The State of Cr(VI) on the Cr/Silica Polymerization Catalyst

M. P. McDANIEL

Phillips Petroleum Company, Bartlesville, Oklahoma 74004

A brief study has been made of the hydroxyl population on silica before and after promotion with CrO_3. The measured $\Delta OH/Cr$ ratios did not equal a constant 1 or 2, as has often been expected for a pure dichromate or chromate surface species. Instead, they decreased smoothly with increasing temperature even to values well below 1. However, an analysis of these data which assumes normal dehydroxylation of Cr/silica indicates initial bonding as a chromate surface species. Anhydrous impregnation of Cr gave a more direct answer, again indicating initial bonding as chromate.

I. INTRODUCTION

Although pure CrO_3 is unstable above 200°C, on silica it remains hexavalent up to 1000°C, and adsorption experiments indicate that each chromium atom is exposed. This implies the formation of a stable surface chromate compound (*1–4*). The commercial importance of this catalyst has created interest in the nature of the surface compound: Is it chromate, or dichromate, or perhaps both?
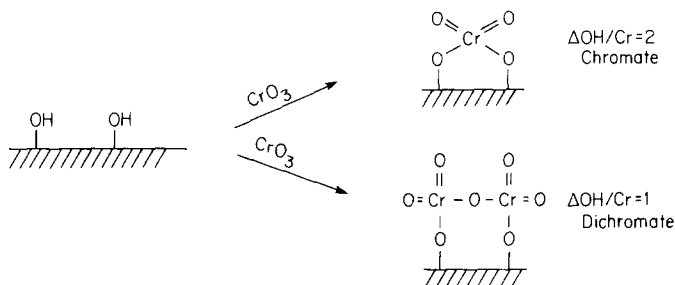
The question is not a simple one because using one form or the other as the starting material makes no apparent difference in the final catalyst after activation. Hogan (*1*) measured the change in weight upon impregnation of CrO_3 onto silica after drying at 150°C. He concluded that more than two hydroxyl groups were lost per chromium atom, and therefore that the binding must take place as chromate. On the other hand, Krauss (*2*), working with silica–alumina, and Zecchina *et al.* (*3*), working with Aerosil, both found only one hydroxyl lost per chromium, and concluded that the chromium must be present as dichromate. Zec-china *et al.* used infrared measurements to determine OH populations after their samples had been activated at 600°C.

In this paper, another brief look into this question has been made, together with an attempt to rationalize some of the previous conflicting evidence.

II. EXPERIMENTAL

Silica preparation. Davison 952 wide-pore silica was used in these experiments. It had a surface area near 280 m²/g and pore volume of about 1.6 cm³/g. Samples were slurried in distilled water, to which enough CrO_3 had been added to yield 1.5 or 3.0%

Cr, based on the weight of the dry silica. These slurries were then dried on a hot plate with constant stirring.

For the activation step, about 10 g of silica was fluidized in 40 liters/hr of dry air (passed through a 13X molecular sieve column) inside a 46-mm-o.d. quartz tube. Heat was supplied by an electrical furnace programmed to rise at 400 C deg/hr until the desired temperature was reached, and then to hold that temperature for 18 hr. After activation, the total Cr content of each sample was determined by neutron activation as well as the Cr(VI) content by titration with Fe(II) to the ferroin endpoint. No evaporation of Cr was detected. Up to 600°C only Cr(VI) was found, but at 800°C some decomposition to lower valence states was noticed, particularly at 3% Cr. X-Ray diffraction indicated Cr_2O_3 crystallites 400 Å in diameter.

Anhydrously promoted samples were impregnated with a hexane solution of di-t-butyl chromate after the activation step. Then they were again activated at the same temperature for another hour to drive off organics.

Silanol measurements. Two methods of measuring the surface hydroxyl population on silicas were used. The first, which has become a common technique (5), used methyl magnesium iodide to react with the OH groups and generate methane. Silica samples of about 0.5 g were charged under N_2 to a 20-cm^3 reaction vessel attached to a mercury-filled burette and oil manometer. About 1 or 2 ml of 1 M CH_3MgI in dibutyl ether was then injected onto the sample. Methane evolved immediately and then stopped after 2 or 3 min. Each mole of methane collected was taken to indicate 1 mole of surface silanol. Blank runs indicated no significant contribution from the vapor pressure of the ether.

For unpromoted silicas, the Grignard method indicated OH levels consistent with reports from other sources. However, samples containing chromium produced far more methane than was reasonable from the expected OH population, suggesting a side reaction with the hexavalent chromium. After the initial reaction, methane continued to evolve at a slower but steady rate for hours. Reducing the chromium in carbon monoxide at 350°C did not stop this autolysis. Instead, $TiCl_4$ was used as a reagent and the liberated HCl was measured. Although $TiCl_4$ has been reported (6) to react completely with silica, hydroxyl populations determined by this method at 25°C were always slightly lower (by about 10%) than by the Grignard method. Therefore, values reported here have been corrected. No autolysis was observed, and again blank runs indicated no contribution other than from the silica.

III. RESULTS AND DISCUSSION

Aqueous impregnation of CrO_3. Figure 1 plots the hydration level of silicas activated in dry air at 200, 400, 600, and 800°C for 18 hr. The upper curve is that of the support alone, containing no chromium, while the lower curves represent silicas impregnated with aqueous solutions of CrO_3 to contain 1.5 or 3.0% Cr. As expected, the presence of CrO_3 decreased the hydroxyl concentration on the silica surface. However, the loss in OH content at the various temperatures was not constant as might be anticipated for
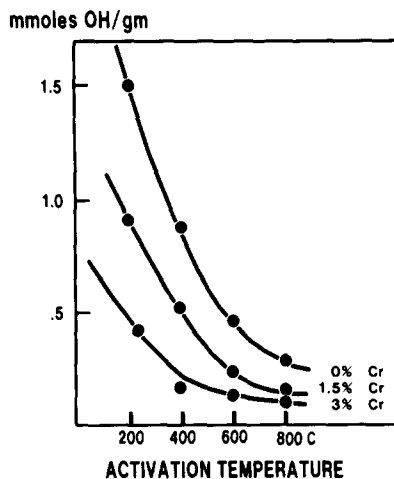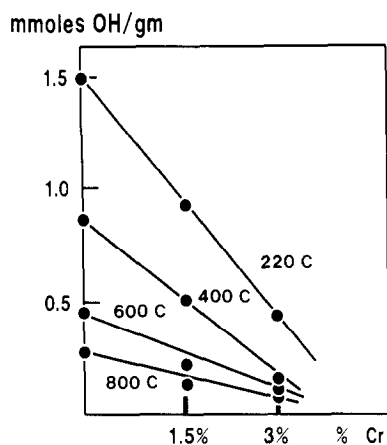

FIG. 1. Aqueous impregnation of CrO_3 on silica.

FIG. 2. Aqueous impregnation of CrO₃ on silica.

a simple displacement of 1 OH/Cr for di-chromate or 2 OH/Cr for chromate. In fact, the ΔOH/Cr replacement decreased smoothly with increasing activation temperature.

Figure 2, a plot of hydroxyl concentration against Cr concentration, shows that for a given temperature, the ΔOH/Cr replacement ratio was about constant, because approximately straight lines were obtained at all temperatures. A similar plot from ir spectra for 600°C only was reported by Zecchina et al. (3), and Krauss (2) has made measurements on silica–alumina. Both concluded that the chromium was present as dichromate because the ΔOH/Cr replacement was about unity. On the other hand, Hogan (1) found by gravimetric analysis that each mole of CrO₃ released 2 moles of OH at 150°C, indicating chromate. Interpolation of Fig. 2 also gives OH/Cr replacement ratios near two at 150°C and near unity at 500°C.

Anhydrous impregnation of Cr. When CrO₃ is impregnated aqueously, the chromium sets down on a fully hydroxylated surface and thus has its choice of possible OH pairs to replace; difficulties in finding proper OH spacing are at a minimum. Therefore, another series of samples was impregnated anhydrously with a chromate ester after activation. In this procedure, the Cr contacts a surface already in a partially

dehydrated state and could have more difficulty finding OH pairs at the right spacing.

Figure 3 shows the hydration level of samples activated, impregnated to 1.5% Cr with a hexane solution of t-butyl chromate, and reactivated at the same temperature for 1 hr to drive off organics. The curve is similar, but not identical, to that found for aqueous impregnation. Again the presence of Cr lowered the surface OH content and again the loss diminished with increasing activation temperature.

Difference curves. Figure 4 is a plot of the difference in OH concentration between untreated silica and silica containing 1.5% Cr, against activation temperature. This difference has been expressed as a replacement ratio, in OH groups lost per Cr atom. The two curves represent aqueous and anhydrous impregnation. In both cases, this difference was not constant or an integer, as might first be anticipated for pure chromate or dichromate, but it decreased smoothly with increasing activation temperature. At 3.0% Cr, the findings are similar.

Figure 4 indicates that some chromate exists on the surface because for several points, ΔOH/Cr values lie well above unity. This was true of both types of impregnation. The other points, however, are
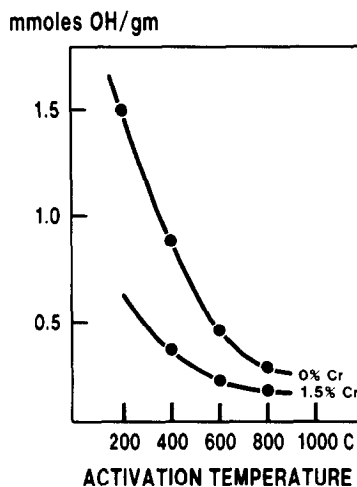

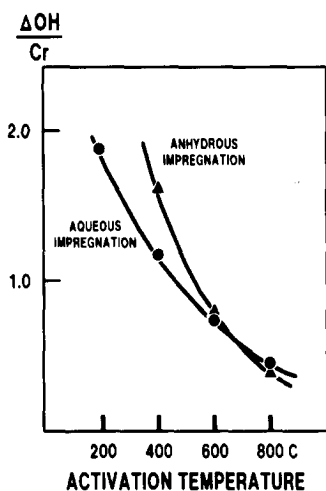FIG. 3. Anhydrous impregnation of t-butyl chromate on silica.

FIG. 4. Change in OH population upon impregnation of 1.5% Cr.

more difficult to explain because they lie below unity. In the case of anhydrous impregnation, the chromate ester could also react with siloxane, producing a surface chromate without replacing any hydroxyl groups. However, for aqueously impregnated samples, reaction with siloxane seems unlikely or even impossible because contact is made with a fully hydroxylated surface.

Analysis. Rather, the effect is just an artifact of the way these experiments, and those of other workers, were done. For illustration, consider a hypothetical portion of the surface, call it Region A, which before activation contains two OH groups. Now consider Region B, which is identical to Region A except that the two OH sites have been replaced by a surface chromate species. At the start of the experiment, that is, before activation, Region A contains two more OH groups than Region B, and $\Delta OH/Cr = 2$. But during activation, Region A begins to dehydroxylate normally, until by 500°C it contains only half of its initial OH population, speaking statistically, and now $\Delta OH/Cr = 1$ even though the Cr is still present as chromate. At higher temperatures, the ratio goes even lower. Therefore the hydroxyl population after impregnation

of CrO_3 should be predictable:

$$[OH]_T{}^c = [OH]_T{}^0 - [OH]_T{}^0\, nc/m, \quad (1)$$

where

n = 1 or 2 for dichromate or chromate,

c = Cr concentration (in mmole/g),

$[OH]_T{}^c$ = OH concentration on silica having a Cr concentration of c and an activation temperature of T,

m = OH density on fully hydroxylated silica.

Notice that the form of Eq. (1) fits the plots in Fig. 2, where the hydroxyl populations are plotted against chromium concentration, and the slope is $n[OH]_T{}^0/m$. If m is taken to be about 1.85 mmole/g (measured by the CH_3MgI technique) then n, calculated from the slope of each line in Fig. 2, lies very close to 2 in every case. The value of n can also be taken from the x intercept, or saturation point, where in principle all OH sites would be occupied by chromium. All four lines intersect the axis around 4.0 to 4.5% Cr (0.9 mmole Cr/g). At this point $n = m/c$ or 2.

In other words, the measured $\Delta OH/Cr$ ratio should be proportional to the OH population of the unpromoted silica at all temperatures because the Cr occupies a fixed fraction of the available sites. On
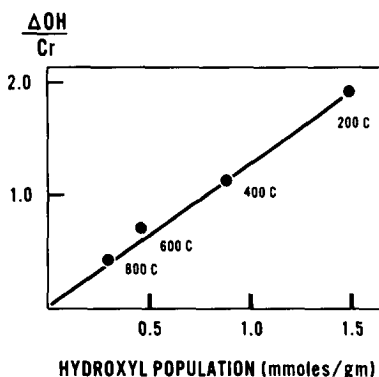

FIG. 5. OH loss per Cr plotted against OH population of the unpromoted silica.

rearranging Eq. (1):

$$\frac{\Delta OH}{Cr} = \frac{[OH]_T^0 - [OH]_T^c}{c}$$

$$= \frac{n[OH]_T^0}{m}. \quad (2)$$

This proportionality is visible in Fig. 4, where the difference curve seems to parallel the parent hydration curve in Fig. 1, and also in Fig. 5, where the measured $\Delta OH/Cr$ ratios have been plotted for each temperature against the OH concentration of the unpromoted silica. A straight line was obtained which went through the origin. The slope of this line (n/m) again corresponds to a saturation coverage of about 4.3% Cr, indicating $n = 2$ or chromate.

The analysis assumes normal dehydroxylation of Cr/silica, that is, that the Cr does not alter the thermal dehydroxylation pattern of the unoccupied portion of the surface. Furthermore, these findings do not rule out that dichromate could be formed at higher temperatures from the chromate, without changing the hydroxyl population. Neither would rearrangement to Cr_2O_3 crystallites at higher temperatures be expected to change the $\Delta OH/Cr$ measurements if the dehydroxylation of Cr/silica were normal. Finally, these findings deal only with the range 0–3% Cr, and therefore say nothing of the bonding at ultrahigh loadings, where an excess of Cr is used. However, such loadings are unstable, decomposing at 400°C to Cr_2O_3 and about 4.5% Cr(VI) (4).

The anhydrously impregnated samples also show a decreasing $\Delta OH/Cr$ ratio with increasing activation temperature. Whereas on the aqueously impregnated samples only one type of surface site was available for binding Cr—the hydroxyls, on the anhydrously impregnated samples there are two types of sites—remaining hydroxyls (perhaps more isolated) and siloxanes (condensed hydroxyls). If on the anhydrous samples the binding were random, that is, if the Cr showed no preference between hydroxyls and siloxanes, then the difference

curve in Fig. 4 would be identical to that of the aqueous samples because in both cases the loss in OH would be determined by the same statistical arguments. Instead $\Delta OH/Cr$ (anhydrous) was slightly higher at 400°C, indicating a selective reaction with the remaining hydroxyl groups in this range. At higher temperatures, where the hydroxyls become more isolated and the siloxanes probably more strained, the preference diminished.

IV. CONCLUSIONS

CrO_3 binds as chromate to the surface of silica when impregnated aqueously at up to 3% Cr. However, measuring the difference in hydroxyl populations between activated silicas containing varying amounts of chromium does not always yield the true $\Delta OH/Cr$ replacement ratio of two. Instead, this ratio should and does vary with the activation temperature in direct proportion to the hydroxyl population of the unimpregnated silica. In fact, $\Delta OH/Cr$ values well below unity can be obtained at high activation temperatures. Of course, the chromium is known to be mobile on the surface during activation, and these findings do not rule out a secondary formation of some dichromate from the initially formed chromate.

Impregnating the chromium anhydrously onto an activated silica does give a true indication of $\Delta OH/Cr$ for any activation temperature. Again, evidence for the formation of chromate was found, as well as binding of the chromium to siloxane.

REFERENCES

1. Hogan, J. P., *J. Polym. Sci. A-1* **8**, 2637 (1970).
2. Krauss, H. L., in "Proceedings, 5th International Conference on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), Vol. 1, p. 207. North-Holland, Amsterdam, 1973.
3. Zecchina, A., Garrone, E., Ghiotti, G., Morterra, C., and Borello, E., *J. Phys. Chem.* **79**(10), 966 (1975).

4. Unpublished data from this laboratory.

5. Fripiat, J. J., and Uytterhoeven, J., *J. Phys. Chem.* **66,** 800 (1962).

6. Armistead, C. G., Tyler, A. J., Hambleton, F. H., Mitchell, S. A., and Hockey, J. A., *J. Phys. Chem.* **73**(11), 3947 (1969).