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The State of Cr(VI) on the Phillips Polymerization Catalyst

II. The Reaction between Silica and CrO_2Cl_2

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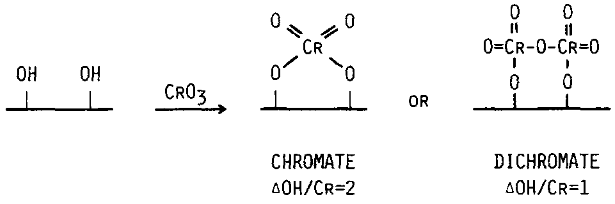
The reaction between chromyl chloride vapor and the hydroxyl population on calcined silica was examined at 200°C in a flow system. When the silica had been calcined at high temperatures ($\geq$800°C) the CrO_2Cl_2 attached by losing one chloride per Cr. This indicates the formation of a surface $\equiv SiOCrO_2Cl$ species which, upon contact with ethylene, failed to develop any polymerization activity. However, when the silica had been calcined at low temperatures ($\leq$400°C), most of the CrO_2Cl_2 attached by losing two chlorides per Cr, indicating the formation of a surface chromate species by reaction with hydroxyl pairs. On contact with ethylene this species developed polymerization activity very much like the conventional CrO_3/silica catalysts, suggesting that here too the active species could begin as a surface chromate.

INTRODUCTION

Owing to its commercial importance, the Phillips polymerization catalyst, Cr/silica, has been well studied since its discovery in the early 1950s. It is now generally accepted that a surface layer is formed during activation in which hexavalent chromium is stabilized against thermal degradation by attachment to the silica surface (*1–6*). Other phases may coexist, such as α-Cr_2O_3 (*7–9*), but it is this hexavalent layer, in which each atom is exposed, that is thought to be the precursor of the active polymerization site, formed by reduction with ethylene, CO, or other compounds to a divalent species (*1–6*).

Hogan (*1*) has proposed that the mechanism of attachment is simple esterification to pairs of surface silanol groups to form a surface chromate or dichromate species. However, the identification of this species has proven difficult and rather controversial. By measuring the weight change upon impregnation of CrO_3, Hogan concluded that about two hydroxyls were lost for each chromium attached and therefore that the initial bonding must occur as chromate. He did not, however, rule out later rearrangement to dichromate during activation at higher temperatures.



Zecchina *et al.* (*2*), working at 600°C, as well as Krauss (*6*) at 500°C, came to the opposite conclusion. Finding only one hydroxyl lost for each chromium, they concluded that dichromate (*3*) was the species present. However, McDaniel (*3*) later of-

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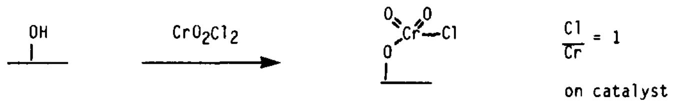
fered a contrary interpretation of the same data. In their straightforward calculations previous workers had implicitly assumed that the chromium selectively occupies only those sites which would be hydroxylated at the temperature in question. The possibility that chromium might occupy "condensable" sites too was not considered. Without this knowledge it is hard to be definitive, and therefore the issue is still unresolved.

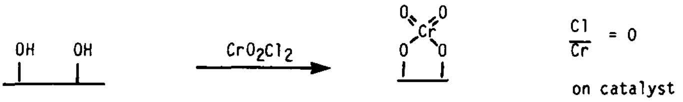
Spectroscopy has proven just as inconclusive. The Turin group (*2*) and Krauss (*6*) again proposed dichromate as the catalytic species because the visible spectrum of the catalyst seemed to match that of known dichromates. However, doubt about this interpretation was expressed in a later publication (*4*) since adequate reference data are apparently lacking.

In still another approach the Turin group also examined the geometry of both species (*2*). They concluded that dichromate fits the silica surface nicely, whereas chromate would introduce strain and is therefore less likely.

This matter is rather important to our understanding of the active site, particularly when mechanisms are proposed based on one or the other species (*5, 14*). Recently Rebenstorf and Larsson (*14*) have proposed that polymerization can take place only when the chromium ions are paired, as in dichromate. This was advanced as the reason why nonsupported Cr(VI) compounds have failed to exhibit any activity, since they were always chromate-like structures. Therefore in this report, yet another approach to the problem has been taken, hopefully one which requires less interpretation. The reaction between chromyl chloride and silica, calcined at various temperatures, has been briefly examined in a flow system. A simple monofunctional reaction yields the surface Cr(VI) monochloride:



Whereas a chromate surface species should result from the difunctional reaction if the silanol spacing is correct.



The reaction products can be easily monitored by measuring the amount of Cr(VI) and chloride remaining on the silica after its reaction with CrO_2Cl_2 vapor. The direct formation of a dichromate species is not possible in the absence of oxygen and at low temperatures where Cr(VI) is stable, allowing a more conclusive interpretation of polymerization and other data.

EXPERIMENTAL

Catalyst Preparation

Catalysts were made from Davison grade 952 MS silica having a pore volume of 1.6 cm^3/g and surface area of 280 m^2/g. Davison purity specifications were reported less than 0.1% Na_2O, 0.1% CaO, and 0.15% Al_2O_3. Our own analysis by X-ray fluorescence indicated 0.012% Na_2O, 0.06% CaO, and 0.57% Al_2O_3.

Samples were first calcined in a fluidized bed as already described (*3*). The entire tube, surrounded by an electrical furnace, was heated to the desired temperature at 400 deg/hr, and held there 2 hr before cooling. Gases were dried through activated alumina.

Afterward the fluidized bed of silica was cooled to 200°C in dry nitrogen or argon and between ½ and 4 ml of chromyl chloride was then injected upstream from the bed. The nitrogen carried the CrO_2Cl_2 vapor up through the silica bed where it either reacted or passed through as a vapor. Since the boiling point of chromyl chloride is 117°C, only that actually attached to the silica remained after N_2 flushing at 200°C. Sometimes when a low loading was desired a solution of CrO_2Cl_2 in CCl_4 was also used after it was determined that CCl_4 vapor did not react with silica at 200°C.

Analyses

To determine the hexavalent chromium population about 0.5 g of each sample was added to 150 ml of hot H_2SO_4 and stirred for about 15 min. The slurry was then titrated with 0.03 *N* ferrous ammonium sulfate to the ferroin endpoint. Afterward, to determine the chloride residue, samples were then titrated with silver nitrate, using a chloride-sensitive electrode to detect the endpoint. Since silver chromate can also be precipitated, the analyses were always done after reduction of Cr(VI) to Cr(III). Blanks and controls indicated no interference from Fe^{2+}, Cr^{3+}, or SO_4^{2-} ions. To measure the hydroxyl population, samples containing no Cr but calcined as described above, were reacted with excess 2 *M* methyl magnesium iodide in dibutyl ether (*10*). The amount of methane produced was then measured volumetrically.

Polymerization

Ethylene polymerization runs were made in a 2-liter stirred autoclave, having a pressurized jacket containing boiling alcohol for accurate control of the reactor temperature. After the catalyst had been charged to the reactor under dry N_2, 1 liter of isobutane was added as diluent and the ethylene (both Phillips polymerization grade) supplied on demand at 550 psig. At 107°C polyethylene was obtained as a slurry and after 1 or 2 hr the isobutane was flashed off leaving several hundred grams of polymer powder.

RESULTS

Step 1: CrO_2Cl_2 at 200°C

The question of whether a chromate species can actually exist on a silica surface is clearly answered by the results in Table 1. Silica samples were first calcined at the temperature listed for 2 hr in a bed fluidized by dry air. Afterward they were cooled in dry nitrogen to 200°C, where chromyl chloride was then injected into the nitrogen upstream from the silica bed. Usually evaporation was complete within 15–30 min but the N_2 purge was always maintained for 1 hr. As the CrO_2Cl_2 vapor passed through the silica at 200°C some reacted and became attached, while the unreacted portion merely escaped through the exit vent. The amount of CrO_2Cl_2 injected was varied from sample to sample so that each would have a different Cr loading. Afterward each sample was analyzed for hexavalent chromium and chloride residue.

The results of these experiments are shown in the first line of each series in Table 1. For example, the first sample listed was dried at 200°C, then exposed to a heavy dose of CrO_2Cl_2 at the same temperature to approach saturation of the surface. Of the 2.29 Cr(VI)/nm^2 which became attached to the silica, 1.31/nm^2 still contained a chloride, implying that 43% must have attached as chromate. As the loading was decreased the percentage of chromium attached as chromate also increased, reaching as high as three-quarters. This trend was also visible for samples dried at 400°C but the amount of chromate was less—by almost

TABLE 1

Reaction of CrO_2Cl_2 Vapor with Predried Silica

Silica drying temp.	Treatment	Cr(VI)/nm^2 attached	Cl/nm^2 left	Percentage OH reacted	Percentage chromate
200°C	CrO_2Cl_2, 200°C	2.29	1.31	82	43
200°C	CrO_2Cl_2, 200°C	1.85	0.91	65	51
200°C	CrO_2Cl_2, 200°C	0.99	0.30	42	69
200°C	CrO_2Cl_2, 200°C	0.53	0.12	24	77
200°C	CrO_2Cl_2, 200°C	0.25	0.07	11	74
300°C	CrO_2Cl_2, 200°C	—	—	—	—
	N_2, 300°C	0.30	0.05	20	85
400°C	CrO_2Cl_2, 200°C	1.68	1.34	86	21
	N_2, 300°C	1.44	0.74	91	49
	O_2, 400°C	1.42	0.27	—	—
400°C	CrO_2Cl_2, 200°C	1.02	0.76	54	26
	N_2, 300°C	0.90	0.41	59	55
	O_2, 400°C	0.91	0.04	—	—
400°C	CrO_2Cl_2, 200°C	0.39	0.20	25	48
	N_2, 300°C	0.39	0.08	30	80
	O_2, 400°C	0.40	0.04	—	—
600°C	CrO_2Cl_2, 200°C	0.93	0.86	67	8
	N_2, 300°C	0.81	0.62	67	24
	O_2, 400°C	0.77	0.09	—	—
600°C	CrO_2Cl_2, 200°C	0.89	0.79	66	11
600°C	CrO_2Cl_2, 200°C	0.63	0.57	43	9
	N_2, 300°C	0.55	0.33	52	39
	O_2, 400°C	0.58	0.05	—	—
600°C	CrO_2Cl_2, 200°C	0.37	0.33	28	11
	N_2, 300°C	0.33	0.24	28	29
	O_2, 400°C	0.33	0.04	—	—
600°C	CrO_2Cl_2, 200°C	0.30	0.28	21	7
	N_2, 300°C	0.27	0.27	18	2
	O_2, 400°C	0.27	0.00	—	—
800°C	CrO_2Cl_2, 200°C	0.57	0.57	70	0
	N_2, 300°C	0.51	0.45	70	13
	O_2, 400°C	0.40	0.24	—	—
800°C	CrO_2Cl_2, 200°C	0.54	0.56	63	0
	N_2, 300°C	0.48	0.48	59	0
	O_2, 400°C	0.28	0.06	—	—
950°C	CrO_2Cl_2, 200°C	0.46	0.47	79	0
	N_2, 300°C	0.40	0.37	76	4
	O_2, 400°C	0.07	0.13	—	—
950°C	CrO_2Cl_2, 200°C	0.31	0.38	42	0
	N_2, 300°C	0.26	0.30	39	0
	O_2, 400°C	0.17	0.06	—	—
950°C	CrO_2Cl_2, 200°C	0.31	0.38	42	0
	N_2, 300°C	0.24	0.28	35	0
	O_2, 400°C	0.15	0.08	—	—

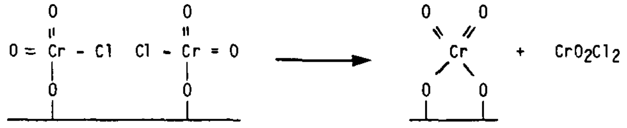
half. However, at 600°C the chromate content was always low, about 10%, regardless of the loading, and samples dried at 800°C and 950°C had no chromate at all after CrO_2Cl_2 treatment at 200°C.

Step 2: N_2 at 300°C

Next each sample (except those dried at 200°C) was heated to 300°C while still in nitrogen and held there one half hour to encourage the chloride species ($\equiv$SiO CrO_2Cl) to further react with silanols where possible. This secondary reaction was evident on samples dried at 400°C by a large decrease in the chloride content of the catalyst. This raised the fraction of chromate present to as high as 80%. On samples dried at 600°C the effect was less and at 800 and 950°C little secondary formation of chromate was observed.

Sometimes the sample also lost a trace of Cr(VI) as well during the 300°C nitrogen treatment. Decomposition to Cr(III) is one possible explanation, but this seems unlikely because CrO_2Cl_2 vapor could sometimes be seen leaving the sample, and because subsequent reoxidation in oxygen at 400°C never restored the lost Cr(VI). Instead, the following rearrangement seems more likely:

(a)

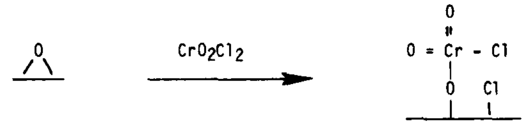


$$\mathrm{O{=}\overset{O}{\underset{O}{Cr}}{-}Cl\quad Cl{-}\overset{O}{\underset{O}{Cr}}{=}O \longrightarrow \overset{O\ \ O}{\underset{O\ \ O}{Cr}} + CrO_2Cl_2}$$

This explanation requires that the loss of chloride always be greater than twice the loss of Cr(VI), which was usually true. One would also expect the reaction to occur more frequently at high loading, where crowding is more common, and at low drying temperatures, where the sites are still close to each other. This also fits the observed pattern.

Samples dried at 950°C sometimes contained a little more chloride than Cr(VI). This probably indicates the formation of some very reactive siloxane, along with a few isolated hydroxyls.

(b)



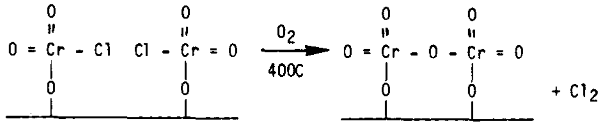
$$\mathrm{\overset{O}{\wedge} \xrightarrow{CrO_2Cl_2} O{=}\overset{O}{\underset{O}{Cr}}{-}Cl\quad Cl}$$

The largest example of this, the last run in Table 1, was 0.07/nm^2 excess chloride or nearly a quarter of the Cr(VI) population.

Step 3: O_2 at 400°C

Next each sample dried at 400°C or above was then exposed to dry oxygen at 400°C for another half hour. On 400 and 600°C samples this treatment usually reduced the chloride level to near zero without changing the Cr(VI) population. Development of dichromate is a possible explanation.

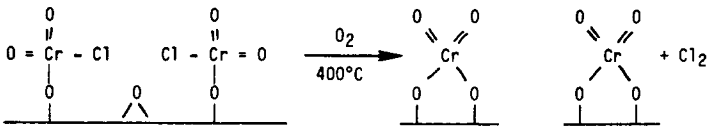
(c)



$$\mathrm{O{=}\overset{O}{\underset{O}{Cr}}{-}Cl\quad Cl{-}\overset{O}{\underset{O}{Cr}}{=}O \xrightarrow[400C]{O_2} O{=}\overset{O}{\underset{O}{Cr}}{-}O{-}\overset{O}{\underset{O}{Cr}}{=}O + Cl_2}$$

However, the oxygen and higher temperature could also encourage further reaction with hydroxyls, or catalyze rearrangement to chromate by reaction with siloxane.

(d)



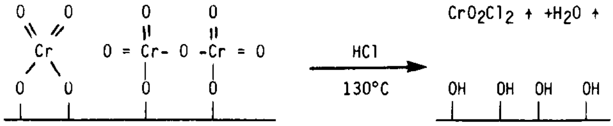
Samples dried at 800 or 950°C also lost considerable Cr(VI) upon treatment at 400°C. On the 950°C samples, this may have been due in part to decomposition of isolated ≡SiOCrO₂Cl groups to Cr(III) since a color change from orange to brown was sometimes observed. However, many samples, particularly those dried at 800°C, released large amounts of CrO_2Cl_2 vapor during this step especially when oxygen was admitted. Some type of rearrangement is indicated, such as in reaction (a), although the role of oxygen is unclear.

One sample dried at 600°C was split in half after step 2. Half was treated at 400°C in oxygen where it lost all of its chloride, the other half in nitrogen at 400°C where it lost nearly two-thirds of its chloride. Cr(VI) content was about the same on both. Hence the bulk of the dechlorination at 400°C was probably just further reaction with the hydroxyl population, which does not require oxygen.

Step 4: HCl at 130°C

As a last step, some of these samples were then exposed to dry hydrogen chloride gas at 130°C for 10 min; about 20% HCl in N_2 was used to fluidize the bed. Although HCl reacted very little with plain silica, it did react exothermically with the Cr(VI), stripping it off as CrO_2Cl_2 vapor and leaving one OH for each point of attachment to the silica.

(e)



If dichromate is present, one-half mole of water vapor will also be released for each mole of Cr. However, the probability of this trace of water rehydrating the surface is low. Silicas annealed at 600°C or above, according to reports (*15*), cannot be rehydrated by water vapor, but require soaking in the liquid. Our own tests have confirmed this and even silicas dried below 600°C did not rehydrate to any significant degree when exposed to large pulses of water vapor under the conditions of these experiments.

Since methyl magnesium iodide reacts with Cr(VI) as well as hydroxyls one cannot use the technique to determine the OH population when Cr(VI) is present. Instead the OH population on the virgin silica was determined before treatment with CrO_2Cl_2, and then again after stripping with HCl. They should, of course, be identical whatever the type of Cr(VI) species present. An increase in the hydroxyl population after stripping with HCl would signify that at some point during the preceding steps the chromium reacted with a siloxane, rather than hydroxyl. Thus the increase in OH population is a direct indication of the extent of reaction with siloxane, as in (d).

These results are listed in Table 2. Sam-

TABLE 2

Change in Surface Hydroxyl Population

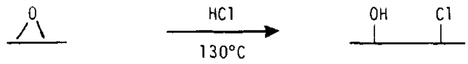
Drying temp. (°C)	Initial loading Cr(VI)/nm^2	OH/nm^2 before CrO_2Cl_2	OH/nm^2 after HCl
200	1.85	3.96	4.01
	0.99	3.96	3.90
	0.53	3.96	3.92
	0	3.96	3.96
400	1.68	2.35	2.62
	1.02	2.35	2.47
	0.39	2.35	2.40
	0	2.35	2.35
600	0.93	1.49	1.80
	0.63	1.49	1.61
	0.37	1.49	1.66
	0.30	1.49	1.62
	0	1.49	1.53
800	0.57	0.80	1.08
	0.54	0.80	1.09
	0.30	0.80	1.05
	0	0.80	0.92
950	0.31	0.53	0.77
	0.24	0.53	0.70
	0.15	0.53	0.74
	0	0.56	0.67

ples dried at only 200°C contained, after all of the Cr was cleanly stripped off by HCl, the same OH population that they had before reaction with CrO_2Cl_2. Thus no reaction with siloxane was indicated. This is reasonable since at 200°C the surface is nearly fully hydroxylated and there are very few siloxanes to react with. Also, these samples were not exposed to oxygen at 400°C like the others.

Samples dried at 400°C presented a different picture. Although silica itself did not react with HCl, samples containing Cr(VI) always showed an increase in the OH population, and the greater the Cr loading, the larger the OH increase. At the highest loading nearly 0.3 Cr/nm^2 were apparently attached by reaction with siloxane, and at all loadings it varied between 10 and 20% of the chromium. Again samples were cleanly stripped of their Cr(VI) leaving a white silica containing no chromium. Thus no decomposition to lower valent states had occurred.

At 600°C the pattern was similar to that seen at 400°C, except that large increases in the OH population were seen for a given Cr loading. In fact, between 20 and 50% of the Cr(VI) may have attached by reaction with siloxane, even higher if one uses the final Cr loading (before HCl) as the basis for comparison instead of the initial loading. Silica itself, dried at 600°C, exhibited a very faint reaction with HCl which could barely be detected by residual chloride or the tiny increase in OH, 0.04 OH/nm^2.

(f)



However, it is likely that these very reactive siloxane sites probably also react with Cr when present so that a "background" correction might be erroneous. Again no evidence for decomposition to Cr(III) was found; the stripping reaction was very clean.

On the 800°C dried samples the fraction of Cr(VI) attached to siloxane went even higher, to between 50 and 85%. However, this amount, about 0.3/nm^2 for each sample, was almost independent of the Cr loading, quite unlike those 400°C results. Again the stripping was clean but the HCl–silica reaction increased to 0.12/nm^2. Even if a background correction is made it is clear that a major fraction of the Cr(VI) after step 3 became attached through reaction with siloxane.

Samples dried at 950°C showed obvious signs of decomposition during step 3. After the HCl stripping treatment all samples had a faint green tint, indicating the presence of lower-valent residue, probably Cr(III). This makes the analyses unreliable, although they present a picture similar to that seen in the 800°C series.

Polymerization Results

Several catalysts were prepared to contain only chromate. For example, in one typical run silica was calcined at 400°C and then treated with CrO_2Cl_2 vapor at 200°C. To encourage complete reaction it was then held in argon at 300°C for 1 hr. It was found to contain 0.39 Cr(VI)/nm^2 (about 1 wt% Cr) but no chloride.

These samples were then tested for polymerization activity in a high-pressure autoclave. On contact with ethylene they became reduced and began to catalyze polymerization, slowly at first but becoming more and more active as time went on. A typical example is shown in Fig. 1 where the increasing rate is plotted against reaction time. This type of kinetics is thought to be caused by the slow reduction and alkylation of the Cr(VI), and it is very typical of the conventional CrO_3/silica polymerization catalyst. For comparison, a typical run with a CrO_3/silica sample is also shown in Fig. 1. This sample also contained 0.39 Cr(VI)/nm^2 and was activated in oxygen at 400°C. The two runs were almost identical.

Not only were the kinetics similar between CrO_2Cl_2/silica (chromate) and CrO_3/silica, but even the polymer properties were close. Both had weight average molecular weights between 250,000 and 300,000, and in both cases $M_w/M_n = 18$. High load melt indices varied only between 3 and 7, and the flexural modulus from both (determined by crystallinity) were similar. Both catalysts were also tested for polymerization activity in the presence of 50 psi H_2, which has the effect of lowering the average molecular weight (*1*). Although the sensitivity of individual catalyst modifications to H_2 sometimes varies considerably, they were nearly identical here.

Some differences, however, were noted. The polymerization activity of CrO_3/silica samples activated at 400°C was almost constant from 0.2 to 0.8 Cr(VI)/nm^2. In contrast CrO_2Cl_2/400°C silica increased in activity up to about 0.4 Cr(VI)/nm^2 and then it declined as the samples began to retain chloride. In fact, the peak activity was nearly 75% greater than that of CrO_3/silica. Even if both types of catalysts contain only chromate, differences in bonding still probably exist owing to the different preparations. On the CrO_2Cl_2/silica samples, the Cr may attach only to sites which still contain hydroxyls at 400°C, whereas on CrO_3/silica samples it can attach anywhere.

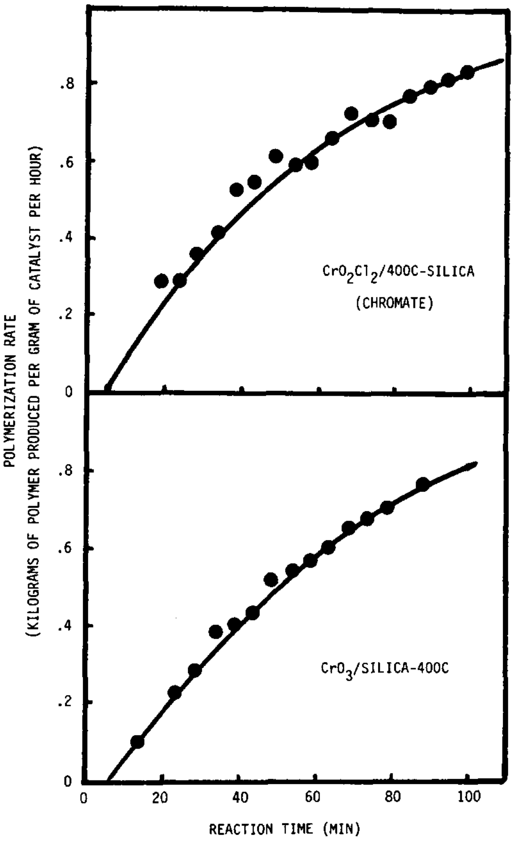


FIG. 1. The polymerization kinetics of CrO_3/silica calcined at 400°C were very similar to those of a sample containing only the chromate surface species, formed by reaction of CrO_2Cl_2 with silica dried at 400°C.

In another test the sample was not given the argon treatment at 300°C. Instead the 400°C silica was merely treated with CrO_2Cl_2 vapor at 200°C and then introduced into the autoclave. It retained 0.13 Cl/nm^2 so that only 64% of its 0.36 Cr(VI)/nm^2 was present as chromate. It also polymerized ethylene with kinetics like that in Fig. 1 but was only about half as active.

As the activation temperature is increased the polymerization activity of conventional CrO_3/silica catalysts also increases. In fact, between 400 and 800°C the rate normally increases by an order of magnitude. The reason is unknown but is suspected to be due to the disappearance of the surrounding hydroxyl population, which may interfere somehow with the polymerization. Despite the preferability of the 800°C activation, however, CrO_2Cl_2/800°C silica exhibited no polymerization activity whatever. This was undoubtedly because, as has already been noted, it contained only the monochloride species ($\equiv SiOCrO_2Cl$) which was apparently not active. Heating these samples in oxygen at 400°C for 1 hr burned off the chloride and polymerization activity developed like that of CrO_3/silica activated at 800°C. The polymer melt indices, which also normally increase substantially with increasing activation temperature, were identical.

Reflectance Spectra

Several spectroscopic studies of CrO_3/silica have been reported, but the discussion of chromate–dichromate identification has hinged in part on the assignment of a band found in the visible spectrum near 460 nm. Most workers have assigned this band to dichromate (*2*, *5*, *6*, *13*) based on comparison to the spectra of potassium chromate and dichromate. However, the Turin group has recently questioned the interpretation (*4*), pointing out that surface species are not completely comparable to those in crystals or solution. They emphasized the need for better reference data.

The reaction studied here, between CrO_2Cl_2 and silica, provides an opportunity to obtain for the first time the spectrum of the pure chromate species on silica. This is shown in Fig. 2 where CrO_2Cl_2 was reacted with silica calcined at 400°C. After a treatment at 300°C in argon, it contained 0.35 Cr(VI)/nm^2 and no chloride, thus indicating chromate. The peak in question was found in the spectrum of this catalyst, centered at 465 nm. It was also found, again at 465 nm, in the spectrum of CrO_3/silica calcined at 400°C, containing 0.42 Cr(VI)/nm^2 which was nearly identical to that of chromate. When CrO_3/silica was calcined at 800°C, however, the peak may have shifted slightly to 470 nm, but otherwise the spectrum was the same.

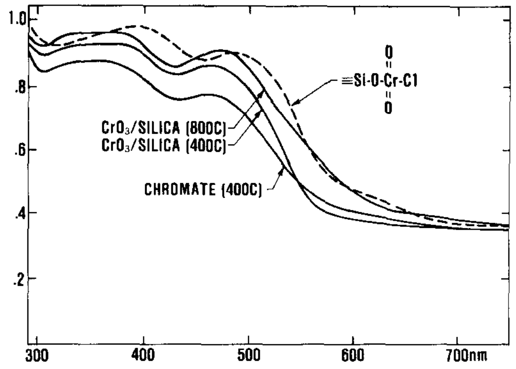


FIG. 2. Visible reflectance spectra of CrO_3/silica calcined in O_2 at 400°C, and at 800°C, and of CrO_2Cl_2/400°C silica (the chromate species), and of CrO_2Cl_2/800°C silica (the chlorochromate species).

Finally the spectrum of the surface chlorochromate is also shown for comparison. Silica calcined at 800°C was reacted with CrO_2Cl_2 at 200°C, leaving 0.58 Cr(VI)/nm^2 and 0.57 Cl/nm^2. Thus the Cr(VI) was present almost exclusively as $\equiv SiO\text{-}CrO_2Cl$. The spectrum is not like the others. The band in question again appeared, but was shifted to 485 nm.

DISCUSSION

These data constitute the most direct evidence yet obtained that a surface chromate species not only can exist on silica but also that this species can polymerize ethylene. It is hard to imagine any way that two chlorides could be lost per chromium in the absence of oxygen other than by formation of chromate. A rearrangement from chromate to dichromate at 200 or 300°C is not only hard to conceive of, but would lead to a decrease in the OH population after treatment with HCl, which was never observed on any sample.

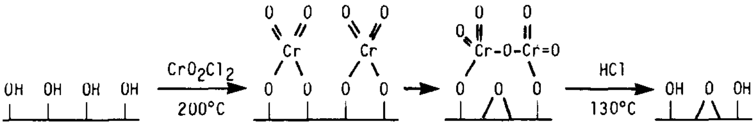


Figure 3 shows the fraction of chromate found on samples containing about 1 wt% Cr, which is a typical commercial loading, as a function of activation temperature. The fraction varied from mostly chromate (or in many cases all chromate) at 200–400°C, to no chromate at 800°C or higher. Since this fraction was governed by the spacing of the hydroxyls on the silica, it is not surprising that the same pattern has been reported for $SiCl_4$, $TiCl_4$, BCl_3, etc. (*11, 12*). At low temperatures most of the hydroxyls were "paired" but by 600 or 700°C only isolated "singles" remained. It is therefore tempting to believe that the trend also holds for CrO_3/silica after activation, where the remainder of the chromium is present as dichromate. The saturation behavior of CrO_2Cl_2/silica, which is shown in Fig. 4, lends some credence to this idea because it is very similar to that seen for CrO_3/silica in Part IV of this series.

However, the differences between CrO_3 and CrO_2Cl_2 must not be ignored. Remember that unlike CrO_2Cl_2 in these experiments, aqueously impregnated CrO_3 attaches to a nearly fully hydroxylated surface, and then is calcined to high temperatures. If it remains fixed on the surface during activation and thus prevents condensation of site pairs (*3*), then the proportion of chromate would not necessarily be the same. In fact this might favor retention of chromate to higher temperatures. Second, anhydrous impregnation of CrO_3 onto precalcined silica (*3*) is perhaps more comparable to these CrO_2Cl_2 experiments but even here there is an important difference.

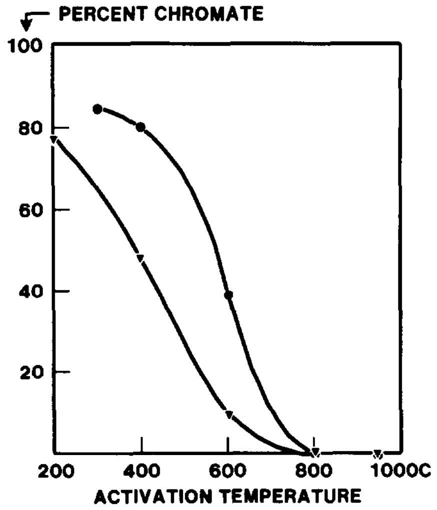


FIG. 3. Percentage chromate found on samples containing near 1% Cr. ▼, silica activated at indicated temperature, then treated with CrO_2Cl_2 at 200°C; ●, then N_2 at 300°C.

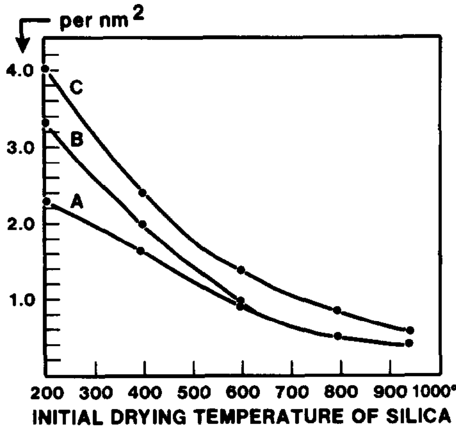
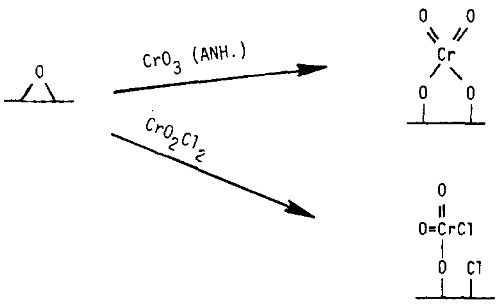


FIG. 4. (A) Highest Cr(VI) concentration observed in this study after CrO_2Cl_2 at 200°C. (B) Number of attachments of Cr(VI) to the surface (2Cr(VI)–Cl). (C) Initial OH population on virgin silica before reaction with CrO_2Cl_2.

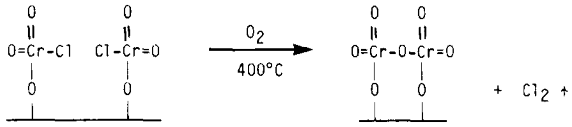
The CrO_3 can still, in principle, attack siloxanes to yield chromate, whereas CrO_2Cl_2 cannot.



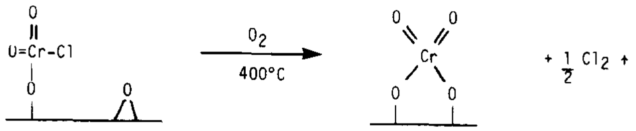
More impressive is the comparison of the polymerization activity of CrO_3/silica versus CrO_2Cl_2/silica. At 1% Cr and 400°C, conditions which produced only chromate, the CrO_2Cl_2/silica catalyst had similar activity to CrO_3/silica and produced similar polymer. To anyone familiar with the extreme sensitivity of Cr/silica catalysts to any change in environment, this is a powerful suggestion that the active sites on both catalysts originated similarly, that is, from chromate. However, even if this is true, it is not to say that all catalysts contain only chromate, because there are many processes and modifiers used commercially to achieve special polymer properties. The existence of dichromate cannot be ruled out on other catalysts.

If their ir assignments are correct, the recent finding by Rebenstorf and Larsson (*14*) of bridged CO adsorption on CO-reduced Cr/silica catalysts constitutes the most direct evidence yet produced for the clustering of Cr(II) species. However, the existence of a dichromate species before reduction is not necessarily indicated since the clustering could also occur during reduction. Certainly the chromocene catalysts cannot exist as dichromate, and yet these too were reported to adsorb CO in a bridged position.

Samples calcined at 800°C or higher and then treated with CrO_2Cl_2 apparently produced no chromate, only $\equiv SiOCrO_2Cl$ species which had no polymerization activity. Heating this species in oxygen at 400°C removed the chloride and also restored the polymerization activity. Although one could argue that dichromate was formed by the oxygen treatment,



the increase in OH population after HCl treatment strongly suggests the formation of mainly chromate,



even though some rearrangement is required. In fact, the quantities of chloride removed, Cr(VI) remaining, and hydroxyls gained, are consistent with this interpretation. Again the polymerization activity and the polymer produced by the CrO_2Cl_2/800°C silica catalyst after oxidation at 400°C were similar to those of CrO_3/silica calcined at 800°C. This again suggests, although admittedly with less certainty, that chromate could also be the active species on CrO_3/silica calcined at high temperatures like 800°C.

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