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

IV. Saturation Coverage

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Cr/silica catalysts were activated in the range 200–900°C to determine the maximum amount of Cr(VI) which could be stabilized by the silica at each temperature. All of the Cr impregnated onto silica remained hexavalent up to a sharply defined saturation coverage, and any excess over this limit merely decomposed, mainly to Cr_2O_3. This saturation coverage declined with increasing temperature, paralleling the silica hydroxyl population, and common modifiers like alumina or fluoride, which increase or decrease the OH population, also enhanced or diminished the stabilization of Cr(VI). Above 500°C moisture quickly destabilized Cr(VI), as did lack of oxygen. These findings have again been discussed in terms of three simple models of occupation.

INTRODUCTION

If one keeps the chromium concentration low, and calcines in dry oxygen, it is possible to prepare a Cr/silica catalyst having high polymerization activity but containing chromium completely hexavalent after activation (*1*). More commonly though (*2–6*), workers have studied preparations and chosen conditions where degradation, particularly to α-Cr_2O_3, accounted for a good portion of the chromium, thus obscuring the results. One factor contributing to degradation was suspected to be overloading since chromium unattached to the silica would probably not be stabilized. However, very little information is available concerning how much Cr(VI) can be stabilized. Hogan (*1*) found it increasingly difficult to stabilize Cr(IV) with increasing temperature. Zecchina *et al.* (*7*), measuring the decrease in the hydroxyl population as they increased the Cr loading, found a breakpoint at about 2.2 Cr/nm^2 which might indicate saturation, but it was not reported how much of this chromium was actually hexavalent. In this report, the saturation coverage by Cr(VI) has been measured as a function of total Cr loading, temperature, activation conditions, and other variables, and a brief attempt has also been made to interpret the findings in terms of three simple models which have been introduced earlier in this series.

EXPERIMENTAL

The catalyst samples used in this report were prepared by the same procedure already described. Analysis and polymerization methods were also the same. X-Ray diffraction powder patterns were obtained on a Norelco basic diffractometer. Samples were mixed with 5% tungsten as a standard. Measurements of signal intensity and breadth were obtained on the peak at 36.2° (2θ). 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.

RESULTS

Saturation Coverage by CrO_3

Figure 1 shows how the suface of silica can become saturated with hexavalent chromium. These samples were made to contain various concentrations of CrO_3,

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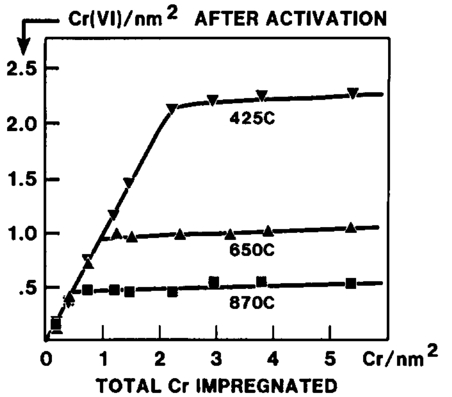


FIG. 1. Stabilization of Cr(VI) on silicas impregnated with CrO_3 and calcined in O_2 at indicated temperature.

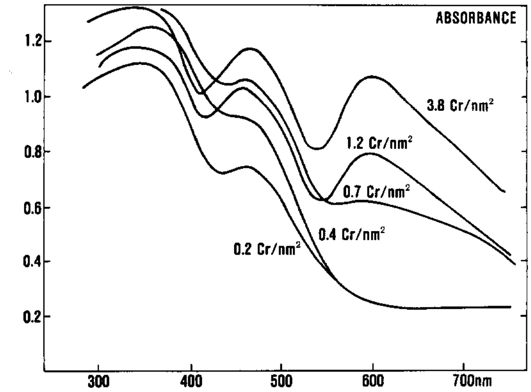


FIG. 2. Reflectance spectra of CrO_3/silica calcined at 870°C.

then they were calcined in dry oxygen at 425, 650, and 870°C. The amount of Cr(VI) stabilized by the silica was then determined. For example, at 650°C on samples containing up to about 1.1 Cr/nm^2 (2.1 wt% Cr), all of the chromium (within experimental error) was stabilized in the hexavalent state. However, at higher loadings the excess CrO_3 merely decomposed, presumably to Cr_2O_3, always leaving 1.1 Cr(VI)/nm^2 no matter how much total chromium was present. We call this sharp limit the saturation coverage.

This same behavior was also observed at 870°C, where the saturation coverage was different—0.55 Cr(VI)/nm^2 (1.1 wt% Cr)—and at 425°C, where it was 2.0–2.3 Cr(VI)/nm^2. Again when the total chromium content was less than the saturation coverage, then all of the Cr was stabilized as Cr(VI). As activation temperature increased, the saturation coverage decreased.

X-Ray diffraction results from these samples yielded the powder pattern of α-Cr_2O_3 above 400°C when the total chromium concentration exceeded the saturation coverage. Below this level, however, no diffraction lines were observed. Neither was any evidence seen in the XRD for any other crystalline species. The intensity of the XRD signal varied in direct proportion to Cr(total) − Cr(VI), suggesting that most of the excess Cr was converted to crystalline Cr_2O_3. The average crystallite size was several hundred angstroms.

The uv–visible reflectance spectra of these samples are shown in Figs. 2, 3, and 4. The band near 460 nm mentioned in Part II is present at every loading and at all three temperatures. At 425°C it was found at about 455 nm, but it seemed to shift to 460 or 465 nm as the calcining temperature was increased to 870°C. The saturation effect is easily seen in the spectra. At each temperature studied, a band at 600 nm appears immediately after the saturation loading is achieved, but not before, and then becomes more intense as the loading is further increased. This band comes from Cr(III); for

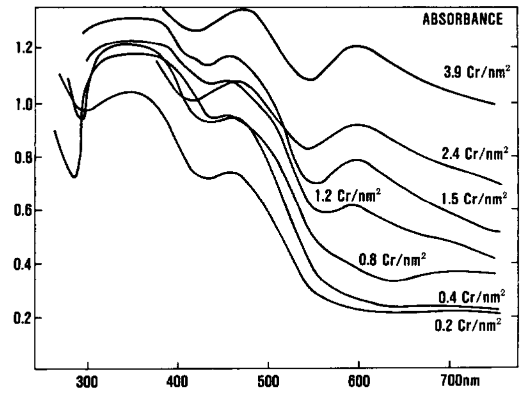


FIG. 3. Reflectance spectra of CrO^3/silica calcined at 650°C.

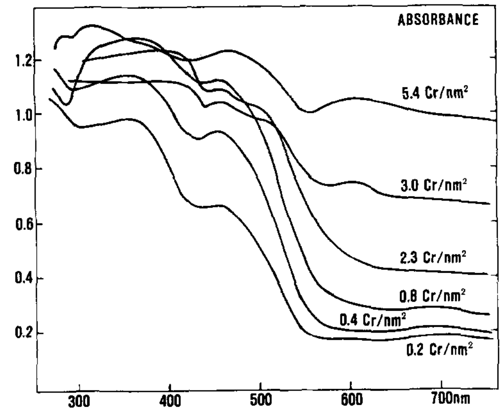


FIG. 4. Reflectance spectra of CrO_3/silica calcined at 425°C.

TABLE 1

Maximum Cr(VI) Coverage Obtained on Silicas Impregnated with Various Compounds and Then Calcined in Dry O_2 at the Temperature Indicated

Compound impregnated	Cr(VI) saturation coverage (Cr/nm^2)		
	870°C	650°C	425°C
CrO_3	0.55	1.1	2.3
$(NH_4)_2CrO_4$	0.54	1.0	1.8
$(NH_4)_2Cr_2O_7$	0.59	1.1	1.9
$Cr(NO_3)_3$	0.53	0.8	1.8
$Cr(OAc)_3$	0.55	1.1	1.9
OH population (OH/nm^2)	0.7	1.2	2.3

comparison, the spectrum of Cr(III)/silica, containing no Cr(VI), is shown in Fig. 11.

These saturation levels in Fig. 1 were not reversible. For example, in one run the catalyst, containing a large excess of total chromium (2.2 Cr/nm^2), was calcined at 870°C for 2 hr. It stabilized 0.55 Cr(VI)/nm^2 as expected. Then it was recalcined at 425°C overnight, but the hexavalent chromium level remained unchanged.

Prolonged calcining lowered the saturation coverage only slightly. One sample was held at 650°C in oxygen for 24 hr instead of the usual 2 hr. The hexavalent chromium content slowly decreased from 1.04 Cr(VI)/nm^2 at 2 hr down to 0.92 Cr(VI)/nm^2 at 24 hr. At 425°C another sample declined from 2.25 Cr(VI)/nm^2 at 2 hr to 1.88 Cr(VI)/nm^2 at 24 hr.

Other Chromium Compounds

This same saturation behavior was also found when the silica was impregnated with several other chromium compounds in place of CrO_3. Two other hexavalent compounds, ammonium chromate and dichromate, and two trivalent compounds, chromium nitrate and acetate, were investigated. The oxidation of samples impregnated with chromium acetate is shown in Fig. 5. At 425°C the Cr(VI) buildup was more gradual than that usually observed, but otherwise the saturation effect is again present.

The saturation coverages found for the five chromium compounds tested are listed in Table 1. At 870 and 650°C they were almost identical, regardless of the source of the chromium. At 425°C, however, the samples made with CrO_3 were somewhat higher than all the others. At lower temperatures the decomposition of excess Cr(VI) was incomplete. At 200–300°C the decomposition of ammonium chromate or dichromate did not yield diffraction lines from α-Cr_2O_3 or anything else. It is doubtful, then, whether saturation can be reliably measured below about 400°C.

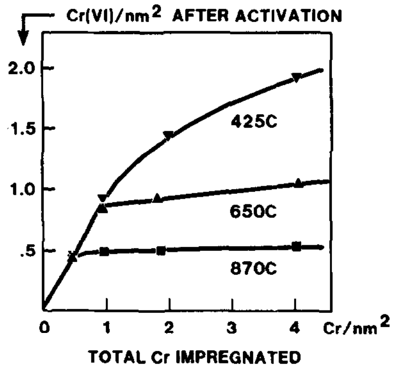


FIG. 5. Stabilization of Cr(VI) on silicas impregnated with Cr(III) acetate and calcined in dry O_2 at indicated temperature.

Saturation and the Hydroxyl Population

Figure 6 plots the saturation coverage of Cr(VI) as a function of activation temperature. Also plotted is the hydroxyl population of the silica containing no chromium. Above 400°C the two curves parallel each other, with the OH population being slightly higher than the Cr(VI) density at all temperatures. Below 400°C the Cr(VI) data became scattered due to incomplete decomposition of excess Cr(VI).

This behavior suggests that the stabilization of hexavalent chromium is somehow related to the hydroxyl population. As the activation temperature increased, the hydroxyl population on unimpregnated silica declined due to condensation and likewise the maximum Cr(VI) population decreased. To test whether the two phenomena are related, the following experiments were done. Silica samples, containing no chromium, were first calcined at 870°C, high enough to remove most of the hydroxyl population. Afterward they were impregnated with an excess of CrO_3, anhydrously as a solution in acetonitrile. In this way the chromium was added but without rehydrating the silica surface. Then they were calcined as usual in oxygen at 425, 650, and 870°C.

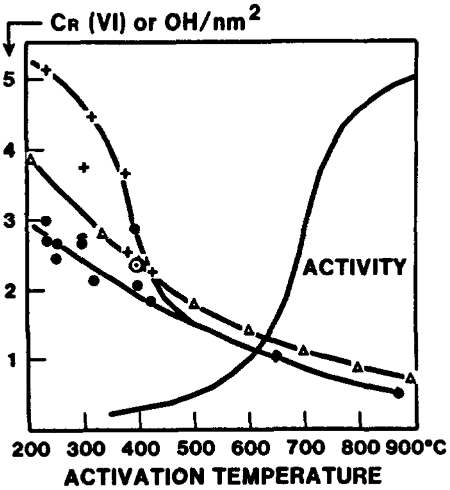


FIG. 6. Maximum Cr(VI) coverage on silicas impregnated with (+) CrO_3, or (●) other Cr compounds such as $(NH_4)_2Cr_2O_7$, and then calcined in O_2 at temperatures shown. (△) hydroxyl population on silica.

TABLE 2

Impregnation	Maximum coverage by Cr(VI)		
	870°C	650°C	425°C
CrO_3/CH_3CN	0.4–0.5	0.8	0.6–0.7
CrO_3/H_2O	0.5	0.7	1.4

Note. Silicas were calcined at 870°C before being impregnated with CrO_3 and calcined again at the temperature shown.

Table 2 lists the results of this experiment. If the Cr(VI) saturation coverage is related to the hydroxyl population, then all three samples should have stabilized the 0.5–0.6 Cr(VI)/nm^2 characteristic of 870°C, the silica pretreatment temperature. On the other hand if it is only a function of how high a temperature the chromium has experienced, then the three samples should have stabilized the usual Cr(VI) density characteristic of 425, 650, and 870°C. Instead the measured Cr(VI) densities were nearly constant at 0.5–0.7 Cr(VI)/nm^2, suggesting a connection with the hydroxyl population.

The experiment was then repeated, only the acetonitrile solvent was replaced by water. That is, the silicas were first calcined at 870°C, then impregnated with CrO_3/water, and finally calcined again in O_2 at 425, 650, and 870°C. These resuts, also listed in Table 2, were intermediate between the virgin (fully hydrated) samples in Table 1 and those impregnated in acetonitrile in Table 2. This also would be reasonable because complete rehydration of silicas annealed at very high temperatures is known to be difficult.

Since surface-bound Cr(VI) is thought to be the precursor of the active polymerization site, one might expect low activation temperatures to be preferred for best activity, since these give the highest Cr(VI) density. However, the reverse is actually true. Figure 6 plots the activity of a typical CrO_3/silica as a function of activation temperature. It rises with increasing temperature until 900°C or so when sintering sets in. In the concentration range studied here (0.5–5 Cr(VI)/nm^2) the activity of the catalyst is affected very little by the Cr(VI) density. Instead, it is far more dependent on activation temperature, whatever the Cr loading. This agrees with what other researchers have concluded from other approaches (*1*, *2*)—that only a small fraction of the total chromium is active in polymerization. It would seem that this number is sensitive to activation temperature, but not so much to Cr(VI) density in this range.

Saturation Coverage by CrO_2Cl_2

To determine how much chromate could be attached, a virgin sample of silica was dried at 150°C and then treated with a large excess of CrO_2Cl_2 vapor as the temperature was slowly increased to 220°C. After an argon flush the samples contained 2.2 Cr(VI)/nm^2 and 1.0 Cl/nm^2 indicating about 1.2 chromate species/nm^2. Further heating in argon to 300°C yielded 1.8 Cr(VI)/nm^2 of which 1.6/nm^2 was chromate. Heating in oxygen at 425, 650, and 870°C produced the same saturation coverages observed for CrO_3/silica.

Modifying Agents

Often in commercial applications a third component is added to the basic Cr/silica recipe to enhance activity or perhaps some polymer property useful in a particular application, such as the molecular weight of the polymer, or its distribution. One example of a modifying agent is fluoride (*8*), which is known to replace surface hydroxyls:

$$\equiv\text{Si—OH} + \text{HF} \rightarrow \equiv\text{Si—F} + H_2O \uparrow .$$

Fluoriding a catalyst sometimes increases its activity and also narrows the molecular weight distribution of the polymer.

To determine the effect of fluoride on the saturation Cr(VI) coverage, silica samples containing no chromium were mixed with ammonium fluorosilicate and then calcined at 425, 650, or 870°C. This causes the fluorosilicate to evaporate and then attack the silica. Most of the fluoride becomes incorporated. Afterward these fluorided samples were impregnated with an excess of CrO_3 in acetonitrile, to prevent hydrolysis of the attached fluoride, and then calcined again at the same temperature in oxygen. This two-step process prevented the chromium from coming into contact with the fluoriding agent.

The results from these experiments are shown in Fig. 7 where the Cr(VI) saturation coverage is plotted against the amount of fluoride added. At all three temperatures the amount of Cr(VI) stabilized dropped as the severity of the fluoride treatment increased. At 425°C the initial slope of the drop was about 0.7 Cr(VI) lost per F added. At 650°C it increased to 1.3 Cr(VI)/F, and at 870°C it further increased to 1.7 Cr(VI)/F. How can one fluoride replace more than one Cr(VI)? Possibly some of the Cr(VI) was present as a dichromate surface species. However, the effect is more likely related to the mobility of the fluoride at the higher temperatures as is demonstrated in Fig. 8 by its ability to flux and sinter the silica. The surface area, plotted against the amount of fluoride added, was completely

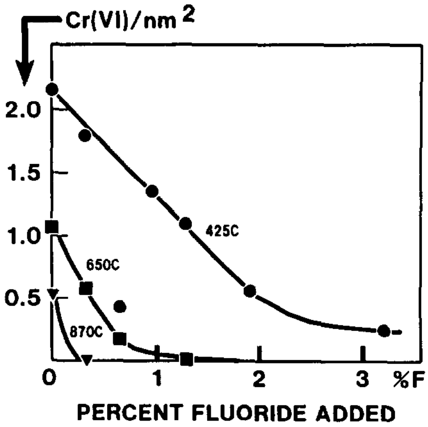


FIG. 7. Maximum Cr(VI) coverage on fluorided silicas impregnated with CrO_3/CH_3CN and activated at temperatures shown.

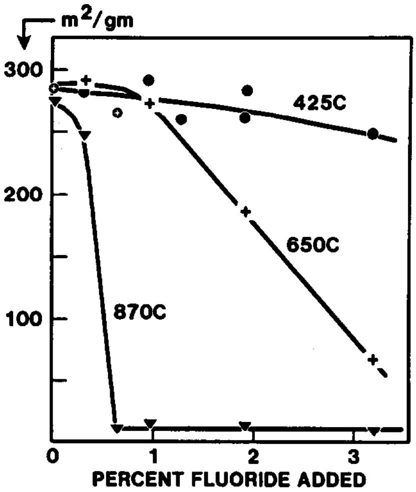


FIG. 8. Effect of fluoride on surface area of silica.

ruined at 870°C by only 0.7% F, but unaffected at 425°C.

This mobility is also evident in another way. Had the fluoride occupied sites randomly and remained stationary, the loss of Cr(VI) might have been uniform. Consider, for example, the addition of 0.3% F (~0.3 F/nm^2). This is only 7% of the total site density or about 10% of the hyroxyl population at the time of fluoriding, so the Cr(VI) population should be decreased by no more than about 10% at all temperatures. Such was the case at 425°C. However, at 650°C the fluoride was more effective, killing 45% of the Cr(VI) (although it should have occupied only 10% of the sites) and at 870°C all of the hexavalent chromium was destroyed by only 0.3% F. Thus the fluoride became mobile enough to attack all sites.

Another common modifier for the Cr/silica catalyst, sometimes used to increase polymer molecular weight, is alumina (*8*). To determine the effect of alumina on the hydroxyl population, silica samples containing no chromium were impregnated with an aqueous solution of aluminum nitrate, to 2.0 wt% Al, and then calcined as usual. At 800–900°C little change was noticed in the hydroxyl population, but at the lower temperatures the OH level was higher than normal—about 25% higher at 600°C and at 400°C. When the silica containing 2% Al was impregnated with an excess of CrO_3, the Cr(IV) saturation coverage also increased at the lower temperatures but was unchanged at 870°C. At 425°C the coverage was 3.5 Cr(VI)/nm^2; at 650°C it was 1.2 Cr(VI)/nm^2; and 0.54 Cr(VI)/nm^2 at 870°C.

Titania, sometimes used to decrease molecular weight (*9*, *10*), seemed to have no great effect on the saturation coverage. CrO_3/silica samples, dried at 150°C, were impregnated with a hydrocarbon solution of titanium isopropoxide to 6 wt% Ti before being calcined. Hexavalent chromium values found were 2.45 Cr(VI)/nm^2 at 425°C and 1.01 Cr(VI)/nm^2 at 650°C.

Atmosphere during Activation

Since the saturation Cr(VI) coverage appears to follow the hydroxyl density on the silica, one might expect higher Cr(VI) levels when the calcining was done in a moist, rather than dry, atmosphere. However, Fig. 9 demonstrates that moisture actually destabilized the hexavalent chromium at higher temperatures. In these experiments CrO_3/silica samples (contain-

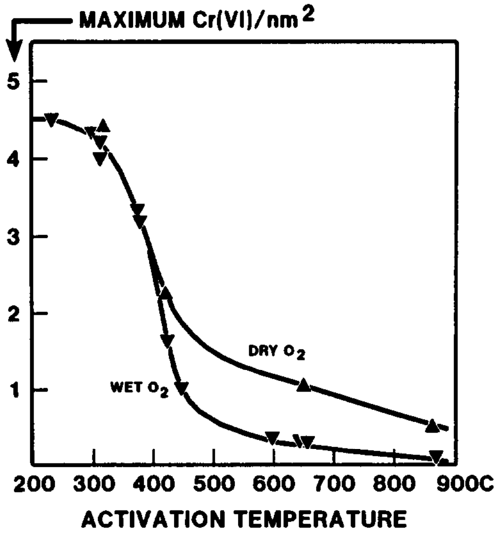


FIG. 9. Maximum Cr(VI) coverage on CrO_3/silica calcined in (▼) wet O_2, (▲) dry O_2. Total Cr density was 4.5 Cr/nm^2.

ing an excess of Cr) were brought to temperature and held there 2 hr in 1 atm flowing oxygen which was first saturated with water vapor at 25°C. Above 400°C the Cr(VI) concentration dropped far below that obtained in dry oxygen, and the polymerization activity of these samples also fell sharply.

The destabilization of Cr(VI) by moisture is probably due to hydrolysis of the Si–O–Cr bond, as has been postulated earlier by Hogan (*1*). Hexavalent chromium is easily and completely dissolved from the catalyst when it is placed in water at 25°C. When not stabilized by the silica, the Cr(VI) merely thermally degenerates. Again X-ray diffraction powder patterns indicated α-Cr_2O_3 in large crystallites (≥600 Å diameter).

Another factor found to affect the stabilization of Cr(VI) was the oxygen concentration in the fluidizing atmosphere. This is demonstrated in Fig. 10 where CrO_3/silica samples were calcined in dry nitrogen, dry air, and the usual dry oxygen. At 425°C all three samples retained approximately the same amount of hexavalent chromium. By 650°C, however, decreased oxygen levels had greatly decreased the Cr(VI) coverage. And by 870°C, the sample calcined in nitrogen contained less than 10% of the Cr(VI) stabilized by oxygen at the same temperature. Air, of course, yielded Cr(VI) values intermediate between those of oxygen and nitrogen. Wet N_2 at 870°C yielded no Cr(VI) at all, only the lines of α-Cr_2O_3 in the XRD pattern. The reflectance spectrum of this sample (containing 0.8 total Cr/nm^2) is shown in Fig. 11.

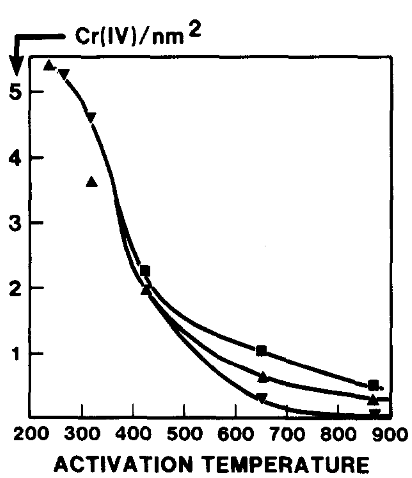


FIG. 10. Maximum Cr(VI) after calcining CrO_3/silica in dry (■) O_2, (▲) air, or (▼) N_2.

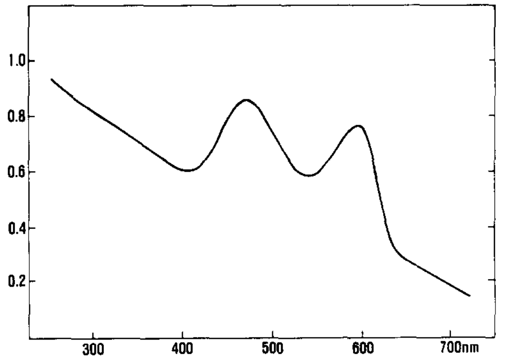


FIG. 11. Reflectance spectrum of CrO_3/silica calcined at 870°C in west N_2.

Calcining the silica in nitrogen instead of oxygen did not affect the porosity or the hydroxyl population. Therefore these results suggest an equilibrium

$$Cr(VI) \rightleftharpoons Cr(III) + \frac{3}{4} O_2$$

between oxidized and reduced forms. The identity of the equilibrium reduced form is debatable. Again large crystallites of α-Cr_2O_3 were detected by X-ray diffraction, but, from experience, these are not easily reoxidized.

Table 3 summarizes these findings and also suggests one additional point. During the heat-up, condensation of hydroxyls constantly releases moisture which can then destabilize Cr(VI). Since in a nitrogen atmosphere there is no possibility of reoxidation, one wonders whether the very low Cr(VI) values are a result of destabilization by moisture during heat-up or by the lack of oxygen during the 2-hr hold period. Therefore, in the last experiment in Table 3, samples were brought to temperature and then held 1 hr in oxygen. Afterward they were held another 2 hr in nitrogen. Activation in this way at 425°C led to no destabilization of Cr(VI), but at 650 and 870°C the Cr(VI)

TABLE 3

Maximum Cr(VI) Coverage on CrO_3/Silica after Activation in the Medium Indicated

Activation	Cr(VI)/nm²		
	870°C	650°C	425°C
Dry O_2	0.55	1.05	2.30
Wet O_2[a]	0.11	0.29	1.60
Dry air	0.39	0.70	1.99
Dry N_2	0.05	0.31	2.03
O_2/N_2[b]	0.23	0.68	1.94
Wet N_2[a]	0	—	—

[a] 23 mm H_2O vapor in 745 mm total pressure.

[b] Brought up to temperature in O_2, then held 2 hr in N_2.

coverages were found to be considerably higher than those obtained from a nitrogen heat-up. Apparently then, especially at 870°C, the destabilization caused by moisture during heat-up was much more rapid and severe than that caused by lack of oxygen at 870°C.

DISCUSSION

One reason sometimes given (*15*) for choosing dichromate as the active species on the Phillips Cr/silica polymerization catalyst is that the catalyst is usually prepared by impregnating silica with an aqueous acidic solution of CrO_3 which does contain mainly dichromate (*16*). But a preponderance of dichromate in solution does not necessarily imply binding to the silica as dichromate because even in acidic solution an equilbrium exists between the two species. In fact, insoluble chromates are often precipitated (*16*) from these "dichromate solutions." Furthermore, the actual attachment to the silica surface by esterification does not occur from solution but after drying at 150–300°C (*13*).

In basic solution Cr(VI) exists mainly as chromate instead (*16*). We made catalysts by impregnating silica samples with various chromium compounds: Ammonium chromate, or ammonium dichromate, or CrO_3 in water, CrO_3 ion acetonitrile, or t-butyl chromate in hexane. Lower-valent chromium compounds, which oxidize to Cr(VI) during calcination, were also tested such as Cr(III) acetate in alcohol or in water, or dicumene Cr(0) in hexane. These samples were then calcined in dry air at 650°C, and also at 870°C, to span the commercial range. No difference was found in the polymerization activity of these samples, or in the kinetics, or in the polymer produced, or in the uv–visible reflectance spectrum, or in the saturation coverage. Whatever species was formed, chromate or dichromate, was likely present on all samples.

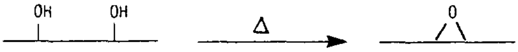
The hydroxyl density on fully hydrated silica is usually accepted to be in the neighborhood of 4.5 OH/nm² (*11*). On this particular silica, which has a large average pore diameter, we have measured up to 4.0 OH/nm² after calcining near 200°C, using the methyl magnesium iodide technique (*12*). Therefore if all sites were populated with Cr(VI) as chromate the maximum possible coverage should be 2.0–2.3 Cr(VI)/nm². As dichromate the maximum coverage could be as high as 4.0–4.5 Cr(VI)/nm².

It is interesting then to examine Fig. 6 with this in mind. Samples impregnated with CrO_3 and calcined at 300°C or lower usually exhibited little decomposition, often containing more than 4.5 Cr(VI)/nm² after calcination. Thus on these samples it is unlikely that all of the chromium was attached to the silica. Fubini *et al.* (*13*) have reported that esterification takes place between 150 and 350°C, but decomposition of the excess CrO_3 to Cr_2O_3 apparently takes place between 350 and 400°C judging from Fig. 6. A rapid degradation in this range always left 2.0–2.3 Cr(VI)/nm² by 425°C, whatever the total Cr content. This could indicate chromate, but remember that by 425°C the OH population on unpromoted silica has also declined to the same 2.3 OH/nm². So the question again is: Which sites are occupied by Cr(VI)? All of them (model 3)? Or only those sites which would ordinarily contain hydroxyls at the temperature in question (model 1)?

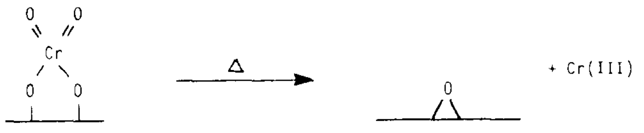
Other hexavalent chromium compounds, like ammonium chromate or dichromate, decomposed at as low as 200°C, but not to α-Cr_2O_3. Without studying the mechanism of decomposition and knowing the intermediates it is risky to assume that the measured oxidizing capacity at this temperature represents only Cr(VI) stabilized by the silica.

Model 1 (Selective Occupation of Hydroxylated Sites)

The correlation between the saturation coverage by Cr(VI) and the hydroxyl population is so compelling that one is tempted to believe the following simple picture: That Cr(VI) initially bonds to a nearly fully hydroxylated surface through esterification with a pair of hydroxyls, and that as the activation temperature is raised those pairs of sites normally prone to condensation



would still condense at about the same temperature even though they happen to be occupied by Cr(VI).



Thus the Cr(VI) population would always follow the OH population, even on those samples which were precalcined and then impregnated anhydrously, since siloxanes would not react. This model has often been implicitly assumed (*1*, *7*, *14*).

The problem with this simple scheme is that it is inconsistent with the saturation pattern observed in Fig. 1. For example, consider a Cr loading considerably less than saturation, say 0.3 Cr(VI)/nm^2. If the initial bonding with hydroxyls is random, then as the temperature is raised the Cr(VI) density should decrease, as pairs of sites condense whether they contain hydroxyls or Cr(VI). Normally by 870°C only about 15% of the OH population remains and therefore one would also expect a corresponding 85% reduction in the Cr(VI) population. Actually the experimental evidence points otherwise. As can be seen in Fig. 1, all of the Cr(VI) population remained intact. In fact, the above model predicts an altogether different pattern of saturation coverage from that seen in Fig. 1; the predicted behavior is shown in Fig. 12.

Of course this problem disappears if one assumes that the displaced Cr(VI) has enough mobility on the surface to always concentrate on those remaining hydroxyl sites which have not yet condensed. That is, as the temperature is increased the Cr(VI) selectively replaces those hydroxyls which do not condense, so that Cr(VI) is not lost until there are fewer available hydroxyls than chromium. The trouble with this view is that, although it fits the general saturation pattern, it contradicts all pre-

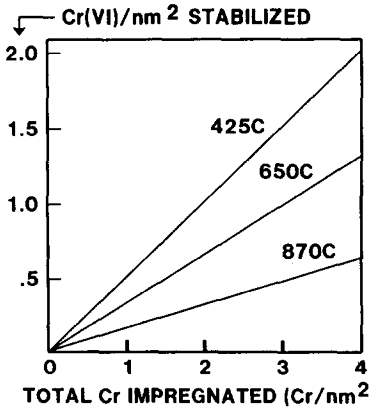


FIG. 12. Cr(VI) saturation coverage predicted by model 1.

vious data in Parts I, II, and III of this series. Consider the following contradictions between actual data and those predicted by the mechanism in question:

		Predicted	Found
Part I	ΔOH/Cr =	never <1	often <1
Part II	ΔOH =	always 0	always ≥ 0
Part III	ΔOH/Cr(HCl) =	always 0	0.8–1.8
	ΔOH/Cr(CO) =	never >-1	mostly >-1

Model 2 (Selective Occupation of Condensed Sites)

Another view is that the Cr selectively occupies and holds open pairs of sites which have the closest spacing and are therefore most condensable. Not only does this scheme not predict any correlation between saturation coverage and OH population, but it was also ruled out by previous data in Parts I and III. It is best considered as the high-temperature limit of model 3.

Model 3—The Ideal Case (Random Occupation of All Sites)

This view supposes that the Cr sits down without preference on a variety of site spacings, some easily condensable, others more separated, and that Cr prevents all of them from condensing during activation. That is, the Cr(VI) remains fixed during activation while unoccupied portions of the surface continue to dehydroxylate normally. In previous data this ideal has approached reality very closely, but unfortunately we now find that it does not predict the correct saturation behavior. Once saturated with Cr(VI) at say 400°C, samples still lost Cr(VI) as the temperature was raised. Thus the Cr(VI) does not totally prevent condensation.

Model 3—Nonideal Case

Rather than preventing it, one might argue that the Cr merely inhibits the condensation of sites, particularly when strain would result. That is, occupied site pairs still condense, but at somewhat higher temperatures than would ordinarily be needed. In fact, we have already noted that the data in Part III point overwhelmingly to some type of inhibited condensation. Thus the site population available to Cr would gradually decrease with increasing temperature, seemingly paralleling the OH population as was observed in Fig. 6. However, the randomness which seemed to fit all previous data would still be approximated.

This view still leaves the saturation pattern in Fig. 1 to be explained. Why does the Cr(VI) content on an unsaturated sample not decay like a saturated one as the activation temperature is raised? There are two possible answers: First, the Cr is mobile enough above 400°C to relocate when displaced from its original site by condensation. The relocation would not necessarily be to hydroxylated sites, as was postulated in model 1, but could also be to other, perhaps more strained, condensed sites. Second, the chromium might itself influence the condensation pattern so that in the absence of saturation the occupied sites are always last to condense.

Alumina and fluoride probably affect the saturation coverage not because they affect the OH population, but because they also affect the total number of sites available for occupation by chromium.

Finally, there are the anhydrous experiments to consider, where the silica was first dehydrated at 870°C, then impregnated anhydrously with CrO_3 before a second activation at 425 or 650°C. The saturation coverage found on these samples reflected the initial 870°C treatment, not that later experienced by the Cr. It is known that silica, once annealed above 600°C, becomes very resistant to rehydration (*11*). Apparently this was also true of attack by CrO_3. Once annealed, only those siloxane sites which would ordinarily be available at 870°C were reactive with CrO_3 at the lower temperatures.

As to whether the chromium exists as chromate or dichromate, these saturation data do not give a conclusive answer, but do agree with trends observed earlier. Had coverages been found greater than 2.3 Cr(VI)/nm^2, dichromate would have been definitely indicated, but this was not the case. Instead 2.3 Cr(VI)/nm^2 was the highest coverage found for CrO_3, and other compounds produced only 1.8 Cr(VI)/nm^2. Since this is within the theoretical limits of chromate coverage according to model 3, and not too far from the 1.6/nm^2 actually attached as chromate by reaction with CrO_2Cl_2, it is still possible that all of the Cr was present as chromate even under these crowded conditions.

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