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

III. The Reaction between CrO_3/Silica and HCl

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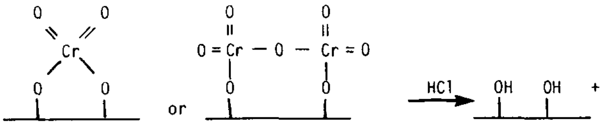
CrO_3/silica catalysts calcined between 400 and 900°C were treated with HCl gas, which stripped off the Cr(VI) as CrO_2Cl_2 vapor leaving one additional hydroxyl for each point of attachment to the surface. The increase in the hydroxyl population has been examined in terms of three simple models to gain insight into how Cr(VI) attaches to the surface and whether it exists as chromate or dichromate. These OH pairs formed by stripping off the Cr were then reacted with CrO_2Cl_2 vapor, which mostly lost two chlorides per Cr and developed polymerization activity similar to that of the original catalyst. This again confirms the activity of the chromate surface species.

INTRODUCTION

The difficulties in identifying chromate or dichromate species on the Phillips Cr/silica polymerization catalyst have already been discussed in Parts I and II of this series. Simply measuring the loss in surface hydroxyl population upon impregnation of CrO_3 (the ΔOH/Cr replacement ratio) does not give a direct identification as had been previously assumed (*1*). Instead these data require an interpretation because one must know whether the Cr selectively occupies certain surface sites, those which would otherwise be hydroxylated, or condensed, or "paired," or whether the occupation of sites occurs randomly without any preference.

In this report the reverse of the chromyl chloride reaction (see Part II) has been examined and the question of selective or random occupation has again become relevant. Samples of conventional CrO_3/silica, calcined between 400 and 900°C, were treated with dry HCl gas which strips off the Cr(VI) as CrO_2Cl_2 vapor leaving one new hydroxyl for each point of attachment:



Dichromate should also release a trace of water vapor during stripping but this does not readsorb very readily (see Part II). Thus the measured increase in hydroxyl population after stripping should provide information into which species was present and the type of occupation.

EXPERIMENTAL

The catalysts used in this study were prepared from the same Davison grade 952 silica described previously in Part II. About 50 g of this wide-pore silica, which is often used as a support for commercial polymer-

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ization catalysts, was slurred in water in which the desired amount of CrO_3 had been dissolved. The water was then evaporated off in a rotoevaporator. Catalyst samples were calcined by fluidization in dry oxygen, as has already been described. Gaseous HCl was purchased from Matheson and used without further purification. The analyses of Cr(VI), Cl, and OH have also been previously described, as well as the polymerization procedure.

RESULTS AND DISCUSSION

Stripping Off Cr(VI) with HCl

In Fig. 1 silicas containing various loadings of CrO_3 were calcined at 400°C in dry flowing oxygen for 2 hr. Afterward they were cooled in oxygen to 130°C and flushed with dry argon or nitrogen. Gaseous HCl was then admitted upstream from the catalyst, enough to comprise about 20% of the stream by volume. When the HCl first contacted the catalyst an immediate rise in temperature was noticed, particularly when the sample contained a heavy Cr loading. In fact, the HCl quite often had to be added slowly at first to prevent the temperature from exceeding 140°C (if not controlled, a runaway could sometimes go as high as 200°C briefly). Usually the exotherm lasted only a few minutes. The red vapor of CrO_2Cl_2 was not seen in the exit stream immediately. Instead it usually appeared only after the exothermic reaction, suggesting that the breaking of the first Si–O–Cr bond released most of the heat. After another few minutes the CrO_2Cl_2 vapor stopped coming off, but the HCl was continued for a total of 10 min. After another 5-min flush in argon or nitrogen the catalyst bed was lowered from the furnace where it could be seen to be white, no longer containing any chromium.

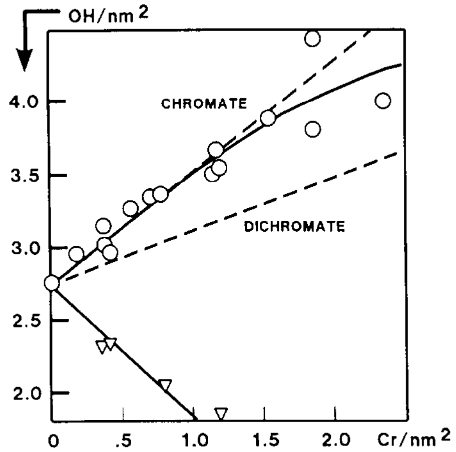


FIG. 1. CrO_3/silica calcined at 400°C and then (○) HCl at 130°C, or (▽) at 400°C.

Figure 1 plots the hydroxyl population found on these samples after HCl stripping, against the amount of Cr(VI) stripped off. Although HCl does not react with the silica itself, it does leave one hydroxyl behind for each former point of attachment to chromium. At the low stripping temperature of 130–140°C it is unlikely that these pairs of hydroxyls would then condense. Care was taken in all of these experiments to stay below the saturation loading (see Part IV of this series) so that all of the Cr was hexavalent.

As expected the higher the Cr loading, the more hydroxyls were left behind; hence the data in Fig. 1 have a large positive slope. However, an interpretation of Fig. 1 again requires a "background" correction (*1*). At the time of esterification with silica, CrO_3 probably reacts with hydroxyls on a nearly fully hydroxylated surface. Then during subsequent activation at 400–900°C, condensation of hydroxyls occurs. The question is: Would the sites occupied by Cr ordinarily remain hydroxylated (model 1, the selective occupation of hydroxylated sites), or condense (model 2, the selective occupation of easily condensable sites), or both (model 3, a random occupation of all sites)? This problem was discussed in Part I (*1*) of this series.

The first possibility above, the selective occupation of hydroxylated sites (model 1), has been implicitly assumed by previous workers (*2–4*) measuring ΔOH/Cr values. In this view the occupied sites are spaced

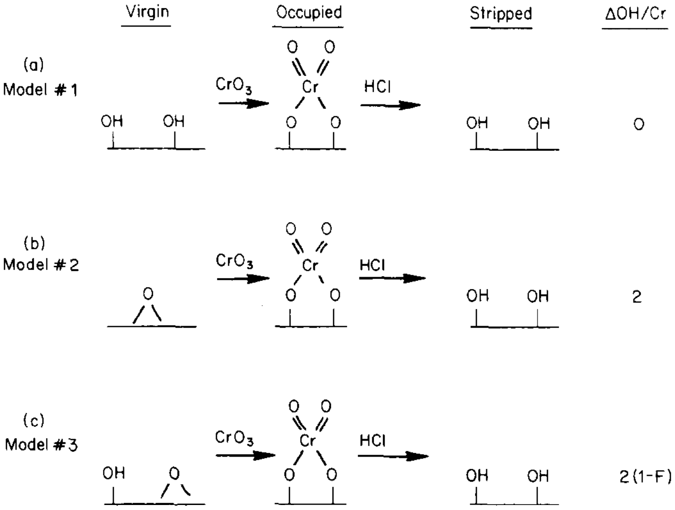


FIG. 2. The measured ΔOH/Cr slope is OH population after stripping minus that on the virgin silica divided by the Cr loading, and F is the fraction of sites which are hydroxylated on the virgin silica.

so far apart that they are uncondensable during activation. Or perhaps the Cr is mobile enough during activation to always occupy those sites which have not yet condensed. Either way, model 1 can be ruled out by the data in Fig. 1 because it instead predicts that a horizontal line should have been obtained, regardless of whether the chromium was present as chromate or dichromate. This is illustrated in Fig. 2a, while Figs. 2b and c illustrate the other two ideal cases. Table 1, then, summarizes the ΔOH/Cr values expected from the three models.

Model 2, the selective occupation of condensed sites, supposes that the occupied sites are spaced so closely that, unless occupied by Cr, they all condense easily during activation. It predicts a ΔOH/Cr of 2 for chromate and 1 for dichromate. Since the actual initial slope in Fig. 1 was 0.8, model 2 would also seem to be ruled out.

Instead of the two previous cases, the best fit was obtained when all sites were considered (model 3). Taking 4.5/nm^2 as the total site population (*5*), at 400°C the fraction of sites hydroxylated was (from Fig. 1) $F = 2.8/4.5 = 0.6$ and therefore for chromate the predicted slope was (from Table 1) $\Delta OH/Cr = 2(1 - F) = 0.8$ as found. Model 3 was also useful in explaining the data in Part I (*1*), and although it too is probably simplistic, it does seem to approach closest of the three to reality.

In Figs. 3 through 7 the results of other HCl stripping experiments are also plotted. The only difference was the initial activation temperature, which was increased from 400°C in Fig. 1 to 900°C in Fig. 7. On

TABLE 1

ΔOH/Cr Slopes Predicted by Three Models

	Occupation by Cr of:		
	Hydroxylated sites only	Condensed sites only	All sites[a]
HCl strip			
Chromate	0	2	$2(1 - F)$
Dichromate	0	1	$1 - F$
CO reduce			
Chromate	−2	0	$-2F$
Dichromate	−1	0	$-F$
Difference[b]			
Chromate	2	2	2
Dichromate	1	1	1

[a] Where F is the fraction of sites which are normally hydroxylated at the temperature in question.

[b] The ΔOH/Cr slope measured from the HCl stripping technique minus that measured after CO reduction.

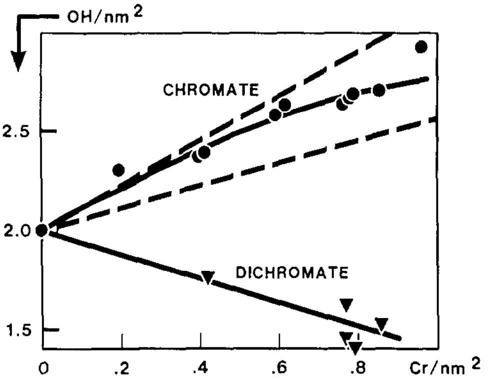


FIG. 3. CrO_3/silica calcined at 500°C and then (●) HCl at 130°C, (▼) CO at 400°C.

each is also plotted the lines expected for chromate and dichromate based on model 3, the random occupation of all sites. Although the data are often rather scattered, in every case the initial slope of the line is closer to that expected for chromate than for dichromate. Often the data seem to bend downward at higher Cr loading. The cause is unknown. A contribution from dichromate at higher loadings is one possibility, but data presented below argue against that explanation.

Reduction in CO

One cannot measure the OH population on Cr(VI)/silica using the methyl magnesium iodide reaction because Cr(VI) also reacts. However, in some experiments the catalyst was calcined first in oxygen as before for 2 hr at the desired temperature, and then in CO at 400 or 500°C for another half hour to reduce the Cr(VI) to Cr(II) (*3*, *4*). A low temperature was chosen for the CO treatment to prevent CO itself from dehy-

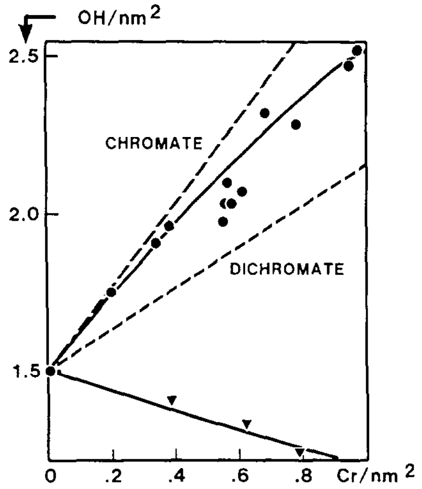


FIG. 4. CrO_3/silica calcined at 600°C and then (●) HCl at 130°C, (▼) CO at 500°C.

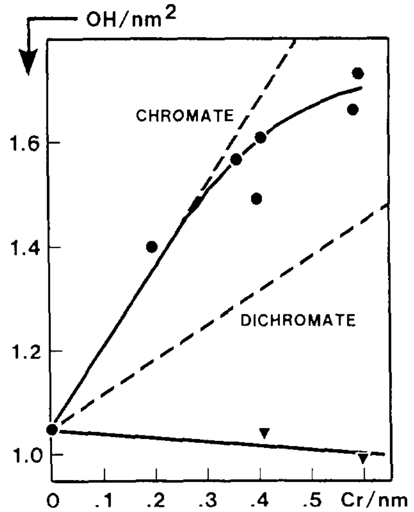


FIG. 5. CrO_3/silica calcined at 700°C and then (●) HCl at 130°C, (▼) CO at 500°C.

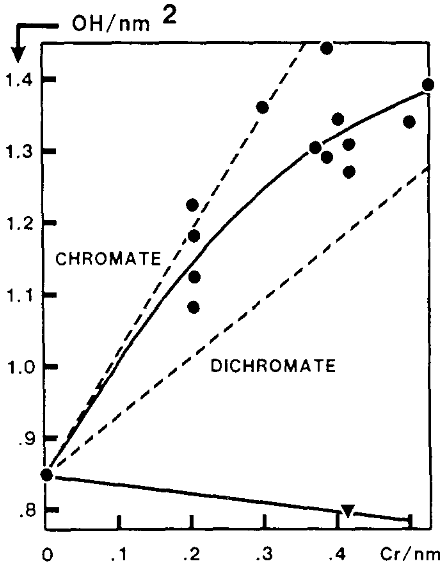


FIG. 6. CrO_3/silica calcined at 800°C and then (●) HCl at 130°C, or (▼) CO at 500°C.

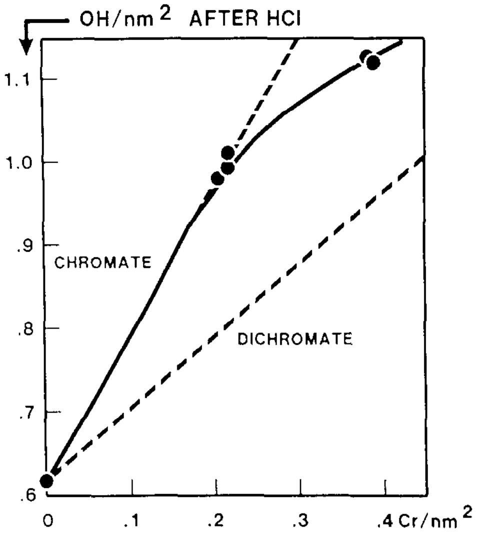


FIG. 7. CrO_3/silica calcined at 900°C and then treated with HCl at 130°C.

droxylating the silica via the water gas shift mechanism (6), which starts at about 600°C. Then samples were cooled in argon and the OH population determined as usual.

These data are also plotted in Figs. 1 and 3–7. This time the OH population decreases as the loading increases. Again, however, a background correction is needed in order to interpret the measured ΔOH/Cr slope. The same three models can be applied and the predicted values are listed in Table 1. This time is it model 2, the selective occupation of condensed sites, which can be quickly ruled out because it predicts a horizontal line. In contrast, the actual line in Fig. 1 points down rather steeply, having a slope of between −1.0 and −1.1. This is again quite close to the −1.2 predicted for chromate by model 3, random occupancy of all sites. It predicts about −0.6 for dichromate.

Actually model 3 approaches model 1 at very low temperatures where most sites are hydroxylated. And it also approaches model 2 at very high temperatures where most sites are dehydroxylated. Therefore in Figs. 3–7 it is reasonable that the lines should become more horizontal as the temperature was increased. However, at 600°C and higher the measured slopes were even more flat than would be predicted by the random site model. This may be related to the fact that paired hydroxyls are completely condensed by 600°C, and afterward only singles remain (see Refs. (7, 8) and also Part II of this series where silica was reacted with CrO_2Cl_2). The chromium may attach to "paired" sites only. A much better fit to the CO data can be obtained from model 3 by considering only the paired sites when computing F. This is summarized in Table 2. For example, consider again the data at 400°C in Fig. 1. If there are 1.1/nm^2 single hydroxyls (7) then $F = (2.8 - 1.1)/(4.5 - 1.1) = 0.5$ and therefore for chromate the predicted $\Delta OH/Cr = 2F = 1.0$, which was observed. This treatment of the HCl data puts the measured slopes between chromate and dichromate, but again usually closer to chromate.

ΔOH/Cr Difference Slope

Actually one can eliminate the need for a model, or a computation of F. Notice in Table 1 that if the CO predictions are subtracted from the HCl predictions, then F drops out and the difference is the same for all three models. That is, ΔOH/Cr(HCl) − ΔOH/Cr(CO) = n, where n is 2 for chromate and 1 for dichromate. A moment's reflection on what is actually being measured makes it clear why this should be true.

This measured difference data, then, are also listed in Table 2. The values all lie a little below 2.0 suggesting mainly chromate. However, the possibility cannot be ruled out that some dichromate might also be present.

Although they were obtained by different methods, the ΔOH/Cr(CO) data in Table 2 agree fairly well with that reported in Part I. The only difference occurs at 600°C and above, where the CO data drop off more quickly. In contrast, the previous data fit model 3 quite well with all sites considered.

TABLE 2

Slopes of ΔOH Plots

Activation temperature (°C)	Measured ΔOH/Cr			Predicted[a] ΔOH/Cr	
	HCl	CO	Difference[b]	CO (All OH)	CO (OH pairs)
400	0.8	−1.0 → −1.1	1.8 → 1.9	−1.2	−1.0
500	1.0	−0.6 → −0.7	1.6 → 1.7	−0.9	−0.5
600	1.1 → 1.3	−0.3	1.4 → 1.7	−0.7	−0.2
700	1.4 → 1.6	−0.1	1.5 → 1.7	−0.5	0
800	1.5 → 1.6	−0.1	1.6 → 1.7	−0.4	0
900	1.7 → 1.8	−0.1	1.8 → 1.9	−0.2	0

[a] Based on model 3. The first column assumes the chromium can attach as chromate to any of the 4.5/nm^2 available sites, whether hydroxylated or not. The second column assumes that it can attach (again as chromate) only to the 3.4/nm^2 paired sites. Divide by 2 for corresponding dichromate values.

[b] This value should be independent of model or interpretation. Chromate = 2. Dichromate = 1.

Subtracted from the HCl data, it gives about 2 at all temperatures.

Dehydration

Whether the chromium exists as chromate or dichromate, stripping it off with HCl should leave pairs of hydroxyls, which can then condense. In Fig. 8 a CrO_3/silica sample was activated at 800°C to remove most of the background OH population, then the Cr was stripped off. This raised the OH level up to about 1.3 OH/nm^2. Figure 8 shows the decline in OH level as the sample was reheated to progressively higher temperatures. Some of the pairs began condensing at as low as 200°C, and by 600°C only half remained. By 800°C all of them had apparently condensed. This indicates that at 800°C the chromium-occupied sites would ordinarily have been mostly condensed, in agreement with model 3, and that some of these pairs were even condensable at rather low temperatures. Thus the chromium prevents (or at least retards) the condensation of site pairs.

CrO_2Cl_2 Post-treatment

Most of the hydroxyl pairs generated by HCl stripping did have the correct spacing to form chromate. This was demonstrated by treating the stripped catalysts with CrO_2Cl_2 vapor. Most of the Cr reattached by losing two chlorides, to form a catalyst with polymerization activity similar to that of the original (unstripped) parent catalyst. Remember that only one chloride was lost when virgin 800°C silica was treated with CrO_2Cl_2.

For example, consider the following cyclic experiment. CrO_3/silica was calcined for 2 hr at 800°C to remove most of the background hydroxyl population. This ma-

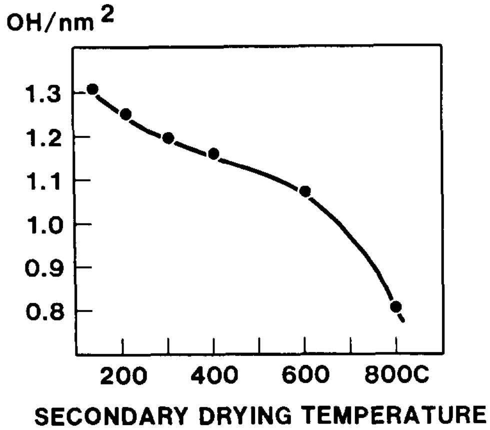


FIG. 8. The condensation of OH pairs resulting from the stripping of Cr/800°C silica.

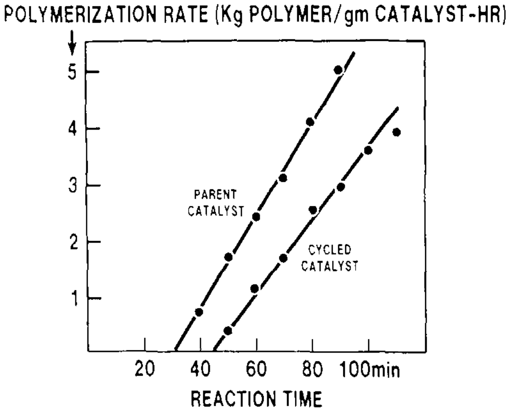


FIG. 9. Polymerization run with CrO_3/800°C silica (parent) and again after the Cr had been stripped off with HCl and replaced with CrO_2Cl_2 as chromate (cycled).

TABLE 3

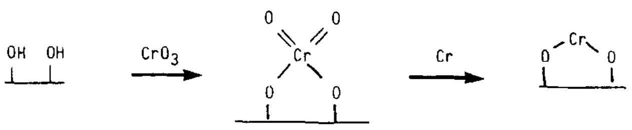
Activation temperature (°C)	Parent	Cycled	
	$Cr(VI)/nm^2$	$Cr(VI)/nm^2$	Cl/nm^2
950	0.26	0.22	0.03
(N_2, 300)		0.20	0.02
800	0.33	0.33	0.04
(N_2, 300)		0.33	0
800	0.51	0.48	0.09
(N_2, 300)		0.45	0
800	0.40	0.28	0.03
800	0.44	0.42	0.08
800 (N_2, 300)	0.40	0.46	0.28
(N_2, 350)		0.38	0
800 (N_2, 300)	0.39	0.36	0
600	0.77	0.36	0.02
(N_2, 300)		0.35	0
600	0.77	0.39	0.04
600	0.90	0.53	0.12
600	0.78	0.40	0

Note. CrO_3/silica samples were activated at the temperature indicated (parent). Then the Cr(VI) was removed by HCl at 130°C, and then put back on again as CrO_2Cl_2 vapor at 150–200°C (cycled). Sometimes they were then held in N_2 another half hour at 300°C to encourage reaction.

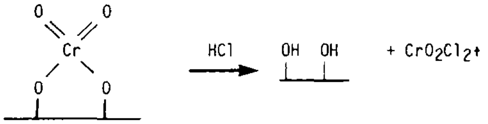
terial contained 0.44 $Cr(VI)/nm^2$ and on contact with ethylene it began to catalyze polymerization, the rate increasing at about 5 $kg/g\text{-}hr^2$. The chromium was then stripped off with HCl at 130°C, and at 150°C a light dose of CrO_2Cl_2 was injected into the argon stream. Afterward the catalyst was held in argon at 200°C for 1 hr. It was found to contain 0.42 $Cr(VI)/nm^2$ and it also had some chloride, about 0.08 Cl/nm^2. Hence 80% of the chromium reattached easily as chromate. It polymerized ethylene with only slightly less activity, having a 10-min-longer induction time and increasing rate at 4 $kg/g\text{-}hr^2$. The polymer melt indices were also very close, 0.2 for the parent and 0.1 for the cycled catalyst. These data are plotted in Fig. 9. The experiment was repeated several times at 800°C activation and also 600°C, where the cycled catalyst had the same activity as its parent. Table 3 lists the results. In all cases the CrO_2Cl_2 attached mainly as chromate.

CONCLUSIONS

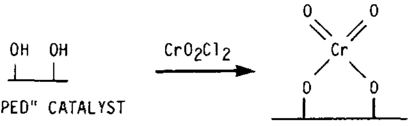
Again the evidence suggests that the commercial CrO_3/silica catalyst contains a high percentage of chromate and that this species could be responsible for the polymerization activity. Three types of experiments point to this conclusion: (1) The decrease in OH population brought about by the attachment of Cr (that is, the experiments using CO-reduced catalysts);



(2) the increase in OH population brought about by stripping with HCl;



and (3) the cyclic experiments in which "stripped" catalysts readsorbed CrO_2Cl_2 as chromate.



However, the possibility of a small contribution from dichromate, especially at heavier loadings, cannot be completely ruled out by this data.

The main difference between CrO_3/silica and CrO_2Cl_2/silica (see Part II) seems to be in the occupation of sites. Whereas CrO_2Cl_2 attached only to hydroxylated sites (model 1), HCl data indicate that CrO_3 also attaches to sites which, if unoccupied, could otherwise condense between 200 and 800°C. Thus the Cr(VI) prevents or retards the condensation of these sites. The best fit to these data was obtained from model 3, which assumes that the chromium attaches randomly and remains fixed while the rest of the surface dehydrates normally.

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