JOURNAL OF CATALYSIS 99, 140–148 (1986)

Silica-Supported Chromium Catalysts for Ethylene Polymerization: The Active Oxidation States of Chromium

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Received August 6, 1985; revised January 3, 1986

The reduction of Cr(III)/SiO_2 to Cr(II)/SiO_2 with CO led to a change in the kinetically significant site for the polymerization of ethylene at low temperatures and pressures. Cr(III)/SiO_2 displayed higher activity than Cr(II)/SiO_2 over the same range of reaction temperatures. Cr(II)/SiO_2 catalysts were characterized by a sharp falloff in polymerization activity at temperatures <40°C. Activation energies for polymerization over Cr(III)/SiO_2 and Cr(II)/SiO_2 were 10.6 and 17.1 kcal mole^{-1}, respectively. Hydrogen sulfide poisoning of Cr(III)/SiO_2 and Cr(II)/SiO_2 indicated that the active fraction of Cr was 13 and 34% of the total chromium, respectively. Infrared spectra of adsorbed CO and NO suggest that the active sites on Cr(II) catalysts are C-type Cr(II) ions with at least two vacant coordination positions available for the growing polymer chain and the monomer. Thermal activation of Cr(II)/SiO_2 catalysts at 700°C (*in vacuo*) resulted in both an increase in the concentration of C-type Cr(II) ions and polymerization activity. A decrease in the activation energy of ethylene polymerization for Cr(II)/SiO_2(700) and a blue shift in the infrared band associated with the nitrosyl complex of this species suggest that the thermal treatment modified the surface coordination of these ions. Most importantly, thermal activation of Cr(II)/SiO_2 produced a Cr(II) catalyst which is active for ethylene polymerization at 25°C. © 1986 Academic Press, Inc.

INTRODUCTION

The technological importance of chromium supported on silica gel as a catalyst for ethylene polymerization has stimulated numerous studies to determine the nature of the active sites. In recent years the groups working in the field have been almost equally divided between the proponents of Cr(II) (*1–3*) and those who favor Cr(III) (*4–8*) as the active valence state. Rebenstorf (*3, 7*) recently suggested that both Cr(II) and Cr(III) might play a role as active sites for ethylene polymerization, with the kinetically significant site being determined by reaction conditions. Although the subsequent results will show that the conclusions of Rebenstorf are essentially correct, experimental difficulties obscure the interpretation of his data. For example, the reaction involved a solid catalyst and ethylene at sufficiently high pressures (500 Torr) so that a thermal excursion occurred; i.e., the reaction was not isothermal. In addition, CO reduction, presumably to Cr(II)/SiO_2, was at 350°C—a temperature at which reduction to Cr(II) is incomplete; and Cr(III)/SiO_2 was formed by reaction of Cr(II)/SiO_2 with H_2O and O_2—conditions which result in higher oxidation states of chromium as well as α-Cr_2O_3.

In view of the controversy between Cr(II) and Cr(III) as the significant oxidation state and the ambiguities in the data of Rebenstorf, the activities of Cr(II)/SiO_2 and Cr(III)/SiO_2 catalysts were explored over a range of temperatures, using catalysts prepared by several techniques. Since a paper describing the activity of Cr(III)/SiO_2 has recently been published from this laboratory (*8*), the present work focuses mainly on Cr(II)/SiO_2.

EXPERIMENTAL

Materials. The support material was Davison grade 952MS silica. All gases used in this study were obtained from Matheson. Carbon monoxide (ultrahigh purity grade)

0021-9517/86 $3.00

TABLE I

Summary of Pretreatments Used in the Preparation of Cr/SiO_2 Catalysts

Catalyst	Pretreatment
$Cr(III)/SiO_2$	Heating *in vacuo* to 900°C
$Cr(II)/SiO_2$	Heating *in vacuo* to 900°C, followed by reduction in CO at 400°C for 1 hr
$Cr(II)/SiO_2(700)$	Same as that for $Cr(II)/SiO_2$, followed by heating *in vacuo* at 700°C for 2–4 hr

was further purified by passage through a reduced Cr/SiO_2 column to remove traces of oxygen. Oxygen (extra-dry grade) was used directly. Ethylene (CP grade) was purified using the freeze–pump technique. Nitric oxide and hydrogen sulfide (both CP grade) were purified by vacuum distillation and freeze-pumping at liquid-nitrogen temperatures.

Catalyst preparation. An extensive description of techniques used in the preparation and pretreatment of $Cr(III)/SiO_2$ catalysts has been provided elsewhere (*8*). The $Cr(II)/SiO_2$ catalysts were prepared by reduction of 0.11 wt% $Cr(III)/SiO_2$ (activated at 900°C *in vacuo*) and 0.3 wt% $Cr(VI)/SiO_2$ (activated at 900°C *in vacuo* followed by oxidation with 200 Torr O_2 at 500°C) with 100 Torr CO for 1 hr at 400°C (Table 1). Catalyst samples were outgassed for 30 min at 400° to remove residual CO and CO_2. An additional treatment on some samples of $Cr(II)/SiO_2$ involved heating to 700°C *in vacuo* for up to 4 hr. These thermally treated Cr(II) catalysts are denoted as $Cr(II)/SiO_2(700)$ (Table 1).

Polymerization kinetics. Low-pressure polymerization studies were performed under static shallow-bed conditions. Catalyst samples were contacted with 100 Torr of C_2H_4 at various temperatures. Temperature control during the polymerization reaction was achieved by precooling the catalyst bed 10–15°C below the desired reaction temperature. Upon exposure to ethylene the temperature rapidly increased to the reaction temperature and thereafter remained constant. 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, which is reported throughout.

Spectroscopic methods. Infrared (IR) spectra were obtained using a Perkin–Elmer Model 580 B spectrophotometer. Spectra were recorded at ambient temperature. Samples were prepared by pressing the catalyst into wafers of typically 10–15 mg cm^{-2}. Samples were pretreated in a fused silica cell equipped with KCl windows. All IR spectra were normalized to a constant wafer density of 10 mg cm^{-2}.

RESULTS

Polymerization kinetics. Catalysts containing chromium(III), denoted $Cr(III)/SiO_2$, displayed a straight-line fit to the Arrhenus equation in the temperature range of 0 to 60°C (Fig. 1A). An extensive examination of the temperature dependence for this catalyst in the range of 0 to 120°C has been described elsewhere (*8*). The region from 25

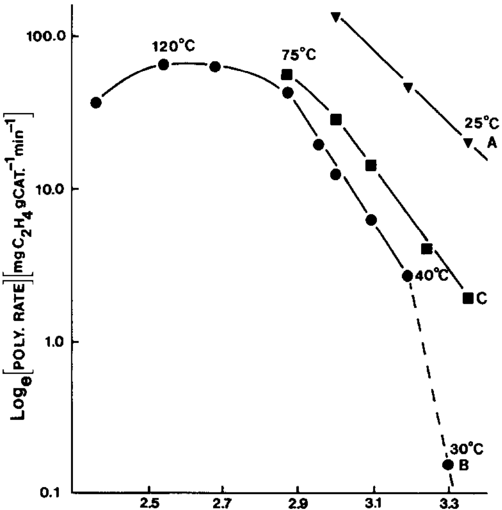

FIG. 1. Arrhenius plots for Cr/SiO_2; (A) $Cr(III)/SiO_2$, (B) $Cr(II)/SiO_2$, (C) $Cr(II)/SiO_2(700)$.

TABLE 2

Arrhenius Activation Energies for Ethylene Polymerization with Cr/SiO_2 Catalysts

Catalyst	E_a (kcal/mole)
$Cr(III)/SiO_2$	10.6 ± 0.5[a]
$Cr(II)/SiO_2$	17.1 ± 0.5[b]
$Cr(II)/SiO_2(700)$	15.5 ± 0.5[c]

[a] Temperature range 0 to 60°C.
[b] Temperature range 40 to 75°C.
[c] Temperature range 25 to 60°C.

to 60°C is shown here for comparitive purposes, and the activation energy obtained over this temperature range is 10.6 kcal $mole^{-1}$ (Table 2). The reduction of $Cr(III)/SiO_2$ with CO (400°C) produced catalysts containing >98% Cr(II) (*8*). These $Cr(II)/SiO_2$ catalysts displayed kinetic properties which were strikingly different from their Cr(III) precursors. The $Cr(II)/SiO_2$ catalysts were characterized by a complex dependence on reaction temperature which is best described by considering three regions (Fig. 1B). The temperature range of principle interest was from 40 to 75°C, where a good fit to the Arrhenius equation was obtained; the apparent activation energy was 17.1 kcal $mole^{-1}$ (Table 2). The activation energy for ethylene polymerization over $Cr(II)/SiO_2$ catalysts was independent of the starting valence of Cr. At temperatures >75°C the dependence became nonlinear, and in the extreme a region of positive slope was observed for temperatures >120°C. By contrast, a precipitous decrease in activity was observed at reaction temperatures <40°C, and these catalysts displayed no measureable activity at 25°C. A first order dependence on metal content was displayed by $Cr(II)/SiO_2$ catalysts containing up to 0.3 wt% Cr when the reaction was carried out at 50°C.

Hydrogen sulfide poisoning and the active site concentration. The number of catalytically active sites present on Cr(III) and Cr(II) catalysts was examined by titrative poisoning using hydrogen sulfide (Fig. 2). The adsorption of H_2S on active Cr(III) and Cr(II) catalysts had a marked effect on their catalytic activity. Both catalysts displayed a sharp decrease in activity on adsorption of H_2S. An estimate to the number of active centers was obtained from the abscissa intercept of the line which describes the loss of activity versus H_2S adsorbed. Each mole of hydrogen sulfide adsorbed was taken to be equal to 1 mole of active sites. The $Cr(III)/SiO_2$ catalysts revealed an active site concentration of 1.6×10^{18} sites g cat^{-1}; whereas, the $Cr(II)/SiO_2$ catalysts had an active site concentration of 4.3×10^{18} sites g cat^{-1}. These sites concentrations are upper limits to the actual concentration of active centers and correspond to 13 and 34% of the total chromium present in catalysts containing Cr(III) and Cr(II), respectively.

Thermal treatment of Cr/SiO_2. The thermal treatment of $Cr(II)/SiO_2$ catalysts at 700°C *in vacuo* was found to enhance their activity for ethylene polymerization over a wide range of reaction temperatures. Most

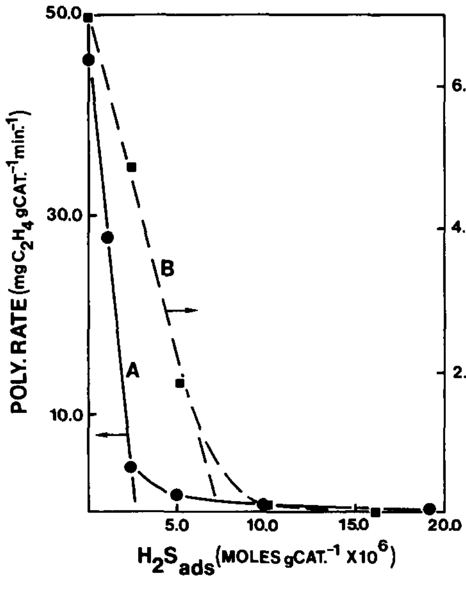

FIG. 2. Polymerization rate as a function of adsorbed H_2S; (A) $Cr(III)/SiO_2$, (B) $Cr(II)/SiO_2$. Tangents represent slopes at zero H_2S adsorption.

notably, these thermally treated Cr(II) catalysts displayed activity at 25°C (Fig. 1C). In the temperature range from 25 to 60°C a good fit to the Arrhenius equation was obtained yielding an apparent activation energy of 15.5 kcal $mole^{-1}$ (Table 2). A similar treatment of Cr(III)/SiO_2 catalysts caused a sixfold decrease in polymerization activity measured at 25°C.

Catalysts initially containing Cr(VI) which were activated at 900°C *in vacuo*, oxidized with O_2 (550°C), reduced with CO(400°C), and thermally treated at 700°C *in vacuo* for 4 hr exhibited an 11-fold increase in polymerization activity measured at 50°C. In addition, it was observed that the length of the thermal treatment at 700°C dictated the magnitude of the increase in catalytic activity. Samples treated for shorter periods (2 hr) displayed larger increases in activity than those treated for longer periods (4 hr).

Infrared studies. Infrared spectroscopy was utilized to examine the coordination state of surface Cr(II) on CO-reduced Cr/SiO_2 catalysts. Background spectra of reduced catalyst samples indicated an absence of residual adsorbed CO or CO_2. In addition, the region from 1600 to 1450 cm^{-1} was devoid of bands, thereby indicating the absence of surface carbonates (*9*). The adsorption of CO (40 Torr at 25°C) on Cr(II)/SiO_2 produced a triplet of IR bands similar to that reported by Lugo and Lunsford (*10*). The first band at 2177 cm^{-1} has been assigned by Garrone and co-workers (*11–13*) to a monocarbonyl complex of a Cr(II) surface species which they designate as Cr(A). A second intense band at 2181 cm^{-1} has been assigned to the monocarbonyl complex of Cr(A) perturbed by a second weakly held CO ligand (*11–13*). The remaining band at 2188 cm^{-1} has been assigned to an additional Cr(II) surface species labeled Cr(B) (*11–13*). On brief evacuation of the gas-phase CO the band at 2181 cm^{-1} disappeared completely, while the two outer bands were attenuated to about 50% of their original intensity (spectra not shown).

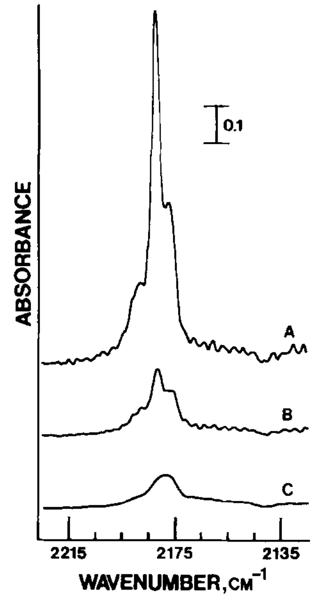

FIG. 3. Infrared (difference) spectra of CO adsorbed on Cr(II)/SiO_2: (A) 40 Torr CO at 25°C; (B) as in (A) following exposure to C_2H_4 at 25°C (3 min); (C) as in (A) following exposure to C_2H_4 at 50°C (3 min).

Evacuation for 2 hr at 25°C completely removed all CO bands and restored an unperturbed background spectrum.

The effect of C_2H_4 and polymer on the surface of reduced Cr/SiO_2 was examined to determine the type(s) of Cr(II) (A, B, or C) which was active for ethylene polymerization. The adsorption of CO (40 Torr at 25°C) on a fresh catalyst sample gave rise to the spectrum shown in Fig. 3A (described previously). Following removal of the adsorbed CO, exposure to 100 Torr of ethylene at 25°C for 3 min, and readsorption of CO, the bands due to complexes of both Cr(A) and Cr(B) were decreased in intensity (Fig. 3B). Notably, the band at 2181 cm^{-1} displayed the most striking loss of intensity. The band at 2188 cm^{-1} was reduced to a poorly delineated shoulder. Removal of the adsorbed CO and reexposure of the sample to ethylene at 50°C (100 Torr for 3 min) led to the growth of IR bands associated with the polymer (not shown). Upon exposure to CO, the IR spectrum (Fig. 3C) was characterized by the presence of one

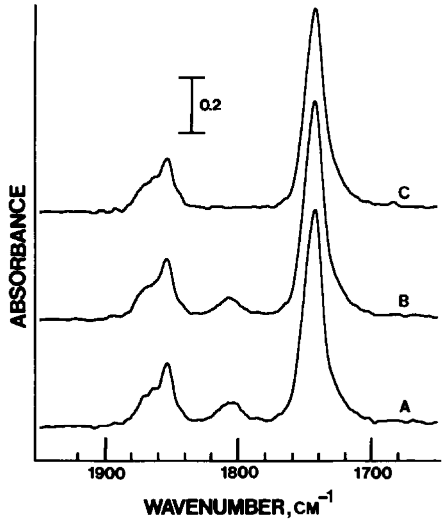

FIG. 4. Infrared (difference) spectra of NO adsorbed on Cr(II)/SiO_2: (A) 15 Torr NO at 25°C (30 min), evacuated 5 min; (B) as in (A) following exposure to C_2H_4 at 25°C for 3 min; (C) as in (A) following exposure to C_2H_4 at 50°C for 3 min.

broad band centered at 2183 cm^{-1}. The asymmetry on the high-frequency side of this absorbance was likely due to the weak and overlapping spectrum of gas-phase CO.

The adsorption of NO (15 Torr at 25°C) resulted in the formation of several Cr(II) nitrosyl complexes. The IR spectrum consisted of four bands assigned to NO complexes of Cr(A), Cr(B), and a third surface species of Cr(II) designated Cr(C) (*14*). It should be noted that Cr(A) and Cr(B) have been identified in the CO and NO spectra; Cr(C) is apparent, at least at 25°C, only from the NO spectra. Chromium (A and B) formed dinitrosyl complexes (*14*) which gave rise to the overlapping bands at 1742, 1856, and 1870 cm^{-1}. The single band at 1805 cm^{-1} has been assigned to a monitrosyl complex of Cr(C) (*14*). Upon coadsorption of NO with ethylene at 25°C the dinitrosyl bands were unaffected (Fig. 4B); however, the band associated with the Cr(C) nitrosyl complex decreased in intensity following C_2H_4 adsorption at 25°C and was completely eliminated following polymerization at 50°C (Figs. 4B and C). In addition, following polymerization the symmetric component of the dinitrosyl band decreased by about 15%.

The thermal treatment of Cr(II)/SiO_2 at 700°C *in vacuo* (4 hr) had a pronounced effect on the spectra of both adsorbed CO and NO. As shown in Fig. 5, the temperature treatment effectively reduced the bands associated with CO adsorbed on Cr(A), while leaving the bands due to the carbonyl complex of Cr(B) unchanged in position and intensity. Adsorption of NO on a thermally treated sample produced the spectrum shown in Fig. 6. It is interesting to note, that the central band, assigned to the nitrosyl complex of Cr(C), exhibited a modest increase in intensity while the outer two bands, attributed to the dinitrosyl complexes of Cr(A and B), decreased.

DISCUSSION

In a recent study (*8*), coordinatively unsaturated, isolated chromium(III) ions were proposed to be the active sites for the low temperature (25°C) polymerization of ethylene. Catalysts containing Cr(III) were prepared either by direct impregnation of silica with $CrCl_3 \cdot 6H_2O$, followed by vacuum pretreatment at 400 to 900°C, or by careful

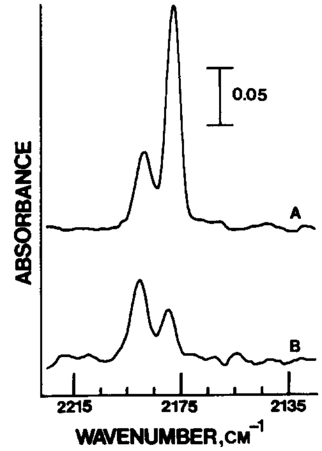

FIG. 5. Infrared (difference) spectra of CO adsorbed on Cr(II)/SiO_2: (A) 40 Torr CO at 25°C, evacuated 3 min; (B) as in (A) following thermal treatment at 700°C *in vacuo* for 4 hr.

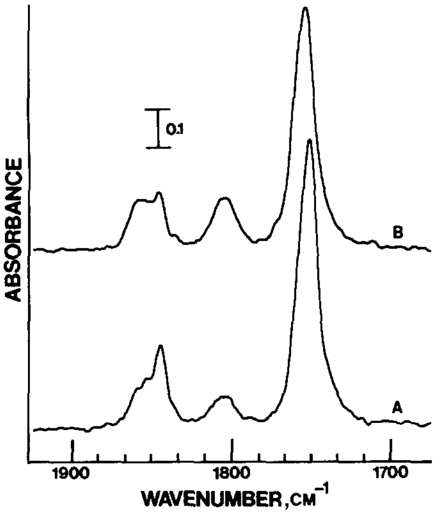

FIG. 6. Infrared (difference) spectra of NO adsorbed on Cr(II)/SiO_2: (A) 15 Torr NO at 25°C, evacuated 5 min; (B) as in (A) following thermal treatment at 700°C *in vacuo* for 4 hr.

reduction (CO, 400°C) of catalysts which contained Cr(VI) initially. It was found that increasing the activation temperature of Cr(III)/SiO_2 from 400 to 900°C greatly enhanced the polymerization activity measured at 25°C. The improved activity was attributed to both a twofold increase in the number of active sites and the removal of surface hydroxyls which may have been coordinated to the site following activation at the lower temperature. The extensive reduction (CO, 400°C) of Cr(III)/SiO_2 or Cr(VI)/SiO_2 produced catalysts containing >98% Cr(II), and these materials were inactive for ethylene polymerization at 25°C. In addition, an inverse correlation was shown to exist between surface Cr(II), detected by chemiluminescence, and the catalytic activity for ethylene polymerization measured at 25°C (*8*).

The kinetically significant site. Rebenstorf and Larsson (*3*) and more recently Rebenstorf (*7*) concluded that both dinuclear Cr(III) and Cr(II) are the active sites for ethylene polymerization over Cr/SiO_2 catalysts. They propose that the kinetically significant site is determined by the reaction temperature, and observed that the Cr(III) site is 100-fold more active at 25°C than the Cr(II) site. Upon reevaluation of our Cr(II) catalysts we found that they were inactive at 25°C, but they began to display activity at higher temperatures (>30°C, Fig. 1B). The higher temperature behavior of Cr(II)/SiO_2 (>75°C) was similar to that displayed by Cr(III) catalysts (*8*) and can be attributed to the denuding of monomer at the catalyst surface due to the unfavorable adsorption equilibrium of ethylene. At low reaction temperatures a falloff in polymerization activity was observed for Cr(II) catalysts, which was totally unlike the behavior of Cr(III)/SiO_2 over the same temperature range. The falloff of polymerization activity at temperatures <30°C, displayed by Cr(II)/SiO_2, represents a change in the slope of the Arrhenius plot, which generally indicates a change in the slow step of the reaction mechanism. The change in the mechanism may involve the initiation step.

The activation energies obtained from the temperature dependence of polymerization over both Cr(III)/SiO_2 and Cr(II)/SiO_2 catalysts provide further evidence in support of a change in the active site on extensive reduction with CO. The activation energy of 10.6 kcal mole^{-1}, obtained for polymerization over Cr(III)/SiO_2, is in excellent agreement with the previously reported value of 10.4 kcal mole^{-1} (*8*). It is significant to note that the activity of Cr(III)/SiO_2 catalysts has improved by roughly a factor of five compared to that reported previously (*8*). The increased activity is attributed to improvements in catalyst pretreatment procedures which include the effective removal of water, thus preventing the formation of α-Cr_2O_3. The activation energy obtained for Cr(II)/SiO_2 catalysts (17.1 kcal mole^{-1}) is significantly higher than that for polymerization over Cr(III)/SiO_2. Rebenstorf (*7*) and Groeneveld *et al.* (*15*) report activation energies of 13.1 and 12.7 kcal mole^{-1}, respectively for polymerization over Cr(II)/SiO_2 catalysts.

It is important to note that both of these researchers used catalysts containing Cr(VI) initially. Groeneveld *et al.* (*15*), activated their catalyst (2.1 wt% Cr/SiO_2) in air at 500°C followed by reduction in CO at 350°C. Rebenstorf (7), calcined his catalyst (0.5 wt% Cr/SiO_2) in O_2 at 850°C followed by reduction with CO at 350°C. Recently, Lugo and Lunsford (10) demonstrated that reduction of Cr(VI)/SiO_2 with CO at 345°C, although extensive, was less complete than at 495°C. It is apparent that the catalysts used by Groeneveld *et al.* (15) and Rebenstorf (7) contained both Cr(II) and Cr(III). Notably, the activation energies they report for polymerization over Cr/SiO_2 are in the range of the values reported here, and are likely the result of an averaging effect caused by the presence of both Cr(III) and Cr(II) in their catalysts.

The relationship between the valence state of chromium and the concentration of active sites. An additional difference between Cr(II) and Cr(III) catalysts is the apparent number of active sites present on each material. In an earlier study of Cr(III)/SiO_2, carbon monoxide was used as a poisoning agent to determine the fraction of chromium active for ethylene polymerization on catalysts which had been activated at 400 or 900°C (*8*). In the present study, hydrogen sulfide poisoning of similar, but more active Cr(III)/SiO_2 catalysts disclosed an increase in the number of active centers over that reported earlier (compare 8.6×10^{17} sites g cat^{-1} (*8*) with 1.6×10^{18} sites g cat^{-1}). This twofold increase in the number of active sites is less than the fivefold improvement in polymerization activity. The difference is believed to be the result of more selective poisoning by H_2S compared to CO.

Hydrogen sulfide poisoning of Cr(II)/SiO_2 catalysts indicated that the active fraction of chromium was larger on Cr(II)/SiO_2 than on Cr(III)/SiO_2. One might have expected the concentration of active sites to be similar on each of these catalysts (assuming that each Cr(II) site was obtained from one which contained Cr(III) by reduction with CO); however, it is possible that some of the inactive Cr(III), perhaps in the form of α-Cr_2O_3, was converted to active Cr(II) during the reduction step.

A comparison of turn-over frequencies compiled from the current literature is shown in Table 3. It is difficult to compare the absolute magnitudes of these numbers because of the various catalyst preparations and methods for estimating the active site concentration. However, a general observation which can be made is that turnover frequencies for Cr(III) catalysts are larger than those reported for Cr(II) catalysts. This supports our results, and is evidence of the greater reactivity of Cr(III) for ethylene polymerization compared to Cr(II).

Spectroscopic characterization of the Cr(II) site. The catalytically active form of chromium(II) was investigated by examining the infrared spectra of CO and NO, adsorbed separately and coadsorbed with both ethylene and polymer. Infrared spectra of CO adsorbed on Cr(II)/SiO_2 following exposure to C_2H_4 at 25°C (Fig. 3B), and a brief polymerization reaction at 50°C (Fig. 3C), indicated that both A- and B-type ions were affected by the presence of ethylene and polymer. The adsorption of monomer substantially decreased the intensity of the carbonyl bands associated with both the A and B ions while in the presence of polymer CO adsorption resulted in a poorly defined band at 2183 cm^{-1}, which appeared to be an average of the original three peaks. These results are not consistent with Garrone and co-worker's (*11*) conclusion that only Cr(A) is active for ethylene polymerization. The coadsorption of CO with ethylene (or polymer) was inconclusive as it did not distinguish between A- and B-type Cr(II) sites, possibly because CO could not compete with C_2H_4 for adsorption on Cr(II).

The coadsorption of nitric oxide with ethylene and polymer provided valuable information concerning the nature of the active Cr(II) site. As shown in Fig. 4 the dinitrosyl bands associated with B-type Cr(II) ions

TABLE 3

Turnover Frequencies for Cr/SiO_2 Catalysts

Catalyst	Activation	Reaction conditions	TOF[a]	Ref.
$Cr(III)/SiO_2$	900°C (*in vacuo*)	50°C, 100 Torr C_2H_4	10.2[b]	This work
$Cr(III)/SiO_2$	850°C (*in vacuo*), reduced CO (350°C), oxidized O_2 and H_2O (800°C *in vacuo*)	20°C, 500 Torr C_2H_4	23[c]	*7*
$Cr(II)/SiO_2$	900°C (*in vacuo*) reduced CO (400°C)	50°C, 100 Torr C_2H_4	0.58[b]	This work
$Cr(II)/SiO_2$	850°C (*in vacuo*), reduced CO (350°C)	80°C, 500 Torr C_2H_4	0.11[c]	*7*
$Cr(II)/SiO_2$	500°C (calcined in O_2), reduced CO (350°C)	25°C, 50 Torr C_2H_4	0.48[c]	*15*

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

[b] TOF based on active site density determined by H_2S poisoning.

[c] TOF based on active site density determined by IR spectroscopy of the polymer.

were completely unaffected by the presence of ethylene or polymer, while the band associated with A-type Cr(II) decreased slightly upon the formation of polymer. The infrared band assigned to the mononitrosyl complex of Cr(C) was narrowed after ethylene adsorption at 25°C, and eliminated following polymerization at 50°C. The disappearance of this band is a direct result of the formation of polyethylene on C-type Cr(II) ions. It is important to remember, that Clark and Bailey (*16*), proposed a Langmuir–Hinshelwood type mechanism for ethylene polymerization over Cr/SiO_2. Such a mechanism requires at least two vacant coordination positions on the active site in order to accomodate two reacting molecules. Ghiotti *et al.* (*14*) have suggested that C-type Cr(II) ions form mononitrosyl complexes at low NO pressures (<10 Torr); the Cr(C) mononitrosyl complexes were converted to Cr(A and B) type dinitrosyls at higher NO pressures (>70 Torr). Clearly the formation of a mononitrosyl complex does not require that only one coordination position is available on a particular ion.

Garrone and coworkers (11, 14) found that the thermal treatment of $Cr(II)/SiO_2$ at 700°C *in vacuo* led to changes in the infrared spectra of adsorbed CO and NO. They concluded that during the thermal treatment surface Cr(II) ions underwent structural changes whereby Cr(A) ions were converted to less coordinatively unsaturated Cr(C) ions, whiile Cr(B) ions were not affected. The decrease in Cr(A) was accompanied by a decrease in the sorptive capacity of the catalyst for CO, which Garrone and co-workers (*11*) interpretated as indicating a loss of C_2H_4 polymerization activity. The infrared spectra of CO adsorbed on $Cr(II)/SiO_2(700)$ (Fig. 5) confirms their observation that the relative amount of A-type Cr(II) ions decreased as a result of thermal treatment at 700°C. Spectra of adsorbed NO indicate an increase in the intensity of the Cr(C) band following the thermal treatment. In addition, the symmetric component of the Cr(A) dinitrosyl (1856 cm^{-1}) decreased in intensity, while the asymmetric component appears shifted to slightly higher frequency. As expected, based on the CO spectra, the dinitrosyl bands associated with Cr(B) were unchanged. The blue shift in the low frequency band at 1746 cm^{-1} may be due to the increased contribution from the asymmetric component of the Cr(B) dinitrosyl. The symmetric component of the Cr(C) dinitrosyl complex also has shifted to higher frequency which is an indication that some structural change may have taken place at this site as a result of the thermal treatment. It is important to note that catalytics samples of Cr(II)/SiO_2 which were thermally treated at 700°C (4 hr) displayed an 11-fold increase in polymerization activity measured at 50°C. Therefore, an inverse correlation exists between the presence of Cr(A) and the catalytic activity for ethylene polymerization, while no correlation exists for Cr(B).

The most significant result of the thermal treatment of Cr(II)/SiO_2 at 700°C was the production of a Cr(II) catalyst which was active for ethylene polymerization at 25°C. It is interesting to note that in addition to a change in activation energy (Table 2) the temperature range over which the Arrhenius relation was obeyed differed following the 700°C treatment. The shift in the stretch of the Cr(C) nitrosyl indicates a small change in its surface environment, in agreement with the observed change in kinetic behavior.

CONCLUSION

The reduction of Cr/SiO_2 catalysts resulted in a change in the kinetically significant site for ethylene polymerization. At low temperature (<30°C) coordinatively unsaturated, isolated Cr(III) ions are the active sites for the polymerization reaction. The Cr(II)/SiO_2 catalysts displayed strikingly different kinetic behavior as compared to Cr(III)/SiO_2. Over the range of reaction temperatures examined Cr(II)/SiO_2 catalysts were significantly less active than Cr(III) catalysts. The difference in activation energy for the polymerization reaction over each of these materials supports a change in the active site following extensive reduction with CO. The active sites on Cr(II)/SiO_2 catalysts are C-type Cr(II) ions which have at least two vacant coordination positions and account for up to 34% of the total Cr in the sample. The thermal activation of Cr(II)/SiO_2 results in a significant increase in polymerization activity measured at 50°C. The infrared spectra of adsorbed NO indicated an increase in the number of C-type Cr(II) ions, and revealed an inverse correlation between the presence of A-type Cr(II) ions and polymerization activity. The shift in the IR band of the Cr(C) nitrosyl complex and the change in activation energy for polymerization over Cr(II)/SiO_2(700) suggest that a modification in the surface coordination of C-type Cr(II) occurred during the 700°C treatment. Thermal activation of Cr(II)/SiO_2 at 700°C yielded a catalyst which was active for ethylene polymerization at 25°C.

ACKNOWLEDGMENTS

This work was supported by the Robert A. Welch Foundation under Grant A-257. The authors acknowledge the helpful comments of Dr. M. P. McDaniel (Phillips Petroleum Co.) and Professor G. L. Haller (Yale University).

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