

The Activation of the Phillips Polymerization Catalyst

I. Influence of the Hydroxyl Population

M. P. McDANIEL AND M. B. WELCH

86-G Phillips Research Center, Bartlesville, Oklahoma 74004

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Parameters in the thermal activation of Cr/silica and Cr/silica-titania polymerization catalysts have been studied. Both the activity and the molecular weight of the polyethylene formed depended on the activation temperature, suggesting a connection with the surface hydroxyl population surrounding each active center. Hydroxyls could be removed by chemical as well as by thermal means to take advantage of this dependence, such as by calcining the unpromoted support in carbon monoxide, sulfur, or halogen, and then afterward adding the chromium anhydrously. This two-step process also provided evidence of two types of chromium centers yielding high and low MW polymer. Combining all three influences—thermal dehydroxylation, chemical dehydroxylation, and the optimum distribution of active centers—yielded catalysts of extremely high activity and melt index potential.

INTRODUCTION

Owing to its commercial importance, the Phillips Cr/silica polymerization catalyst has been studied by an army of researchers during the past two decades, mostly in quest of the "true" active valence (1). The catalyst is not active until it has first been calcined, and these investigators, not always aware of the subtleties of the system, activated their particular catalyst preparations by whatever heat treatment each fancied, sometimes *in vacuo*, sometimes air, He, H₂, CO, or SO₂, and at any temperature between 300 and 800°C. Little attention was given, at least in the open literature, to the effect of these varied activation conditions on the polymer. Actually, this heat treatment controls, perhaps more than any other variable, the activity of the catalyst and, more important, the properties of the polyethylene produced.

Clark (2) has observed briefly that for a silica-alumina catalyst the molecular weight of the polymer varied according to the activation temperature between 500 and 850°C. This effect he attributed to an unspecified influence by hydroxyls on the surface of the catalyst. Others replaced the hy-

droxyls with another group such as fluoride (3, 4) or titania (5-8) to achieve variations in activity and molecular weight or other properties. Pullukat *et al.* (6-8) who studied the influence of titania in some detail, concluded that it increases activity and decreases the molecular weight by affecting the electronic environment at the chromium active center. They also felt that the effect could be enhanced by using CO followed by air during activation.

Since under commercial slurry conditions the high molecular weight polymers are easily made by the Phillips catalyst, the usual desire has been to modify the catalyst so as to decrease molecular weight. In this paper we have taken a more detailed look into the relationship between the hydroxyl population and the activity of the catalyst and the molecular weight of the polymer. We have then used these principles to develop a simple method of achieving low molecular weight polymers.

EXPERIMENTAL

Catalysts

Two commercially typical supports were used in these experiments. Catalyst A, or

Davison grade 952 silica, had a pore volume of 1.6 cc/g and surface area of about 280 m²/g. The other support, catalyst B, was a co-precipitated silica-titania (3.3 wt% TiO₂) with a surface area of about 450 m²/g. X-ray photoelectron spectroscopy indicated that much of the titania was found on the surface of the support. When the one-step activation process was used, both supports were first treated with chromium(III) acetate to yield 1 wt% Cr. Activation was accomplished in a shallow bed fluidized by air or another gas predried through alumina columns. Gases other than air were also deoxygenated through columns of specially reduced Cr/silica-alumina catalyst.

Polymerization

Ethylene polymerization runs were made in a two 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 N₂, one liter of isobutane was added as diluent and the ethylene (both Phillips polymerization grade) was supplied on demand at 550 psig. At 100–110°C polyethylene was obtained as a slurry, and after one or two hours the isobutane was flashed off leaving several hundred grams of polymer powder.

Relative Melt Index Potential

Melt indices were obtained from polymer samples by the standard test (ASTM D 1238-73) at 190°C using a weight of 2160 g. However, melt index values are not just affected by activation parameters, but also by catalyst porosity and by reactor conditions, such as the temperature, monomer concentration, and residence time. Therefore for clarity in this report we have normalized melt index values against those of a reference catalyst run under the same reactor conditions. We call the normalized value the relative melt index potential (RMIP) because it is independent of reactor conditions or catalyst type. Its value reflects only the activation parameters. The RMIP was

defined as unity for catalysts A and B after activation in air at 870°C by the one-step process.

There was also a slight tendency for the melt index to decrease as the yield from a particular catalyst increased. Although this effect was minor, care was taken to hold the yield constant in these experiments. Polymerization reactions were stopped when a yield of 5000 g polymer/g catalyst had been reached.

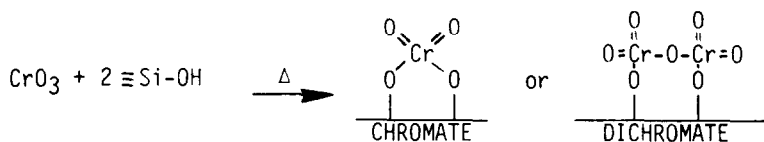
RESULTS AND DISCUSSION

A. One-Step Activation

Activity and the OH population. The Phillips Cr/silica polymerization catalyst is prepared by impregnating a chromium salt in almost any oxidation state onto a wide pore silica and then calcining this combination in oxygen to activate the catalyst (3). If a trivalent chromium salt is used, the activation step converts it to hexavalent form, the precursor of the active center. Ammonium chromate or dichromate can also be used as the chromium source, but most often the oxide CrO₃ has been employed. Whatever the starting material, no difference in the catalyst after activation is observed.

Cr/silica-titania catalysts, which are also commercially important, behave like their Cr/silica cousins in most respects, and in this report and the next they have been used almost interchangeably as examples. The titania is not active itself, but does act as a promoter for the chromium, improving its activity and affecting some of the polymer characteristics. In the third report of this series we look specifically at the effect of the titania.

Although pure CrO₃ begins to decompose above 200°C into O₂ and eventually Cr₂O₃ (8), a certain amount (0.4 Cr/nm²) is stabilized on silica or silica-titania up to 900 C in O₂ (10, 11). This is thought to be due to the formation of a surface chromate or dichromate ester in which each Cr atom is directly linked to the support (9–11).



While heat is necessary to effect the esterification, this is probably not the only purpose of the high temperature activation step. Figure 1 shows how the polymerization rate of a typical catalyst developed as the activation temperature was increased. A respectable activity did not appear until about 500°C, whereas the stabilization of Cr(VI) begins at as low as 200°C (9) and the actual esterification has been reported at between 150 and 300°C (12). Furthermore, other sources of chromium behaved similarly in activity to Fig. 1 even though the particular mechanism and temperature of binding must vary somewhat. Therefore the activation step must achieve some other necessary effect in addition to formation of the surface chromate or dichromate ester.

Notice in Fig. 1 that the catalysts were not active immediately after introduction into the reactor, but underwent a dormant

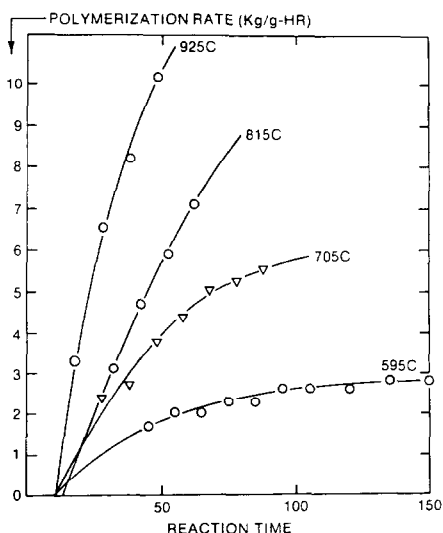


FIG. 1. Samples of Cr/silica-titania were activated in dry air at the temperatures listed, then allowed to polymerize ethylene in a high pressure autoclave. The rate of ethylene consumption has been plotted against reaction time (min) for each sample.

period or induction time. Afterward the rate then increased during the rest of the experiment. This is thought to be due to slow reduction of Cr(VI) to the active valence (1, 2, 9), probably Cr(II), by ethylene. Thus the concentration of active sites on the catalyst is probably not constant. The higher the activation temperature the more quickly the polymerization rate developed, although the induction time itself did not vary greatly. Figure 2 shows more completely this relationship between activity and activation temperature. Here activity was defined as the inverse of the time needed to make 5000 g of polymer per gram

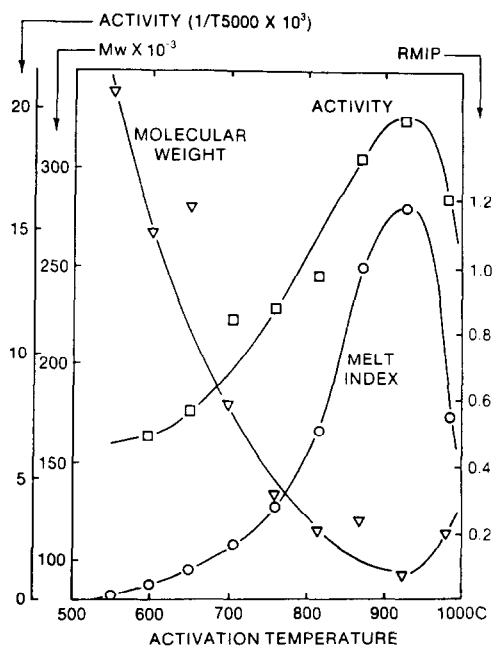


FIG. 2. Samples of Cr/silica-titania were activated at the temperatures shown, then allowed to polymerize ethylene. The weight average molecular weight of the polymer produced has been plotted, together with the relative melt index potential (RMIP), and the overall activity of each catalyst (defined as the inverse of the time needed to produce 5000 g polymer per g catalyst).

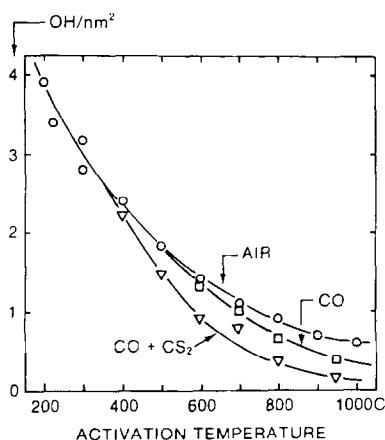


FIG. 3. Samples of silica were calcined at the temperatures shown in either dry air, CO, or a mixture of CO and CS₂ vapor. Surface hydroxyl populations were then determined by reaction with methyl magnesium iodide.

of catalyst. Activity increased with increasing activation temperature up to a maximum at around 925°C, and then declined as sintering developed. This says nothing about the rate constant, only the overall activity of the catalyst, which also includes the active site population.

Thus although the Cr was fully attached by 300°C, the activity continued to increase right up to the point of sintering. During this range, all of the Cr remained hexavalent and no obvious changes were observed in the crystallinity or porosity of the support, just a gradual dehydration of the surface as hydroxyl groups condensed to release water. Figure 3 plots this decrease in the hydroxyl population. Silica, containing no Cr, was calcined at various temperatures and then reacted with CH₃MgI solution. The amount of methane released was taken as an indication of the surface hydroxyl content, which decreased with increasing activation temperature but never actually reached zero. These facts suggest a connection between surface bound moisture and the activity of the catalyst.

Molecular weight and the OH population. Even more sensitive to the activation temperature was the rate of termination relative to the rate of propagation, which determines the average molecular weight of the polymer produced. Termination is thought to occur through beta elimination.

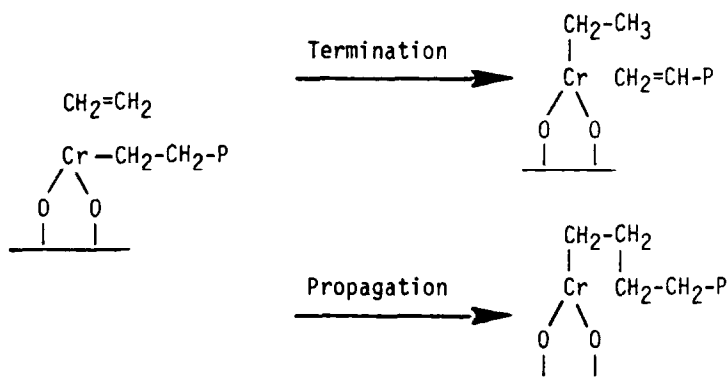


Figure 2 shows how the weight average molecular weight varied with activation temperature. The more dehydrated the catalyst became, the lower the molecular weight of the polymer produced, up to 925°C, and then the trend reversed as the catalyst began to sinter. Thus the relative rate of termination of chains behaved much

like the overall rate of polymerization. It increased with increasing dehydroxylation up to the point of sintering, and then declined.

Relative melt index potential (RMIP). The molecular weight of the polymer is usually more important from a commercial point of view than the activity of the cata-

lyst. Manufacturers and customers of polyethylene tend to be concerned with the viscosity of the polymer melt, which is related to the molecular weight, because it gives a direct indication of the flow of the molten polymer during processing. One common measure of this parameter is melt index (MI), which determines the flow of polymer through a standard orifice at 190°C under a standard load.

In the experiments which follow, melt index has been used as an indication of the relative rate of termination. It is a more sensitive measurement than molecular weight and far more reproducible. We have found for these systems that melt index varies approximately with the inverse fourth power of the weight average molecular weight.

$$MI \propto MW^{-4}$$

This can be seen in Fig. 2, which plots both MI and MW for a series of polymers. Thus a high MI indicates a high rate of termination relative to propagation. However, the melt index values reported here have been normalized to a standard set of reactor parameters (see Experimental section) so that the resultant value depends only on activation conditions and not on catalyst type or reactor conditions. We call this normalized value the relative melt index potential, or RMIP.

Thus in Fig. 2 the RMIP increases with increasing activation temperature up to the point of sintering, and then declines. This again indicates that the rate of termination, relative to propagation, behaved in the same way. In fact, since we know that the overall activity also increased up to 925°C, we conclude that the trend is probably the same or more exaggerated for the absolute termination rate as well.

Rehydration. Catalysts generally changed from yellow to a deeper orange color as the activation temperature was raised. On exposure to moisture, however, the orange samples immediately reverted back to yellow and lost their activity. A

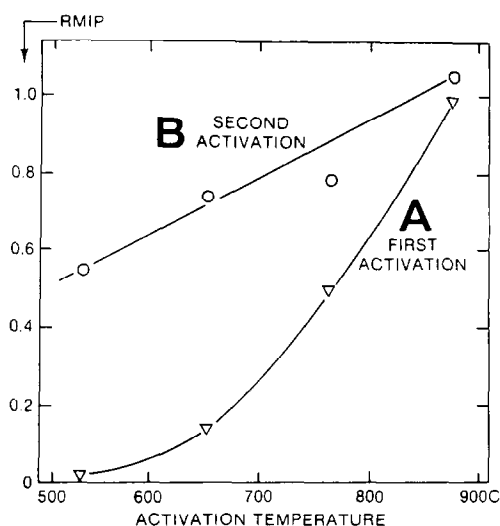


FIG. 4. (A) Samples of virgin Cr/silica-titania were calcined in dry air at the temperatures shown, then allowed to polymerize ethylene. (B) Samples calcined at 870°C were exposed to moisture and then reactivated at the temperatures shown, followed by polymerization.

second calcining step then restored activity and RMIP. One such experiment is shown in Fig. 4, which compares the RMIP obtained after the first and second activation steps. In 4-A a virgin catalyst was activated at various temperatures up to 870°C. In 4-B samples calcined at 870°C were then bathed in moist air at 250°C for 1 h and finally reactivated in dry air at the temperatures shown. Higher RMIP values were obtained after the second activation because the water vapor treatment probably did not rehydrate the surface to the same extent as on a virgin sample. Rehydration of pure silica annealed above 600°C is known to be difficult (13, 14), but the Cr-O-Si bonds are easily hydrolyzed. Thus rehydration lowered the RMIP, but at each temperature the rehydrated-reativated sample was more dehydrated than its virgin counterpart and this resulted in a higher RMIP. The two curves merge at 870°C, the original calcining temperature.

All of these facts indicate a connection between the hydroxyl population on the surface and the catalyst's activity and rela-

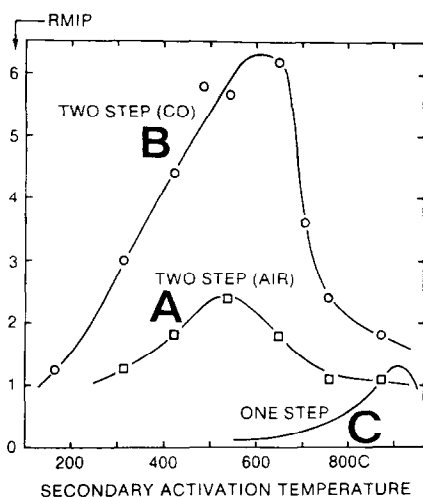


Fig. 5. Silica-titania was calcined in (A) dry air, or (B) dry CO, at 870°C, then Cr was impregnated anhydrously. Samples were reactivated in dry air at the temperatures shown before being allowed to polymerize ethylene. (C) Virgin Cr/silica-titania calcined in air at the temperatures shown (same as Fig. 2).

tive termination rate. This relationship provides a commercially valuable means of controlling the molecular weight of the polymer as well as other properties.

B. Two-Step Activation (Anhydrous Impregnation of Cr)

Two types of sites. Other experiments also implied this connection. For example, silica-titania samples containing no Cr were first dehydrated at 870°C, and then impregnated with a chromium compound anhydrously to avoid rehydrating the support. A short secondary activation in dry air at 400°C removed the solvent and converted the chromium to the surface-attached hexavalent species. This two-step activation produced a very active catalyst having a high RMIP even though only the support, and not the chromium, had experienced the high temperature. Thus we again conclude that the RMIP is controlled by (or at least related to) the level of surface dehydroxylation.

Figure 5-A plots the RMIP obtained from this two-step activation. That is, the support was precalcined at 870°C, anhydrously

impregnated with Cr, and then reactivated. RMIP is plotted as a function of the second activation temperature, so all samples were equally dehydrated. For comparison, a normal one-step activation of aqueously impregnated Cr/silica is shown in 5-C. As expected, the two curves merge at 870°C, where they had the same level of dehydration. Below 870°C the two-step activated catalysts in 5-A had higher RMIP values, because the support had already been dehydrated at 870°C.

But apparently some other factor besides dehydroxylation must also contribute to RMIP, because 5-A goes through a maximum at 500–600°C even though all samples had the same level of dehydration, this being fixed by the initial calcining at 870°C. This effect was observed on all supports tested, both silicas and silica-titanias, although the position of the maximum varied sometimes. For example, on one silica-titania it occurred at as low as 300°C.

The samples in Fig. 5 were impregnated with dicumene chromium (0) in hexane, but other chromium compounds yielded similar results provided the solvent was incapable of rehydrating the support. Some other examples were CrO₃ in CH₃CN, di-*t*-butyl chromate in hexane, chromium(III) octoate in toluene, or even CrO₂Cl₂ vapor. However, the position and exact height of the RMIP maximum varied slightly with the particular compound, suggesting that conversion to the active surface Cr(VI) species is the critical process in the second activation step.

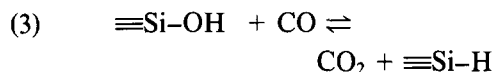
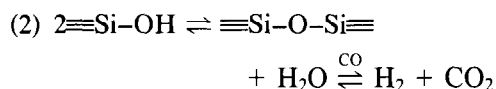
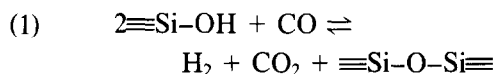
Since the OH level was constant in these two-step experiments this behavior suggests the existence of a second type of chromium(VI) active center which was responsible for the extra high termination rates. Let us call it Cr_B to distinguish it from the usual Cr_A sites produced in the one-step activation. Cr_B sites are apparently formed by the attachment of chromium at low temperatures on a highly dehydrated support. Thus one would expect the reaction to be primarily with siloxane or other oxide

bridges, instead of hydroxyls as with the Cr_A sites, and this was confirmed in earlier work (10). The secondary activation temperature should be only high enough to oxidize the Cr (when a lower valent compound is used) and bind it to the support. As the temperature was further raised, Cr_B sites reverted back to the usual Cr_A sites, lowering the RMIP back to that expected from the one-step activation.

Catalysts rich in Cr_B sites tended to be slightly more active than Cr_A type catalysts. The polymers from such catalysts exhibited a molecular weight distribution broadened slightly to the low MW side, again suggesting two types of sites. Cr_B sites were probably also sensitive to the hydroxyl population because in the two-step activation the RMIP values varied with the temperature of the initial dehydration in the same manner that was observed in Fig. 2 for the one-step process.

Dehydroxylation by carbon monoxide. The connection between activity, RMIP, and dehydroxylation by thermal means, also seems to apply to dehydroxylation by chemical means. Hydroxyls can be replaced by other nonoxidizable chemical groups, like fluoride (3, 4), but this usually interferes with the attachment of the chromium. A cleaner method of removing hydroxyls is to encourage their condensation. For example, the hydroxyl population on silica was found to decrease when exposed to carbon monoxide above 600°C. This is shown in Fig. 3 where the OH concentration is plotted against activation temperature for silica calcined in various gases. The curve representing the OH population in carbon monoxide split away from that in air at 600°C, and the separation increased up to sintering at 900°C. We believe that this is primarily due to the water gas shift mechanism in which surface moisture is removed by conversion to CO_2 and H_2 . The CO might act through a direct attack on hydroxyls (1), or perhaps indirectly by eliminating moisture in the gas stream and thereby shifting the hydration equilibrium

(2). The formation of a surface silane (3) is also conceivable, although we have no evidence for this species and the lost hydroxyls were not restored by oxidation.



When catalysts were made anhydrously (two-step process) from supports first calcined in carbon monoxide rather than air, a significant increase in the termination rate (the RMIP) was noticed (15). Figure 5-B compares silica-titania treated in CO at 870°C with that treated in air. Afterward both were impregnated anhydrously with dicumene chromium (0) and given a secondary activation in air to oxidize the Cr to the surface hexavalent state. The catalysts made from CO treated samples in 5-B always gave higher RMIP values than those in 5-A where the supports were treated only in dry air, in some cases as much as two times higher. Again Cr_B sites were formed at the lower temperatures, but changed back into Cr_A sites as the secondary activation temperature increased. Thus both Cr_B and Cr_A sites responded to the decreased hydroxyl population brought about by reaction with CO. When the experiment was repeated with H_2 instead of CO, no benefit over activation in air resulted. Nor was the OH population diminished.

Sintering in carbon monoxide. Not only did calcining the silica support in CO rather than air result in a lower surface hydroxyl population, but it also retarded the usual sintering process. This is shown in Fig. 6 where the surface area of Cr/silica is plotted after some samples were calcined in dry air and others in CO. As the temperature was raised, the onset of sintering became evident by the rapid drop in surface area. The

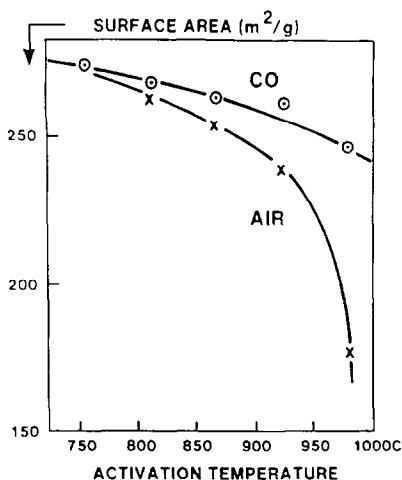


FIG. 6. Samples of Cr/silica were calcined at the temperatures shown in dry air or in CO, then surface areas were taken. Sintering was less pronounced in CO.

effect was more pronounced in air than in CO. This protection by CO could also be seen in the pore volume of the catalyst, which likewise decreased during sintering. Just why catalysts should be less susceptible to sintering in CO is not clear, unless it results from decreased moisture in the gas stream (reaction (2)). The effect was found whether or not Cr or TiO₂ were present.

Dehydroxylation by sulfur. Even more effective than carbon monoxide for removal of hydroxyl groups, and thereby increasing the RMIP, was sulfur in the presence of carbon monoxide (15). Sulfur compounds containing no hydrogen seemed to work best, such as CS₂ or COS, but even organic sulfur compounds like CH₃SH, Et-S-Et, or Et-S-S-Et, produced a large increase in the RMIP over that attainable by CO alone. All decomposed into elemental sulfur at the high temperatures, and in some cases a black sulfur-carbon residue was left. However, this residue played no part in the polymerization because in most cases it was burned off in O₂ at 870°C before the chromium was impregnated, with similar results. In fact, one of the cleanest compounds, COS, which left no detectable sulfur residue, also

TABLE I

The Effect of Chemical Dehydroxylation on RMIP in the Two-Step Activation of Catalyst B

Treatment ^a	RMIP
Air	2.5
Carbon monoxide	6.0
Carbonyl sulfide	150.0
CO + I ₂ , O ₂	12.0
CO + Br ₂ , O ₂	21.0

^a Silica-titania was calcined at 870°C in the composition shown, then impregnated with ½% Cr (as dicumene chromium (0) in hexane) which was oxidized in O₂ between 315 and 650°C to achieve maximum RMIP.

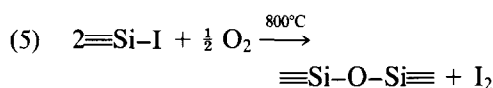
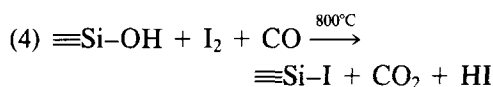
yielded among the highest increases in RMIP. Sulfur treatment in the absence of carbon or carbon monoxide, such as elemental sulfur vapor or SO₂ or H₂S, did not yield the same beneficial effect.

Figure 3 plots the hydroxyl population on silicas treated with CS₂ vapor and carbon monoxide. The OH level separates from that of the air treated samples at as low as 400°C, and by 950°C almost no hydroxyl population remained. Table I lists RMIP values obtained when several different chemical dehydroxylation treatments were used in the two-step process. The sulfiding treatment yielded increases of nearly two orders of magnitude over the usual dry air treatment. The exact mode of action of the sulfur in these experiments is unknown, but one possibility is that it somehow affects the water gas shift equilibrium, because best results were obtained when the sulfur compound also contained carbon or was used with CO. Selenium and tellurium also produced this same effect (16).

Again the effect could be reversed by exposure to moisture. For example, in one run the support was sulfided at 870°C. Any residue was burned off by O₂ at 870°C and then the sample was exposed to water va-

por (23 mm) at 250°C for half an hour. Afterward dicumene chromium (0) was impregnated anhydrously and oxidized at 480°C. The RMIP obtained was 1.5, only a little above that expected from the one-step activation and far below that normally expected from sulfiding in the two-step procedure.

Dehydroxylation by halides. Another treatment which lowers the hydroxyl population is halogenation of the silica surface (15, 17). This removes hydroxyls not by condensation as with CO and sulfur, but by replacement with halide, which prevents later attachment by Cr. The presence of halide probably also changes the electronic environment on the silica. Thus, fluoriding has long been used to increase activity but decrease RMIP (3, 4). The chloride, bromide, and iodide of silica also depress RMIP. However, these latter two have recently been studied (17), and it was possible to burn off most of the iodide or bromide with oxygen above 600°C, leaving a partially dehydroxylated surface.



When this surface was then impregnated with chromium by the usual anhydrous impregnation (two-step process) (15), large increases in the melt index were obtained, as much as an order of magnitude over that obtained from samples activated similarly but in air only. An example is shown in Table 1.

Although the surface chloride of silica cannot be burned off as easily, it will react with H₂ or CH₃OH and these can then be burned off. This treatment sometimes also produced an increase in RMIP (18). However, the effect was minor by comparison to the bromide and iodide, probably because water was formed during the burnoff.

TABLE 2

Effect of Oxidizing the Support on RMIP in the Two-Step Activation

Support Oxidation temperature	RMIP
None	3.0
315°C	4.4
425°C	4.8
540°C	6.2
650°C	6.8
760°C	3.4
870°C	5.6

Notes: Samples of silica-titania were calcined 4 h in CO at 870°C, then oxidized one hour in dry air at the temperature shown. Afterward they were impregnated with dicumene Cr and oxidized at 315°C.

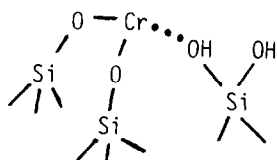
Oxidation of the support. In the two-step activation of silica-titania when the support had been treated with CO, we consistently obtained a small additional increase in RMIP when the support was also oxidized before being impregnated with chromium. For example, in Table 2 samples of silica-titania were calcined in CO at 870°C for 4 h, then oxidized at the temperature shown for 1 h in dry air. Afterward, they were treated with dicumene chromium (0) in hexane, and finally given a secondary activation in air at 315°C. The RMIP more than doubled as the support oxidation temperature increased to 650°C. The effect was most noticeable when the secondary activation temperature was kept low, hence the choice of 315°C in Table 2. It was also observed, in about the same magnitude, on sulfided samples.

The cause of this effect is unknown. It could result from the burnoff of some carbonaceous deposit laid down by the CO, but none was ever detected. A more likely explanation is that some of the titania became reduced to Ti(III) by CO, then reoxidized to Ti(IV) by the O₂. The light blue

color sometimes seen on reduced samples would support this view.

DISCUSSION

These experiments raise two fundamental questions. First, why should the behavior of the catalyst be so dependent on the activation temperature? From about 400 to 900 C, where both activity and the relative termination rate dramatically increase, the only change on the catalyst known to occur is the declining hydroxyl population. Perhaps these hydroxyls coordinate to the active centers, blocking ethylene and thus poisoning the catalyst much as free water would do in the reactor. In some detailed experiments Krauss *et al.* (19–21) have indeed found, by measuring the amount and ΔH of chemisorption by CO, N₂, and O₂, an inverse correlation between the coordinative unsaturation of Cr(II) centers and the surrounding hydroxyl population.



Possible coordination between Cr and Si-lanol groups after reduction by ethylene from Cr(VI) to Cr(II)

However, it is hard to see from the common models of the silica surface just how the hydroxyls could come close enough to chromium to coordinate. For example, in the model of Peri and Hensley (14), with the chromium occupying vicinal pairs (21), the nearest hydroxyl neighbor still seems to be 3 or 4 Å away. Nonetheless, the same problem is often encountered in explaining how neighboring silanols condense, so it is clear that our understanding of the silica surface is incomplete. Some type of distant electronic effect might even be possible between chromium and hydroxyls which does not completely block the active center but still influences its behavior. Thus both the number of active sites as well as the propagation rate constant could be affected.

A variant of this explanation would have the Cr(II) active center not coordinated to

the hydroxyl, but oxidized by it to Cr(III) and H₂. There is even evidence that this may happen when the catalyst is reduced in CO at 300°C or higher (20, 22). The conversion to Cr(II) is always more complete when the catalyst has first been highly dehydrated. Otherwise Cr(III) is also formed. However, both the surface protons and the chromium would probably have little mobility at 100°C, where reduction by ethylene occurs in the reactor, so again the hydroxyl would have to be in close proximity to the Cr.

Still another possibility is that the hydroxyls are not directly involved at all, but only reflect some other important change such as the strain introduced onto the surface by their condensation. The RMIP always drops sharply with the first signs of sintering, which probably relaxes the strain. And we have seen that calcining the support in CO, which increases RMIP, also retards sintering. But without a more concrete knowledge of the silica surface it is difficult to examine this possibility in much detail.

Whatever the reason, there is definitely a strong inverse correlation between the activity of the catalyst and the hydroxyl population on the silica. As the catalyst becomes more dehydroxylated with increasing activation temperature, it also becomes more active for the polymerization of ethylene. This makes it difficult to see how these hydroxyls could be a necessary part of the active site, say by furnishing the initiating proton, as has been suggested by Schuit and coworkers (23). Replacing hydroxyls with fluoride also improves activity (3, 4, 11). In fact, we have removed all hydroxyls from some catalysts by haliding, and found them to be highly active.

In most of the examples described here, termination and activity seemed to be linked together. When one increased, the other did too. However, there is no reason why this should always be the case, and in fact one example to the contrary is known. Fluoriding the silica increases the activity

but decreases the termination rate. One would like to approach the problem from a more rigorous kinetic view, but without an independent measure of the changing active site population this is difficult.

The other question raised by these data is: What are the two types of active centers Cr_A and Cr_B ? Pullukat *et al.* (6–8) have proposed two types of centers which differ in their RMIP, one attached to silicon, the other to titanium. However, that cannot be the distinction here between Cr_A and Cr_B because Cr/silica exhibited the same behavior in the two-step activation as did Cr/silica–titania. So both supports must have contained Cr_A and Cr_B . Neither could the Cr_B sites have resulted from incomplete oxidation because in most two step activations all of the chromium was converted to Cr(VI), just like in the one-step activation. Furthermore all sources of chromium, from hexavalent to zerovalent, displayed Cr_B type behavior after oxidation.

Perhaps Cr_B centers represent a dichromate surface species, where Cr_A centers are chromate. In earlier reports (10, 11) we have shown that chromate exists on silica, is active for polymerization, and does not exhibit an unusually high RMIP. Thus the ordinary Cr_A centers probably do originate from chromate. However, we have no information to confirm or deny the existence of dichromate surface species, and earlier work suggests that even under Cr_B conditions the predominant bonding occurs as chromate (10, 11).

The one known distinction between Cr_A and Cr_B centers lies in their formation. In the one-step activation the chromium is impregnated aqueously onto a fully hydrated support, and it attaches by esterification with hydroxyls probably more or less randomly (9–11). These Cr_A centers have already been shown to hold open surface site pairs which would otherwise condense during activation to form siloxane (11). Their presence may even alter the pattern of dehydroxylation (14). In the two-step process, however, the anhydrous chromium

compounds have been shown to react primarily with oxide bridges (10, 11) since only a few isolated hydroxyls remain. This probably directs the chromium into a more selective occupation of those oxide bridges which are most strained. This alone may somehow account for the increased RMIP. Just as silicas become resistant to rehydration once annealed above 600°C, they may also show a new selectivity in the choice of sites which can stabilize chromium(VI). Certainly the pattern of strain will be different between silica and Cr/silica both annealed at 800–900°C.

The mobility of Cr(VI) at the higher temperatures may also be important. Only on Cr_A -type catalysts does the Cr experience the full mobility possible. Not only could this affect the occupation of sites, but there is even evidence that it accelerates the relaxation of the silica surface (catalysts containing Cr may sinter slightly more easily than the support alone). In contrast, Cr_B type preparations treat only the support at 800–900°C; the temperature is kept low once the chromium has been added. As the temperature is increased, however, Cr_B sites do revert back to Cr_A sites, and this may also reflect the increased mobility.

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