for 60 min. It is important to note that increased luminescence, measured for $Cr(VI)/SiO_2$ samples that were more extensively reduced, mirrored the declining polymerization activity displayed by these catalysts.

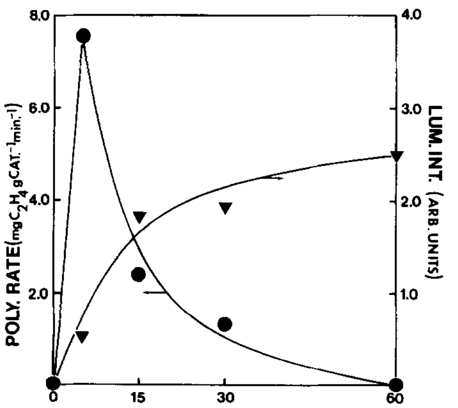


FIG. 5. Polymerization rate (●) and chemiluminescence (▼) of $Cr(VI)/SiO_2$ as a function of CO reduction time (400°C).

To determine if the inverse relationship between polymerization activity and luminescence intensity (displayed by reduced $Cr(VI)/SiO_2$) existed for other Cr/SiO_2 catalysts, the chemiluminescence of $Cr(III)/SiO_2(900)$ was examined. $Cr(III)/SiO_2$ activated *in vacuo* at 900°C chemiluminesced with an intensity equivalent to $Cr(VI)/SiO_2$ catalysts which had been reduced in CO for 5 min. The luminescence was attributed to Cr(II) which had formed during the vacuum activation, through reduction of Cr(III) by organic impurities in the vacuum system. Samples of $Cr(III)/SiO_2$ activated at 900°C in a special grease-free environment were found to display no chemiluminescence. It is interesting to note that samples of $Cr(III)/SiO_2$ prepared both in the conventional vacuum system and under grease-free conditions displayed identical polymerization activity. Samples of $Cr(III)/SiO_2(900)$ which were reduced (CO, 400°C) for 60 min displayed intense chemiluminescence and *no* polymerization activity at 25°C. Gas chromatographic analysis of the CO_2, produced during the 60-min reduction of this catalyst, indicated 98% of the Cr(III) had been reduced to Cr(II). It was determined, therefore, that an inverse correlation exists between surface Cr(II) and the polymerization activity measured at 25°C for both the $Cr(III)/SiO_2$ and the reduced $Cr(VI)/SiO_2$ catalysts.

DISCUSSION

The $Cr(III)/SiO_2$ and prereduced $Cr(VI)/SiO_2$ catalysts examined in this study readily initiated the gas–solid polymerization of ethylene at room temperature. As shown in Fig. 6, the polymerization rate decreased over time due to fouling of the catalyst by

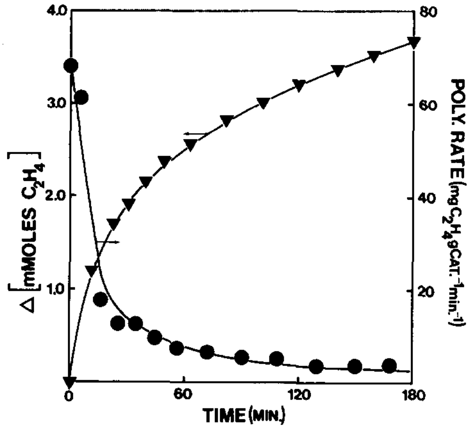


FIG. 6. Consumption of C_2H_4 (▼) and polymerization rate (●) as a function of reaction time for Cr(III)/SiO_2(900) (120°C, and 100 Torr C_2H_4).

solid polymer. The deactivating effect of the polymer restricted our study to the examination of initial rates. This behavior is in contrast to commercial systems where it has been demonstrated that the polyethylene which forms inside the pores of the silica, during a reaction, fractures the catalyst particles (*20*). The fracturing process together with a solvent or diluent act to maintain a high level of catalytic activity and ensures high yields of polyethylene, which are commercially desirable (*1*, *8*, *20*).

The kinetics of ethylene polymerization differ for solution/slurry and gas–solid reactions due to the deactivating effect of the polymer in the latter. It is important to note, however, that the ambient concentration of monomer is more easily determined for a gas–solid versus solution/slurry reaction, and that although the polymer yield is poor, the initial kinetics provide valid information concerning the nature of the active site (*8*).

The Effects of Activation on the Chemistry of the Active Site

The effect of activation temperature on Cr(III)/SiO_2 catalysts (Table 1), provides evidence that the polymerization activity is inversely proportional to the surface hydroxyl population of the silica. Samples pretreated at 900°C *in vacuo* displayed 10 times the activity of those heated to 400°C *in vacuo*. In addition, longer pretreatments at 400°C (12 hr as opposed to 5 hr) had a positive influence on the activity of the catalyst.

McDaniel and Welch (*11*) found that the polymerization activity of Cr/SiO_2 was increased through extensive dehydroxylation of the silica. The activity of thermally treated Cr/SiO_2 catalysts was maximized by calcination at 900°C; higher temperatures led to a loss of activity due to sintering of the chromium (*11*). Measurements of the surface hydroxyl population on catalysts calcined at various temperatures indicated that the reactivity of the catalyst was inversely proportional to the number of hydroxyl groups surrounding the active site (*11*).

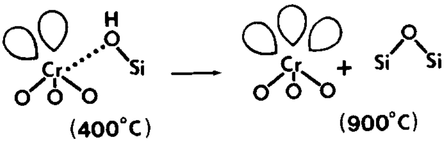
The inverse relationship between polymerization activity and surface hydroxyl population raises major questions pertaining to the effect of high-temperature dehydroxylation on the active site: (1) Does the increased activation temperature modify the site, thereby increasing its reactivity toward ethylene, i.e., does the reaction occur on a different type of site after treatment at 900°C, or (2) can the higher polymerization rate be attributed to an increase in the concentration of active centers? Insight into answers to these questions was provided by an examination of the temperature dependence of the polymerization, and the active site concentrations present in these catalysts.

The temperature dependence (Fig. 3, Table 2) of Cr(III)/SiO_2 (400 and 900) displayed good fits to the Arrhenius equation for temperatures up to 50°C. Activation energies for the catalysts examined were found to be nearly identical, within experimental error. Assuming the polymerization mechanism to be independent of activation temperature leads one to conclude that little change or modification of the active site had occurred. Careful consideration of the magnitude of the activation energies, however, indicates that a small change in their absolute value would translate into a significant alteration of the polymerization rate, thus indicating the active site or its immediate environment had been influenced by the high-temperature treatment. A likely modification of the site might have been the removal of adjacent surface silanol groups which, following activation at 400°C, had remained coordinated to the active center.

Groeneveld *et al.* (*21*) have postulated that a silanol group must be adjacent to the active site for maximum activity, a situation that is not plausible in light of our findings. It is evident that the removal of surface hydroxyl groups enhances activity. In order to attribute the 10-fold enhancement of activity measured for those catalysts treated at 900°C vs 400°C, to a modification of the active site, we might expect a change of 1–2 kcal $mole^{-1}$ in activation energy. Unfortunately the error in our E_a values masks changes of such magnitude. It is significant to note that the integrity of the site seemed to be preserved regardless of metal content. As illustrated by Table 2, both 0.017 and 0.11 wt% $Cr(III)/SiO_2(900)$ show similar activation energies, and the polymerization rate was found to be first order in metal loading over this range.

While consideration of the activation energies of polymerization over variously treated catalysts was somewhat inconclusive, further insight as to the effect of activation temperature was gained through examination of the active site concentration. The technique employed, CO adsorption prior to polymerization, led to a decrease in rate with increased amount of CO adsorbed. Our assumptions that adsorption occurred first on Cr active for polymerization, and that 1 CO molecule poisoned 1 active site seem valid. Hogan (*9*) reports that CO adsorbed on one coordination position of the surface chromium site destroys its activity for polymerization. Additional confirmation of our assumptions was provided by the agreement between our site densities (4.9×10^{17} and 8.6×10^{17} sites g cat^{-1}) and the average site density determined by Zakharov and Ermakov (*10*) (6.8×10^{17} sites g cat^{-1}). Increasing the catalyst activation temperature from 400 to 900°C effects at most a twofold increase in the active site concentration (Table 3). Clearly, this increase in active sites cannot be solely responsible for the 10-fold enhancement of polymerization activity observed for $Cr(III)/SiO_2(900)$ versus $Cr(III)/SiO_2(400)$.

We believe that dehydroxylation, effected by the increased activation temperature, enhances the reactivity of the active site through the removal of surface silanol groups coordinated to the chromium site viz.:



Statistically, there is a greater probability for coordination between the chromium site and surface hydroxyl groups at 400 than at 900°C (viz. 0.0016 active Cr nm^{-2} vs 2.3 OH nm^{-2} (*14*) at 400°C and 0.0026 active Cr nm^{-2} vs 0.65 OH nm^{-2} (*14*) at 900°C). Also the higher temperature treatment causes at most a twofold increase in the active site density. These two phenomena combine to yield catalysts of significantly improved activity for ethylene polymerization.

Turnover frequencies (TOF) based on the active site concentrations given above, compare favorably with values reported by others (*7, 21–23*) (Table 4). It is interesting to note that higher activation temperatures favor high TOF's, supporting our results. Care must be exercised in comparing the absolute values of TOF's reported by other researchers, however, as a variety of techniques have been employed both in the measurement of active site concentrations and in the conditions used to determine activity.

TABLE 4

Comparison of Turnover Frequencies

Catalyst	Activation	Reaction conditions	TOF[a]	Reference
Cr(III)/SiO_2	400°C (*in vacuo*, 5 hr)	25°C, 300 Torr C_2H_4	1.1[b]	This work
Cr(III)/SiO_2	400°C (*in vacuo*, 12 hr)	25°C, 300 Torr C_2H_4	3.2[b]	This work
Cr(III)/SiO_2	900°C (*in vacuo*)	25°C, 300 Torr C_2H_4	6.4[b]	This work
CrO_x/SiO_2	500°C (calcined in O_2, reduced in CO)	25°C, 50 Torr C_2H_4	0.48[c]	*21*
CrO_3/SiO_2	600°C (calcined in air)	100°C, 180 Torr C_2H_4	1.0[d]	*22, 23*
Cr(III)/SiO_2	350°C (*in vacuo*)	25°C, 300 Torr C_2H_4	0.013[e]	*7*

[a] Molecules C_2H_4 site^{-1} sec^{-1}.

[b] TOF based on active site density determined by CO poisoning.

[c] TOF based on active site density determined by ir spectroscopy.

[d] TOF based on active site density determined by H_2O poisoning.

[e] TOF based on active site density determined by EPR spectroscopy.

The Relationship between the Silica Surface and the Active Site Concentration

The relationship between the catalytic activity and metal content of Cr(III)/SiO_2 catalysts disclosed a possible link between the nature of the silica surface and the concentration of active sites. It was observed that for chromium loadings below approximately 0.1 wt% Cr the polymerization rate was linear, and above this level the rate became zero order in metal content (Fig. 1). The zero-order behavior illustrated in Fig. 1 is an unusual phenomenon, commonly thought to indicate that a reaction has become diffusion controlled. Analysis of our results according to the criteria of Weisz and Prater (*16*), however, indicated that pore diffusion did not play any role as a rate-controlling phenomenon. It was concluded, therefore, that the zero-order dependence on metal loading was related to the nature of the catalyst. It is important to note that the range of metal loadings which displayed the zero-order dependence was independent of activation temperature. In addition, as shown in Fig. 1, for metal loadings above 0.1 wt% Cr, the polymerization rates measured for samples activated at 900°C (*in vacuo*) were a constant factor greater than those activated at 400°C (*in vacuo*). These facts point toward the existence of sites on the silica which, when occupied by chromium, generate active centers.

The surface chemistry of silica has been cited as an influencial parameter in controlling the reactivity of Cr/SiO_2 polymerization catalysts (*11*). McDaniel (*24*) measured the "saturation coverage" of Cr(VI) on the surfaces of a series of Cr/SiO_2 catalysts prepared from a variety of chromium complexes. After impregnation the catalysts were calcined in O_2 at temperatures ranging from 400 to 900°C. Using a titrative method, McDaniel determined that the amount of chromium present as isolated hexavalent ions was inversely proportional to the calcination temperature, ranging from 2.0 Cr(VI) nm^{-2} at 400°C to 0.5 Cr(VI) nm^{-2} at 900°C. Chromium present in excess of the saturation coverage, decomposed to form a surface α-Cr_2O_3 phase, which could be detected by X-ray diffraction (XRD) (*24*). Notably, McDaniel observed that the polymerization activity of these catalysts was affected very little by chromium loading (*24*). This, he suggests, indicates that above some chromium content the number of active sites becomes sensitive only to activation temperature, not to metal loading.

The range of metal loadings examined in this study was *below* the saturation coverage of chromium reported by McDaniel (*24*). The active site density measured for

0.11 wt% $Cr(III)/SiO_2$ (400 and 900) represents a small fraction of the total chromium present in our catalysts (4 to 7%). The remaining chromium was presumed to have decomposed to a surface α-Cr_2O_3 phase. The zero-order dependence of polymerization rate on metal content (>0.1 wt%) appears to be the result of a saturation phenomenon similar to that observed by McDaniel. We believe that at 0.11 wt% Cr a saturation density of active sites was achieved. It is possible that the saturation density may be related to the presence of defect structures on the silica surface, which when occupied by a chromium ion(s) generate an active site for polymerization. The temperature treatment of the catalyst activates these chromium sites for the catalytic reaction. The initially linear dependence of rate on metal loading (<0.1 wt%) can be attributed to a very random occupation of these support sites by chromium, leading to an increase in the active site concentration up to the saturation density. The saturation density measured for $Cr(III)/SiO_2(900)$ (0.0026 active Cr nm^{-2}) in this study is significantly lower than McDaniel's saturation coverage (0.5 Cr(VI) nm^{-2}). This difference arises because the saturation density described here accounts for *only* active chromium, whereas McDaniel's saturation coverage includes *all* surface-isolated hexavalent chromium, without reference to the active site concentration.

It is worth noting that catalysts prepared from CrO_3 (0.3 wt% $Cr(VI)/SiO_2$) which had been calcined in O_2 at 850°C, and carefully reduced with CO for 5 min at 400°C, displayed polymerization activity characteristic of $Cr(III)/SiO_2(900)$ catalysts in the same loading range (>0.1 wt% Cr). This indicates that the saturation phenomenon observed here, similar to that reported by McDaniel (*24*), was not peculiar to samples prepared from any particular chromium complex.

The Valence State of the Active Chromium

It has been common practice to prepare Cr/SiO_2 catalysts by methods wherein the chromium is initially in the hexavalent state. Thus the chromium must be reduced to a lower valence in order to achieve activity. While several reducing agents can be used to accomplish this reduction, the extent of reduction is seldom clean, and reduced catalysts often contain a spectrum of oxidation states (*8*).

In the present study we sought to avoid the complications which arise through the use of catalysts containing Cr(VI). This was accomplished through the impregnation of the silica with a Cr(III) salt, followed by a vacuum activation, which was found to effect no change in the metal's oxidation state. We have also studied a catalyst containing Cr(VI) initially, as a basis for comparison with other systems (*4, 12, 21*).

The $Cr(VI)/SiO_2$ catalyst was also used in the determination of the active valence of chromium in ethylene polymerization. The reduction of $Cr(VI)/SiO_2$ with CO reportedly involves surface isolated Cr(VI) and, in the extreme case, results in the near quantitative production of Cr(II) (98% yield) (*5*). The chemiluminescence associated with the adsorption of O_2 on this Cr(II) (25°C) indicated that the surface concentration of Cr(II) was *inversely* proportional to the activity of all Cr/SiO_2 catalysts examined at 25°C. Under conditions where severe reduction of $Cr(VI)/SiO_2$ occurred, it was found that the chemiluminescent intensity reached a maximum, and the catalytic activity was destroyed. Chromium(II), therefore, is not a prerequisite for polymerization activity at low temperatures.

In the past, several researchers (*1, 5, 10, 12*) have relied heavily on the average oxidation state of chromium present in reduced catalysts as providing evidence for the active valence state. It has been concluded that the active component is Cr(II) since the average oxidation state of reduced Cr(VI) catalysts is generally between 2.0 and 2.5 (*1, 5*). Zakharov and Ermakov (*10*) measured the average oxidation state of $Cr(VI)/SiO_2$ treated with CO (300°C) or C_2H_4 (75°C). They found the average oxidation state to be not more than 3 following CO reduction, and around 3.4 following C_2H_4 reduction. Since it has been established that the chromium responsible for the catalytic activity represents only a small fraction of the total (*9*, *10*), it would be difficult to clearly establish the active valence based on an average oxidation number. For example, in the 0.11 wt% Cr(III)/SiO_2(900) catalyst the active component represents *only* 0.0075 wt% Cr!

Rebenstorf and Larsson (*25*) have suggested that Cr(III) is the active site for the low-temperature (<50°C) polymerization of ethylene, while Cr(II) becomes active at higher temperatures (~100°C). Recently we have discovered that catalysts which contain a large percentage (~98%) of the total chromium as Cr(II) begin to display polymerization activity at temperatures >40°C, and low ethylene pressures. A complete description of our active Cr(II)/SiO_2 catalysts will be presented in a forthcoming note.

CONCLUSION

The dehydroxylation of Cr(III)/SiO_2 catalysts at 900°C was found to increase their activity for ethylene polymerization. The increase in activity is linked to the removal of surface silanol groups which were coordinated to the active site following activation at 400°C. The high-temperature treatment also effected at most a twofold increase in the concentration of active sites which, combined with the apparent increase in the coordinative unsaturation of these sites, leads to the increased polymerization rates measured for catalysts activated at 900°C over those activated at 400°C. In addition, there appears to be a saturation density of active sites, which likely is influenced by the presence of defect structures on the silica surface. The active sites at low reaction temperatures are most likely isolated Cr(III) ions, which are only a small fraction of the total chromium present in our catalysts. Although the influence of residual chloride ions left by the impregnation of the silica with $CrCl_3 \cdot 6H_2O$ is still under investigation, we conclude that the active site for ethylene polymerization at low temperatures is a coordinatively unsaturated surface-isolated Cr(III) ion.

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