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The Active Site for Ethylene Polymerization over Chromium Supported on Silica

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Nitric oxide has been used as a probe molecule to investigate the state of chromium supported on silica gel which is active in the polymerization of ethylene. Chromium(III) ions, formed either by the reduction of Cr(VI) or by the direct addition of Cr(III) from solution, coordinate with nitric oxide as the $[Cr^{III}(NO)_2]^{3+}$ complex. This complex has been identified by epr and infrared spectroscopy. The initial activity for ethylene polymerization correlates well with the concentration of isolated Cr(III) ions, as determined from the epr spectrum of the $[Cr^{III}(NO)_2]^{3+}$ complex. This correlation persists over a variety of catalyst pretreatments, including oxidation and reduction of the chromium. Chromium(V) was excluded as the active site on the basis of a negative correlation with catalytic activity, and chromium(II) was excluded because reduction of $Cr(III)/SiO_2$ samples and extensive reduction of the $Cr(VI)/SiO_2$ samples with CO resulted in catalysts having very low activity. Mononuclear chromium(III) ions with at least two available coordination sites are identified as the active species for ethylene polymerization.

INTRODUCTION

The industrial importance of supported chromium as a catalyst for the polymerization of ethylene has stimulated numerous investigations to determine the reaction mechanism and the nature of the active site. With respect to the latter there is much disagreement in the literature and every oxidation state from Cr(II) to Cr(V) has been reported to be active in polymerization. In early studies it was determined that reduced chromic oxide catalysts were more active than unreduced catalysts (*1*). Moreover, chromic oxide catalysts required an induction period prior to becoming active when exposed to 20 atm of C_2H_4 at 150°C (*2, 3*).

Tetrahedral or square planar chromium(V) was favored as the active site, first by Kazansky and co-workers (*4–6*) and later by Eley *et al.* (*7*). In addition to kinetic and spectroscopic evidence, it was noted that high valence ions tend to be more efficient in polymerization over Ziegler–Natta catalysts and to better satisfy the model postulated by Cossee for active sites (*8*). By contrast, Krauss *et al.* (*9–12*) have provided evidence which supports the role of Cr(II) (obtained by the reduction of the catalysts with carbon monoxide) as the active oxidation state of chromium. Eden *et al.* (*13*) postulated that the active site consisted of Cr(IV) ions. In earlier work Miesserov (*13*) postulated that Cr(III) associated with a Lewis acid forms the active site, and more recently in support of Cr(III) involvement Kazansky and co-workers (*14*) showed that catalysts prepared from Cr(III) salts and complexes were much more active than catalysts prepared from Cr(II) salts. In addition, they noted that catalysts prepared from Cr(VI) were more active after mild reduction in CO than after extensive reduction.

Much of the disagreement concerning the nature of the catalytic site arises from (i) the complexity of the surface when one forms the active catalyst from supported chromic oxide and (ii) the inability to identify specific oxidation states rather than an average oxidation state for the catalyst. With respect to the complexity of the surface one should note that in addition to

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having a variety of oxidation states, it is possible to have both two- and three-dimensional aggregates of chromium oxides (*15*).

Probe molecules such as nitric oxide and carbon monoxide provide insight into the oxidation state and available coordination sites of supported metal ions. Of particular interest in the present study was a paramagnetic complex which formed when NO was adsorbed on a partially reduced surface of chromium on alumina. This nitrosyl complex was originally attributed to $[Cr^{I}(NO^{+})]^{2+}$ (*16*); however, Pearce *et al.* (*17*) have concluded that the complex $[Cr^{III}(NO)_2]^{3+}$ is formed in related studies of chromium-exchanged zeolites in which the chromium is also coordinated by three oxygen atoms of the zeolite. In this paper we will demonstrate that this latter nitrosyl complex is also formed on silica, and that the epr and infrared spectra of the complex may be used to determine the concentration of isolated Cr(III) ions on the surface. Furthermore, the evidence suggests that those chromium ions which form the nitrosyl complex are also those ions responsible for ethylene polymerization.

EXPERIMENTAL

Materials. The CrO_3 and $CrCl_3 \cdot 6H_2O$ employed in this study were certified grade supplied by Fisher Scientific. The silica gel was a 28 mesh Davison granular I. D. gel, having a surface area of 300m^2 g^{-1}. The CO, O_2, N_2, NO, and C_2H_4 gases were supplied by Matheson. All except NO and C_2H_4 were ultra-high purity grade, and were used directly. The C_2H_4 was purified using the freeze-pump technique whereby the ethylene was frozen at the boiling point of *n*-pentane (−135°C). Nitrogen-15-labeled NO supplied by Stohler Isotope Chemicals was purified similarly.

Sample preparation. A silica-supported chromium(VI) catalyst was prepared by impregnating the silica gel with 0.02 *M* chromic acid solution. The gel was dried in air at 110°C, rinsed with deionized H_2O, and dried again. The resulting concentration of chromium in the gel was determined to be 0.42 weight percent by standard chemical methods.

In a similar manner a supported chromium(III) catalyst was prepared by impregnating the silica gel with aqueous 0.02 *M* $CrCl_3 \cdot 6H_2O$. After drying the gel at 110°C, chemical analysis revealed a chromium concentration of 0.48 weight percent. The low chromium concentration was used to minimize the formation of bulk phase Cr_2O_3 or other cluster forms of chromium and to avoid diffusional limitations. In this regard a linear relationship has been demonstrated between catalytic activity and chromium loading below 2.5 weight percent (*18*). Neutron activation analysis of a sample degassed at 350°C (see below) revealed a chloride ion concentration of 0.031 weight percent which is less than 0.1 chloride ion per chromium ion in the catalyst.

Spectroscopic methods. The epr spectra were obtained with a Varian E6S spectrometer at a microwave frequency of 9.1 GHz. The spectra were recorded with the sample at −196°C. The g values and spin concentrations were calculated relative to a phosphorus-doped silicon standard. The spin concentrations were calculated by comparison of the doubly integrated sample and standard spectra (*19*).

A Beckman IR-9 spectrophotometer was used to obtain the infrared (ir) spectra. Samples were prepared by grinding the catalyst to a powder and pressing it into wafers typically 2 to 10 mg cm^{-2}. Samples were individually pretreated in a Pyrex cell fitted with KCl windows. The absorbance of gas phase NO at 1876 cm^{-1} served as a frequency standard. Absorbance spectra allowed the measurement of the optical density of observed bands. Band intensities were determined from the half-height band width multiplied by the peak height.

Kinetics. The initial activity of catalyst samples was determined from the rate of ethylene consumption usually in a static system (ca. 200 mL), although in one experiment a closed recirculating reactor was employed. Samples of 300 mg were placed in a cylindrical fused-quartz reactor and activated in the manner described in the subsequent section. The temperature was monitored by means of a thermocouple which was positioned in a well extending into the shallow catalyst bed.

Prior to the polymerization reaction, the catalyst bed was cooled to 0°C with an ice-water bath. When ethylene was admitted into the reactor the ice-water bath was exchanged with a 24°C bath. The precooling of the sample was intended to compensate for the heat of adsorption of ethylene. The temperature of the catalyst bed increased to 24°C in <1 min when ethylene was admitted into the chamber. The reaction rate was therefore determined at 24°C and at an initial C_2H_4 pressure of 300 ± 1 Torr. The physical adsorption of ethylene on degassed silica gel was found to be negligible under these conditions.

The decrease in total pressure was plotted as a function of time, and the initial rate of reaction was determined by a numerical method which was capable of splining several different functions to obtain the best theoretical fit. In this particular application a single knot was chosen as the point where the linear rate of ethylene consumption began to decrease. The slope was computed for the theoretical curve at various intervals, and the slope at zero time was chosen as the initial rate of reaction.

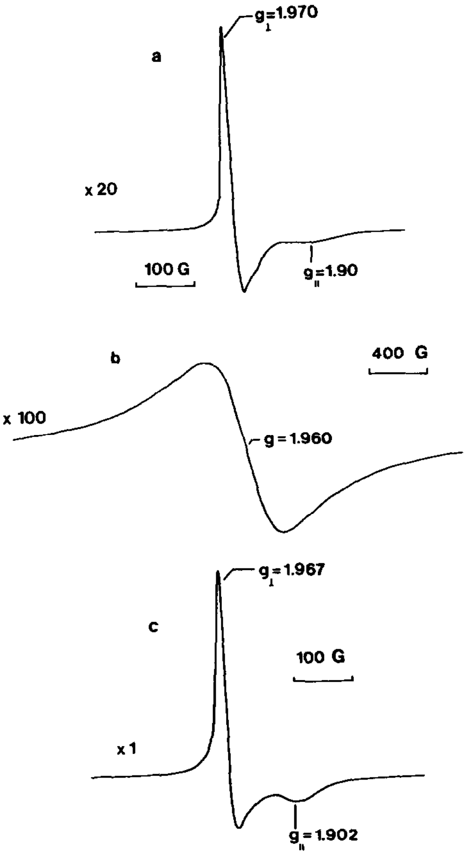

FIG. 1. Epr spectra of chromium on silica gel: (a) Cr(VI)/SiO_2 sample heated *in vacuo* at 400°C for 4 hr; (b) Cr(VI)/SiO_2 sample reduced in CO at 400°C; (c) sample b exposed to 10 Torr NO at 25°C for 1 hr, and gas phase NO removed.

RESULTS

Spectroscopic Studies

A 200 mg sample of the catalyst prepared from chromic acid was activated by heating *in vacuo* to 400°C over a period of 4 hr, and by maintaining the catalyst at that temperature for an additional 4 hr. Similarly, other samples were activated at 300, 350 and 450°C, and in each case, a weak axial epr signal with $g_\perp = 1.970$ and $g_\parallel = 1.90$ was observed (Fig. 1a). The signal originating from the yellow catalyst has been attributed to chromium(V), or γ-phase chromium ions (*5*, *20*). Samples activated at 500 and 600°C appeared yellow-green in color, and exhibited a fivefold increase in the epr signal intensity.

In marked contrast, if the chromic acid derived material was degassed for several hours at 25°C, at 100°C for 3 hr, at 250°C for 3 hr, and then at the final activation temperature for 4 hr, the sample readily attained the yellow color but failed to exhibit a Cr(V) epr spectrum, even at final activation temperatures of 500 and 600°C. Activated samples were subsequently heated in the presence of 200 Torr of O_2 at 400°C for 6 hr. The resulting yellow catalyst exhibited no epr signal, and it was concluded that the majority of chromium ions were in the (VI) oxidation state.

Chromium(VI) supported on silica has been reduced to a variety of lower oxidation states by pretreating the catalyst with CO, H_2, C_2H_4, and other olefins (*7, 21, 22*). Reduced samples are not homogeneous with respect to chromium oxidation state, but contain a distribution of several oxidation states and phases (*14, 16*). This was evident in the present study by the appearance of several different signals from a single sample. Two of these signals, classified by Poole and McIver (*20*) as δ-phase and β-phase ions, arise from isolated chromium(III) and clustered chromium(III) ions, respectively. The distribution of ions in the several possible states was controlled by varying the contact time between the catalyst and reducing agent. This technique was previously used by Eley *et al.* (*7, 22*). The reducing agent used exclusively in the present study was CO. The use of H_2 or olefins was avoided since one of the products of reduction would be H_2O, which is capable of further reaction with supported chromium.

A sample originally containing chromium(VI) was activated at 350°C and reduced by exposure to 50 Torr of CO at 400°C for 30 min. At the end of the reduction period, the sample was degassed for 1 hr at 400°C in order to remove CO_2 along with unreacted CO. This degassing procedure was adopted for all subsequent reduction pretreatments. The epr spectrum of this particular sample displayed a rather broad, symmetric absorption with a line width of 300–400 G and $g = 1.96$ (Fig. lb). The spectrum is characteristic of clustered chromium(III) ions, or the β-phase (*20*). The spectrum of isolated chromium(III) ions in a distorted octahedron (δ-phase) with $g = 3.9$ and line width of 200 G was present but weak (*23*). For this sample, the chromium(V) signal was weak; however, as evident from the results shown in curve a of Fig. 2, at shorter reduction times a higher intensity chromium(V) signal was observed. The concentration of Cr(V) went through a maximum after ca. 3 min of reduction.

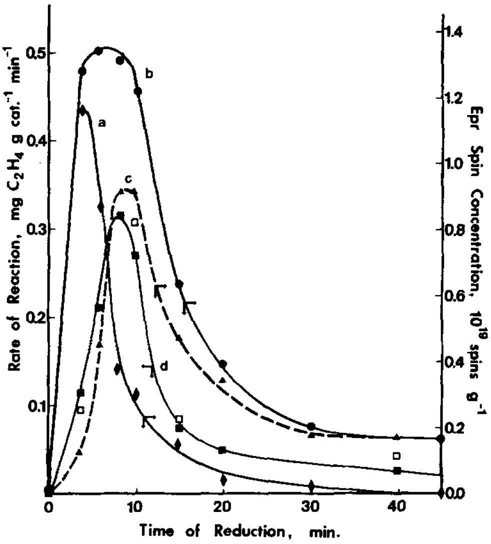

FIG. 2. Variation of spin concentration and catalytic activity for $Cr(VI)/SiO_2$ sample as a function of reduction time at 400°C: (a) spin concentration of Cr(V); (b) spin concentration of composite signal observed after exposure to NO; (c) spin concentration of $[Cr^{III}(NO)_2]^{3+}$ obtained by subtracting curve a from curve b; (d) polymerization activity; ■, samples degassed at 350°C; □, samples degassed at 700°C.

A sample originally containing chromium(VI) was activated at 350°C and After an hour, a strong epr spectrum was observed with $g_\perp = 1.967$ and $g_\parallel = 1.902$ (Fig. 1c). Brief evacuation of the gas phase NO resulted in a slight increase in the epr signal which was expected since gas phase NO is paramagnetic. Prolonged evacuation at 25°C failed to change the axial signal further. Following the adsorption of NO on a partially reduced sample of chromium on alumina a comparable epr signal was observed and attributed by Shelef (*16*) to the $[Cr^{(I)}(NO^+)]^{2+}$ complex. We will subsequently argue that the complex is actually $[Cr^{III}(NO)_2]^{3+}$.

It was noted that the intensity of the epr signal (Fig. 1c) also varied with the period of CO reduction. Individual samples which initially contained only chromium(VI) were activated at 350°C, and exposed to 50 Torr of CO at 400°C for different lengths of time. The spin concentration of Cr(V) was first determined, and after the addition of NO the total spin concentration of Cr(V) and $[Cr^{III}(NO)_2]^{3+}$ was determined from the overlapping spectra. The variation in this spin concentration with reduction time is shown by curve b of Fig. 2. By subtracting the spin concentration due to Cr(V) from the total, the spin concentration of the $[Cr^{III}(NO)_2]^{3+}$ complex was obtained, and this is depicted by curve c of Fig. 2. After 8 min of reduction the contribution of the Cr(V) signal to the spectrum was relatively small, and the concentration of $[Cr^{III}(NO)_2]^{3+}$ went through a maximum. The spin concentration of $[Cr^{III}(NO)_2]^{3+}$ at this maximum corresponded to 20% of the total chromium in the catalyst. Following 2 hr of reduction and subsequent NO treatment no epr spectrum due to Cr(V) or $[Cr^{III}(NO)_2]^{3+}$ was observed.

Similar epr signals were also observed for catalysts prepared from $CrCl_3 \cdot 6H_2O$. A sample of Cr(III) on silica was degassed at 25°C, and activated *in vacuo* at 350°C for 5 hr; no reduction step was incorporated. The characteristic β-phase and δ-phase signals were observed. Exposure to 10 Torr of NO for 1 hr yielded the anisotropic epr spectrum exhibited in Fig. 1, curve c, and brief evacuation resulted in a twofold increase in the signal to 1.9×10^{19} spins g^{-1}, which was equivalent to 40% of the total chromium present.

The amount of Cr(III) on the surface, estimated from the concentration of $[Cr^{III}(NO)_2]^{3+}$ complexes, was determined after oxidation or reduction of the catalysts. Again, individual samples were activated at 350°C, and then the catalysts were exposed to either 50 Torr of O_2 or CO at 400°C for different lengths of time. After the addition of 10 Torr of NO, followed by brief evacuation, the epr spectra were recorded. Oxidation resulted in the appearance of the Cr(V) signal, and as described previously, the spin concentration due to Cr(V) was subtracted from the total spin concentration to give the concentration of $[Cr^{III}(NO)_2]^{3+}$. Following reduction no interfering spectrum of Cr(V) was observed. The spin concentration of $[Cr^{III}(NO)_2]^{3+}$ is plotted in Fig. 3 as a function of the time of oxidation or reduction. It is evident that both treatments resulted in a significant decrease in the concentration of the complex, which in turn reflects the concentration of Cr(III). After 60 min of oxidation or 120 min of reduction the complex concentration was below the limits of detection, which was four orders of magnitude less than the initial concentration.

It was also possible to oxidize the Cr(III) with NO, but not at temperatures below 100°C. When a sample containing the $[Cr^{III}(NO)_2]^{3+}$ complex was heated under vacuum at 50 and 100°C, the spin concentration decreased with half-lives of 15 and 60 min, respectively, and no Cr(V) signal was observed. Removal of the NO at

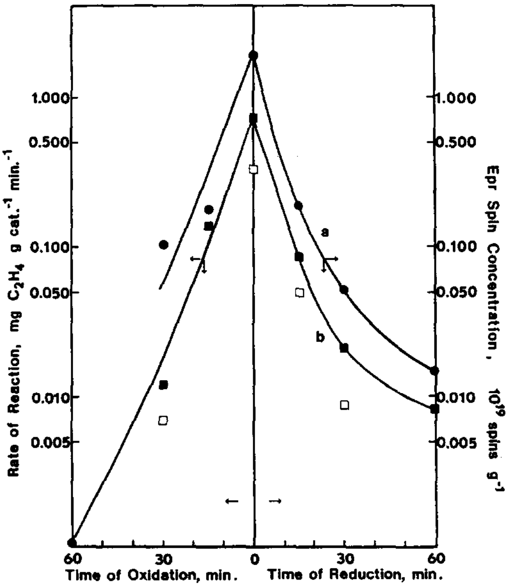

FIG. 3. Variation of spin concentration and catalytic activity for $Cr(III)/SiO_2$ sample as a function of oxidation or reduction at 400°C; (a) spin concentration of $[Cr^{III}(NO)_2]^{3+}$; (b) polymerization activity; ■, samples degassed at 350°C; □, samples degassed at 700°C.

300°C, however, resulted in the formation of a more intense signal which is attributed to Cr(V). The spin concentration of this signal was equivalent to 80% of the chromium in the sample.

In the study of the chromium–nitrosyl complex in zeolites the comparison between the epr and infrared spectra played a major role in the identification of the species as a dinitrosyl complex. It was of interest to compare the results of the two spectroscopic techniques in the present study. In the region of interest (1600–2000 cm^{-1}) two rather broad bands at 1650 and 1880 cm^{-1} were observed for the silica gel. These bands are commonly observed in studies of silica-supported metals, and have been attributed to overtones of the Si–O stretching mode (*7, 24, 25*). Exposure to NO resulted in the appearance of two bands at 1753 and 1880 cm^{-1} (Fig. 4). The bands could be destroyed only by evacuation at temperatures ≥ 50°C. The frequencies of the bands are consistent with the symmetric and asymmetric stretching modes observed in dinitrosyl complexes (*24*).

It was found that the bands were related and that they could be correlated with the chromium–nitrosyl epr signal. Two samples of chromium(III) on silica were activated, one in a reactor equipped with an epr side arm and the other as a wafer in the ir cell. After the simultaneous addition of identical doses of NO (190 nmole) to the samples, the epr and infrared spectra were recorded. The spin concentration of the chromium–nitrosyl complex is compared with the corresponding intensity of the 1753 cm^{-1} band in Fig. 5. The correlation leaves little doubt that both the epr spectrum and the infrared doublet arise from the same complex. Moreover, a comparison of the intensity of the 1753 and 1880 cm^{-1} modes (figure not shown) indicates the association of the two infrared bands.

The use of nitrogen-15-labeled NO shifted the bands 30 cm^{-1} to lower frequencies, 1720 and 1845 cm^{-1}. The latter band appeared only as a shoulder on the strong SiO_2 background band. The infrared spectrum of NO adsorbed on a well-reduced sample in which the chromium presumably was present as Cr(II) exhibited a pair of bands at 1745 and 1875 cm^{-1}, which were shifted 8 and 5 cm^{-1}, respectively, from those of NO complexed with chro-

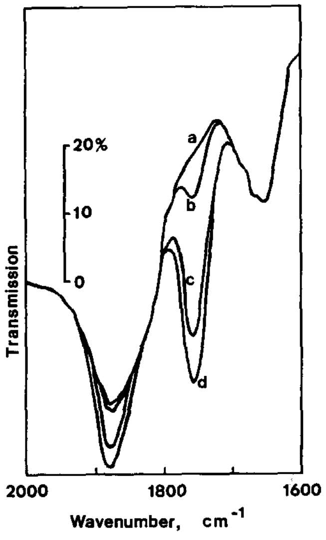

FIG. 4. Infrared spectrum of $[Cr^{III}(NO)_2]^{3+}$ complex on silica gel: (a) background; (b)–(d) after successive additions of 190 nmole of nitric oxide.

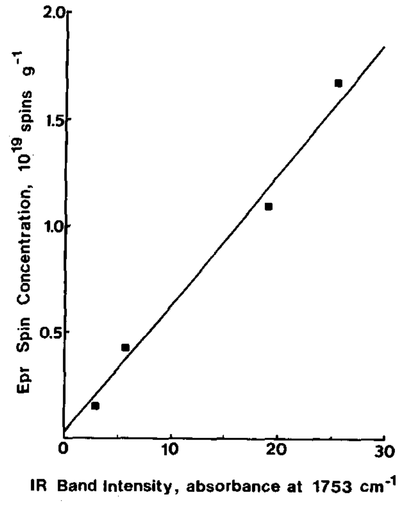

FIG. 5. Epr spin concentration versus infrared band area after successive additions of 190 nmole of NO to an activated $Cr(III)/SiO_2$ sample.

TABLE 1

Comparison of the Infrared Absorption Bands (cm^{-1})

Support	Adsorbed species			Reference
	$[Cr^{III}(^{14}NO)_2]^{3+}$	$[Cr^{III}(^{15}NO)_2]^{3+}$	$[Cr^{II}(^{14}NO)_2]^{3+}$	
SiO_2	1880, 1753	1845[a], 1723	1875, 1745	This work
SiO_2	1880, 1755	— —	1865,1747	*24*
NaY zeolite	1900, 1775	1870, 1745	— —	*17*
NaX zeolite	1895, 1770	1865, 1740	1880, 1763[b]	*17*

[a] Approximate value because the band appears as a shoulder on the background spectrum.

[b] Alternatively, these bands may be due to Cr^{III} in another site.

mium(III). These infrared results are summarized in Table 1.

Polymerization Activity of Chromium on Silica

Individual samples, initially consisting of chromium(VI) on silica, were activated at 350°C and reduced in 50 Torr of CO at 400°C for different lengths of time. Typical reaction curves describing the change of C_2H_4 pressure with time appear in Fig. 6. In each instance the rate of change in pressure gradually decreased to zero with time. The initial activity of each sample for the polymerization of ethylene was determined and compared with the time of reduction pretreatment. As depicted in Fig. 2, curve d, the initial reaction rate passed through a maximum after about 8 min of reduction with CO. Reduction for 120 min resulted in a catalyst which had no measurable activity. A similar procedure was used with supported chromium(III) samples reduced in 50 Torr of CO at 400°C or oxidized in 50 Torr O_2 at 400°C. The activity in this instance decreased both with reduction and with oxidation as shown in Fig. 3, curve b, and listed in Table 2.

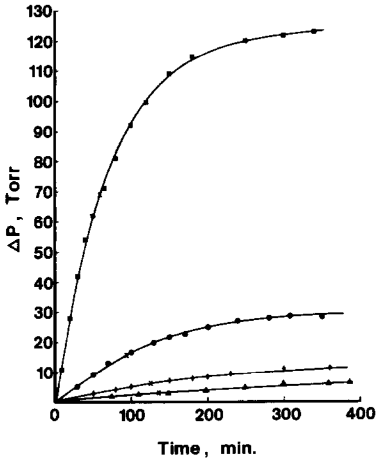

FIG. 6. Decrease in ethylene pressure versus time of reaction for $Cr(III)/SiO_2$ samples: (a) activated at 350°C *in vacuo;* (b) reduced in CO for 15 min; (c) 30 min; (d) 60 min. The solid line is the curve determined from the splining calculation; x denotes the location of the knot.

The rate of polymerization for the most active Cr(III) sample was obtained at 24°C in a recirculating system to determine whether the reaction was diffusion controlled. The initial rate of polymerization was found to be 0.77 mg C_2H_4 $gcat^{-1}$ min^{-1}, compared to a rate of 0.72 mg C_2H_4 $gcat^{-1}$ min^{-1} for the same catalyst in the static reactor. Since the two values are within experimental error, external diffusion was not rate limiting.

The most obvious explanation for the rate maximum observed in Fig. 2, curve d, is that the active site for polymerization is some intermediate oxidation state between Cr(VI) and Cr(II) and that extensive reduction to Cr(II) results in an inactive catalyst. One might argue, however, that the decrease in activity is due to the formation of Cr_2O_3 which is promoted by water in the system (*2*). The water could be derived

TABLE 2

Spin Concentration of Cr(III) and Catalytic Activity of Samples Initially Containing Cr(III)

Pretreatment[a]	$[Cr^{III}(NO)_2]^{3+}$ epr spin concentration (10^{19} spins/g)	Percentage of total Cr	Reaction rate (mg C_2H_4/g cat min)	TOF[d] (molec/site sec)
No reduction	1.93	40	0.72	0.013
15 min reduction[b]	0.190	3.9	0.085	0.016
30 min reduction	0.0518	1.1	0.022	0.015
60 min reduction	0.0148	0.31	0.0082	0.020
120 min reduction	0.0017	0.035	0.001	0.02
15 min oxidation[c]	0.173	3.6	0.136	0.028
30 min oxidation	0.0981	2.0	0.014	0.005
60 min oxidation	<0.0001	<0.002	<0.001	

[a] Separate samples degassed at R.T. for 6 hr, then activated at 350°C *in vacuo*.

[b] Reduced in 50 Torr CO at 400°C.

[c] Sample initially containing Cr^{III} oxidized in 50 Torr O_2 at 400°C.

[d] Site based on epr spin concentration of $[Cr^{III}(NO)_2]^{3+}$.

from hydroxyl groups on the silica which were not effectively removed upon evacuation at 350°C.

In order to test this hypothesis several samples initially containing chromium(VI) were pretreated and reduced in CO in the manner described previously, except that an evacuation temperature of 700°C was used. The activity toward ethylene polymerization was determined and compared (open squares in Fig. 2, curve d) with the activity of samples activated at 350°C. Clearly, there is no significant difference in the activity of catalysts prepared by the two pretreatments. The same experiment was conducted using the trivalent chromium catalyst, and the results are depicted by the open squares in Fig. 3. The polymerization rates for these catalysts were somewhat less than those observed for the catalysts activated at 350°C, but the trends with respect to oxidation and reduction were the same. Thus, water is not responsible for the decrease in activity upon reduction.

To further test the hypothesis that Cr_2O_3 was not formed during reduction a sample of chromium(VI) on silica was thoroughly reduced in 200 Torr of CO at 400°C for 3 hr, oxidized to chromium(VI) in 200 Torr of O_2 at 400°C for 12 hr, and again reduced in 50 Torr of CO at 400°C for 8 min to the point of maximum activity. The rate of polymerization determined for this catalyst was observed to be 0.26 mg C_2H_4 $gcat^{-1}$ min^{-1}, which was comparable to 0.32 mg C_2H_4 $gcat^{-1}$ min^{-1}, observed for a chromium(VI) catalyst that had been reduced in 50 Torr of CO at 400°C for 8 min. This reversibility seems unlikely if a bulk Cr_2O_3 phase was formed during reduction.

Characterization of the Polymer

A sample of chromium(III) on silica in the form of a wafer was activated in the infrared cell, and C_2H_4 was admitted at 25°C. After the polymerization reaction had occurred, the infrared spectrum of the product on the support exhibited doublets at 2920 and 2853 cm^{-1} and at 732 and 720 cm^{-1}. In addition, a band with low frequency shoulders appeared at 1465 cm^{-1}.

The product was recovered from the catalysts used in previous kinetics experiments with *p*-xylene solvent. The residue was weighed and redissolved in *p*-xylene. Using an Ostwald apparatus, the intrinsic viscosities were determined for several concentrations at 105°C. From the intrinsic viscosities an average molecular weight of 6000 ± 1000 g $mole^{-1}$ was determined.

DISCUSSION

Identification of the Chromium–Nitrosyl Complex

Since a correct assignment of the chromium–nitrosyl complex observed in this work is essential for the identification of the active site for polymerization, considerable discussion will be devoted to this topic, particularly in view of the assignment of a similar epr spectrum to $[\mathrm{Cr^{I}(NO^{+})}]^{2+}$ by Shelef (*16*), and by others who have followed (*26*). In a related study from this laboratory, Pearce *et al.* (*17*) have investigated the formation of a chromium–nitrosyl complex in a Y-type zeolite which had been exchanged with Cr(III) ions and degassed under vacuum at elevated temperatures. The advantages of this system are (i) that the infrared spectrum is dominated by a single nitrosyl complex which is not perturbed by a large background spectrum of the support, and (ii) that metal ions take up well defined sites. Based upon the latter advantage, molecular orbital calculations have been carried out on models of chromium in several oxidation states coordinated to three oxygen atoms of the zeolite and one or two nitrosyl ligands (*17*). These calculations lead to the conclusion that the unpaired electrons in a linear $[\mathrm{Cr^{I}(NO^{+})}]^{2+}$ complex would be in a degenerate ground state which would not give rise to the observed epr spectrum, although a bent nitrosyl complex may not be excluded. For $[\mathrm{Cr^{III}(NO)_2}]^{3+}$ the calculations are consistwith an $S = \frac{1}{2}$ spin state, and the theoretical *g* values were in good agreement with the experimental values. Although the complex is written as $[\mathrm{Cr^{III}(NO)_2}]^{3+}$, the ligands possess fractional positive charge corresponding to an effective chromium charge of +2.4. The *g* values for the chromium–nitrosyl complexes on alumina, silica, and zeolites are compared in Table 3.

Perhaps the most straightforward evidence for the assignment of the complex on silica to a Cr(III) species is the observation that a maximum signal was observed when the sample was prepared from a Cr(III) salt, followed by simple degassing of the catalyst under vacuum. Moreover, as shown in Fig. 3, either oxidation or reduction of the sample before addition of NO caused a large decrease in the concentration of the complex. Here it is important to emphasize that the maximum concentration of the complex constitutes ca. 40% of the total chromium

TABLE 3

Comparison of the Epr Parameters

Support	Cr(V) (γ-phase)		Cr(III) (δ-phase)		Cr(III) (β-phase)		$[\mathrm{Cr^{III}(NO)_2}]^{3+}$		Reference
	$g_\perp$	$g_\parallel$	g	width (G)	g	width (G)	$g_\perp$	$g_\parallel$	
SiO_2	1.970	1.90	3.9	~200	1.96	~400	1.967	1.902	This work
SiO_2	1.980	1.90	3.8	~200	1.98	~400	—	—	*15*
SiO_2	1.98	1.90	—	—	—	—	—	—	*6*
γ-Al_2O_3	1.970	1.90	3.8	~200	1.98	~400	—	—	*20*
Al_2O_3	—	—	—	—	—	—	1.982[a]	1.92[a]	*16*
NaY, NaZ zeolites	—	—	—	—	—	—	2.000[a]	1.917[a]	*26*
NaY zeolite	1.991	1.910, 1.883	—	—	~2.0	Several hundred	2.000	1.895	*17*
NaX zeolite	1.985	1.985	—	—	~2.0	Several hundred	2.001	1.906	*17*

[a] Assignment based on conclusions of this study and Ref. (*17*).

in the sample, thus one is not observing a phenomena which is related to only a minor fraction of the total chromium.

The behavior of the samples with respect to reduction was particularly significant since it is generally accepted that chromium may not be reduced with CO to oxidation states lower than Cr(II). If this is true, then the maxima in Fig. 2, curve c, and Fig. 3, curve a, must be due to a higher oxidation state, which for the sample of Fig. 3 is logically Cr(III).

The spectrum of Fig. 1c also requires that the paramagnetic ions be isolated from one another by distances greater than ca. 10Å. For the samples prepared from Cr(VI)/SiO_2 it is conceivable that the paramagnetic chromium was associated, perhaps through bonding oxygens, with diamagnetic Cr(IV) or Cr(VI); however, for the Cr(III)/SiO_2 samples this seems to be an unlikely situation because the epr spectra do not exhibit the presence of strong magnetic dipole interactions. Since the epr spectra were identical for both types of samples, we conclude that the chromium which formed the nitrosyl complex was indeed isolated on the silica surface.

Another important clue in the identification of the complex comes from the infrared data. In the present work it was observed that the bands were formed and destroyed concomitantly, both with respect to each other and with respect to the epr spectrum of the nitrosyl complex. With the CrY zeolite, mixtures of ^{14}NO–^{15}NO were used to confirm that the vibrational modes of the ligands were strongly coupled (*17*). This evidence, together with the wavenumbers of the bands, confirms that the spectrum is due to a geminal dinitrosyl complex. In a study of chromium on silica Zecchina *et al.* (*24*) previously observed a pair of nitrosyl bands at the same wavenumbers as reported in this study and concluded that they were due to a chromium(III)–dinitrosyl complex. In addition, this group observed a pair of bands in a more completely reduced sample at 1747 and 1865 cm^{-1}, which they attributed to a $[Cr^{II}(NO)_2]^{2+}$ complex. This shift to lower wavenumbers was also noted in the present study. Moreover, no band due to a mononitrosyl complex was observed in the reduced samples, which indicates that both Cr(II) and Cr(III) on silica favor the formation of dinitrosyl complexes.

The Nature of the Active Site

Upon comparing the polymerization activity with the concentration of $[Cr^{III}(NO)_2]^{3+}$ complexes one finds that there is a remarkable correlation. Here it is important to recall that NO was only used as a probe molecule and that the samples used in the catalytic experiments had not been exposed to nitric oxide. From a comparison of curves c and d of Fig. 2, it is evident that an 8 min reduction of Cr(VI)/SiO_2 by CO resulted in maxima for both the activity and the $[Cr^{III}(NO)_2]^{3+}$ concentration, but the concentration of Cr(V) went through a maximum at a significantly shorter reduction time. After 8 min of reduction the turnover frequency (TOF) for polymerization based on the concentration of $[Cr^{III}(NO)_2]^{3+}$, was 0.013 molecule $site^{-1}$ sec^{-1}.

A more convincing quantitative relationship was found upon reduction of the Cr(III)/SiO_2 sample, since the Cr(V) spectrum did not interfere with the spectrum of $[Cr^{III}(NO)_2]^{3+}$. As shown in Table 1 the TOF for the set of experiments remained constant, within experimental error, over a two order of magnitude decrease in concentration of Cr(III) and reaction rate. Moreover, the initial TOF of 0.013 molecule $site^{-1}$ sec^{-1} was identical to the maximum TOF found upon reduction of the Cr(VI)/SiO_2 catalyst. Oxidation of the Cr(III)/SiO_2 sample likewise resulted in a significant decrease in both the catalytic activity and the concentration of Cr(III).

From the asymptotic values of polyethylene formed, as determined from the curves of Fig. 6, and from the concentration of active Cr(III), a turnover number of 230 molec site^{-1} was calculated. This is in good agreement with the average molecular weight of 6000 g/mole, which suggests that a single polymer chain grows at each active site until termination occurs. The infrared spectrum is consistent with the formation of linear polyethylene (*27*).

Involvement of chloride ions in the active site can be discounted since these ions were effectively removed prior to the use of the catalyst in the polymerization reaction. Thus we conclude that the active sites for polymerization are isolated chromium(III) ions which are coordinated only to the silica lattice. At least two, and perhaps three (*24*), coordination sites are available for coordination to ethylene and intermediates in the polymerization reaction. The results of this study indicate that no other oxidation states or coordinated forms of chromium on silica are active in polymerization, at least at the low temperatures and pressures used in these experiments.

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