

The Activation of the Phillips Polymerization Catalyst

III. Promotion by Titania

M. P. McDANIEL, M. B. WELCH, AND M. J. DREILING

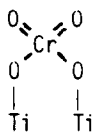
86G Phillips Research Center, Bartlesville, Oklahoma 74004

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Cr/silica polymerization catalysts are rendered much more active by the incorporation of a small amount of titania either in or on the support. The molecular weight of the resultant polymer is also affected. In this report the promotional influence of titania has been examined under different activation conditions. Results varied widely with the type of incorporation and the method of activation. Cr_B centers were more sensitive to titania than Cr_A centers.

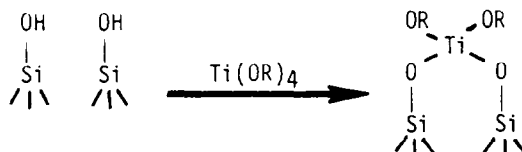
INTRODUCTION

Although titania is not usually considered as a carrier itself for Cr(VI), its presence in small amounts on Cr/silica catalysts does have a promotional effect both on polymerization activity and the termination rate. Numerous patents were filed about a decade ago (1-3), but only Pullukat and Shida (4) and Pullukat *et al.* (5, 6) have ventured any contribution to the scientific literature on the subject. Using X-ray photoelectron spectroscopy, optical spectroscopy, and polymerization kinetics they concluded that the Cr(VI) becomes attached to the titania directly such as



and that the beneficial effect derives from the resulting change in electronic environment around the chromium. As evidence of this, decreases in the XPS binding energy of Cr(VI) were noted when titania was added.

Two ways of incorporating titania onto Cr/silica catalysts have been described in the patent literature. In the earliest method the surface of the silica was coated with a layer of titania by treating it with a titanium ester capable of reacting with silanols.



Unreacted ester groups were then burned away during calcination. How the Cr becomes attached to Ti is not always clear in some procedures. Pullukat *et al.*, who added Ti(OR)₄ either to CrO₃ in solution or to CrO₃ on the virgin catalyst, believed that the resulting redox reaction yielded a chromic (III) titanate, Cr(OTi(OR)₃)₃, in which some Ti-O-Cr bonds remained intact even during later calcination. As proof they noted a maximum promotional effect at a Ti/Cr stoichiometry of 3.0. However, in other procedures where Cr(VI) salts were not employed or where titanium was not introduced as an ester, we must assume a slightly different mechanism of attachment.

For example, the second method of incorporating titania onto the catalyst consists of coprecipitating hydrous titania along with the silica gel (7). This can be accomplished by adding a water soluble titanium salt to the silicate solution before gellation. Although the degree of dispersion is unknown, presumably some of the titania is exposed on the surface and later, during calcination, chromium may attach to it.

This report examines some aspects of

promotion by titania, and compares the two methods of incorporation. In particular we note the effect of titania on the formation of Cr_B -type centers.

EXPERIMENTAL

Conditions of catalyst activation and polymerization have already been described in Part I of this series. For comparison in this report titania concentrations were always expressed as titanium atoms per square nanometer of surface. This convention was used even when much of the titania was probably in the bulk (coprecipitated samples) and in these cases the value serves only as a limit.

The relative melt index potential, or RMIP, has been defined in this paper as before in Part I. Again two families of catalyst preparations were used. The RMIP of coprecipitated Cr/silica-titania catalysts has been expressed relative to a standard catalyst containing 3.3 wt% titania and activated at 870°C in air for 5 h. Other catalysts, those made by impregnating a titanium ester, were based on Davison grade 952 silica. Here the standard catalyst was the untitanated base, again calcined at 870°C for 5 h.

RESULTS AND DISCUSSION

1. Experiments Using a Simple One-Step Activation in Air

Coprecipitated silica-titania catalyst. Figure 1 demonstrates the promotional effect of titania on the activity of Cr/silica catalysts. These samples were made by gelation of solutions (sols) containing both silicate and titanium salts. Chromium was added later as the acetate. After being dried they were calcined at 760°C in dry air which oxidized the chromium to Cr(VI) and fixed it to the surface. For comparison titania concentrations are expressed as titanium atoms per square nanometer of surface. However, this value can only serve as a limit because much of the titania was probably in the bulk.

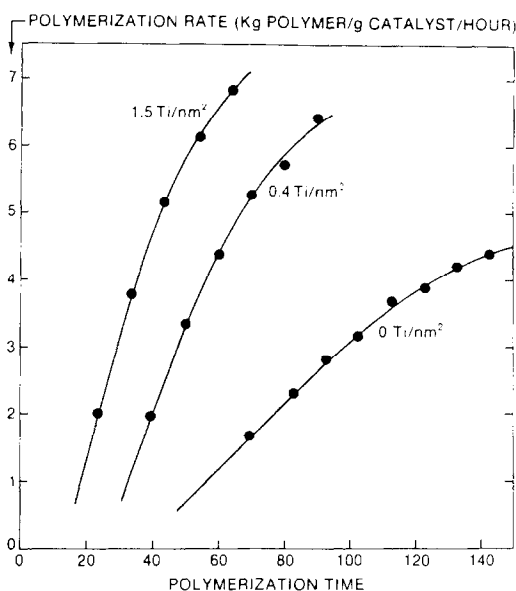


FIG. 1. Samples of silica-titania were made by coprecipitation to contain different levels of titania, then impregnated with Cr and calcined in dry air at 760°C. Afterward each was allowed to polymerize ethylene in a high pressure autoclave. The rate of ethylene consumption is plotted against time (min).

It is clear in Fig. 1 that titania increases the activity of the catalyst, first by shortening the induction time, then by allowing higher polymerization rates. The shortened induction time suggests that titania makes Cr(VI) more easily reducible because the lower valent active sites came to life more quickly. The faster increase in polymerization rate also suggests this, and the higher maximum rates may even indicate an increase in active site concentration, although this is not certain.

That titania also increases the termination rate can be seen in Fig. 2. Here the relative melt index potential (RMIP; see Part I of this series), which reflects the termination rate, of some coprecipitated samples is plotted against the titania concentration. After activation in dry air at 650°C, the termination rate increased with increasing titania concentration, at least up to 1.5 Ti/nm². This was also true after activation at 760°C. Pullukat and Shida (4) and Pullukat *et al.* (5-6) reported a sharp drop in melt

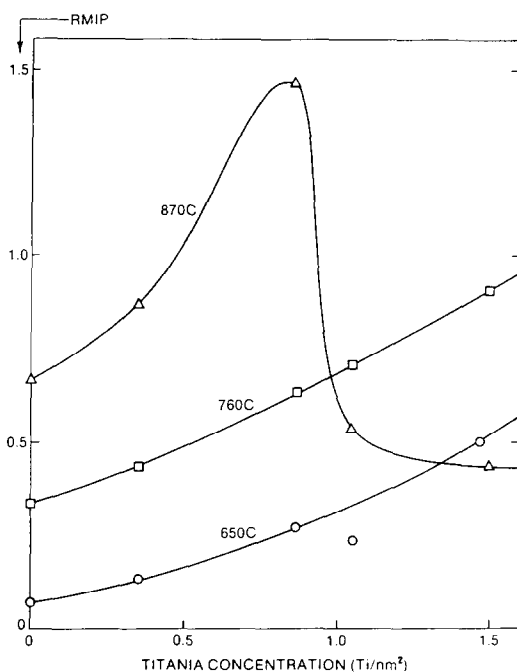


Fig. 2. Samples of coprecipitated silica-titania containing varying levels of Ti were impregnated with Cr and activated at the temperature shown before being allowed to polymerize ethylene. The relative melt index potential of the polymer (see Part I) has been plotted.

index at the stoichiometry $\text{Ti}/\text{Cr}=3$. We did not find this transition at 650 or 760°C even though these catalysts contained only about $0.27 \text{ Cr}/\text{nm}^2$. However, a break was indeed observed after activation at 870°C. At about $0.9 \text{ Ti}/\text{nm}^2$, not too far from $\text{Ti}/\text{Cr}=3$, the relative melt index potential dropped sharply.

Why did the break occur at 870°C but not at the lower temperatures? Closer inspection reveals that it does not reflect any particular stoichiometry between Ti and Cr, but instead it corresponds to sintering of the support. Although Cr/silica itself does not sinter at 870°C, the added titania does promote sintering. And, as we have seen in Part I of this series, melt index and activity decline sharply as sintering begins.

This is more obvious in Fig. 3 which plots the relative melt index potential against activation temperature for a series of copre-

cipitated samples varying in titania content. The RMIP of each sample rose with increasing temperature up to a maximum and then dropped off sharply. This drop-off marks the sintering temperature, which was found to depend on the titania concentration. The more titania present, the lower the temperature at which sintering began. Below the sintering temperature, however, RMIP increased steadily with titania content; there was no optimum Ti/Cr stoichiometry.

The onset of sintering, even in high titania samples, was not readily apparent by X-ray diffraction. However, it could be confirmed by changes in porosity. This is shown in Figs. 4 and 5 where pore volume, as determined by alcohol adsorption (8), and BET surface area are plotted against activation temperature for several samples of varying titania content. The presence of titania during gelation tended to increase

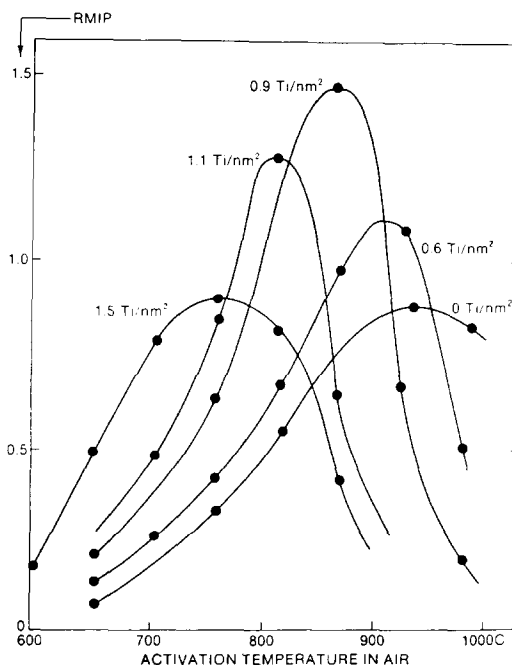


Fig. 3. Samples of Cr/silica-titania (coprecipitated) containing varying levels of Ti were calcined at the temperature shown and then allowed to polymerize ethylene. A drop in melt index marks the onset of sintering.

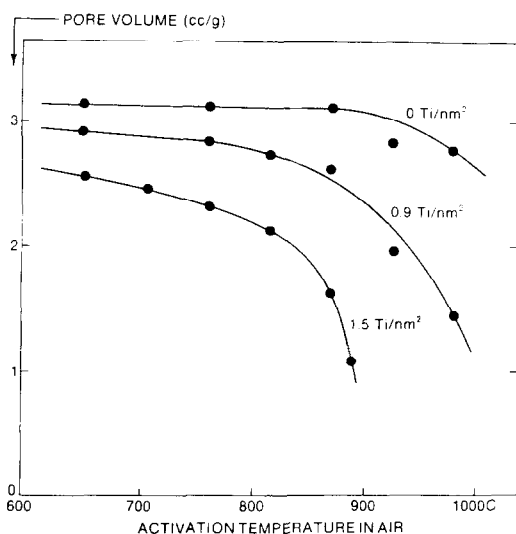
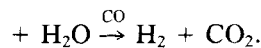
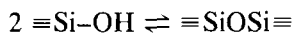


FIG. 4. Samples of Cr/silica-titania (coprecipitated) were calcined at the temperature shown, then the pore volume was determined by alcohol adsorption. Titania decreases the initial porosity of the catalyst and also its thermal stability.

the initial surface area and to decrease the initial pore volume slightly. But it is clear that the thermal stability of both variables was decreased by titania. The more titania

a sample contained, the lower the temperature needed to cause thermal breakdown of porosity, and the more pronounced was that drop in surface area or pore volume. For each sample the loss in porosity occurred at the same temperature that the drop in RMIP had been observed in Fig. 3.

Again the sintering process was found to be retarded in carbon monoxide, even for samples containing a high level of titania. This is demonstrated in Table 1 which lists pore volumes of coprecipitated silica-titania samples after calcination in dry air or CO at 870°C. In air the drop was more pronounced than in CO. The effect was most evident at high titania levels because 870°C is above the sintering temperature of these samples. Again sintering may depend on traces of moisture which are removed by CO:



Titania surface layer. Applying a surface coating of titania to Cr/silica catalysts

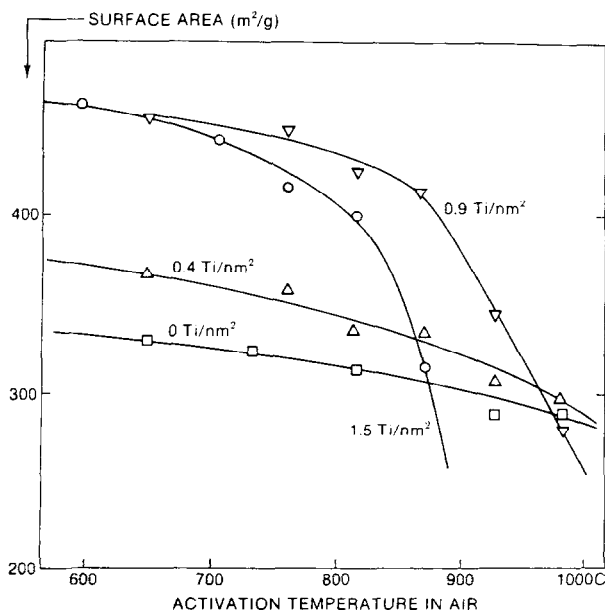


FIG. 5. Samples of Cr/silica-titania (coprecipitated) were calcined at the temperature shown, then the BET surface area was determined. Titania increases the initial surface area but decreases its thermal stability.

TABLE 1

Coprecipitated Silica-Titania Catalysts Are More Prone to Sinter in Air than in CO

Titania concentration	Pore volume (cc/g)		
	Initially ^a	CO 870°C	Air 870°C
0.4 Ti/nm ²	2.64	2.48	2.43
0.9 Ti/nm ²	2.90	2.76	2.61
1.1 Ti/nm ²	2.58	2.37	1.78
1.5 Ti/nm ²	2.55	2.33	1.59

^a After air at 650°C.

should in principle provide a more efficient use of the titania because most of it should be exposed. In one series of experiments one of the materials used in Figs. 1-3, that containing no titania promoter, was impregnated from alcohol solution with titanium ester, Ti(OR)₄, at various levels. The catalyst already contained 0.3 Cr/nm² as chromic acetate. After evaporation of the alcohol, these samples were calcined in dry air at 760°C. Saturation occurred at about 3.0 Ti/nm²; above this level Ti(OR)₄ usually evaporated off. This value corresponds nicely to two-point attachment to the 3.2/nm² paired hydroxyls (1.6 Ti/nm²) plus one point attachment to the 1.4/nm² single hydroxyls (1.4 Ti/nm²) reported to exist on silica (9).

Again the activity of the catalyst was improved by the presence of titania as in Fig. 1, and the RMIP was enhanced just as in Fig. 2 at 760°C. The more titania added, the higher the RMIP. However, one important difference was noticed. This surface layer of titania did not promote the sintering process at higher temperatures as coprecipitated titania had done.

When the RMIP of these samples containing surface titania was plotted against Ti concentration as in Fig. 2, a curve corresponding to that in Fig. 2 (760°C) was obtained. Surprisingly this indicated that the two procedures, coprecipitation versus surface coverage, were approximately equally efficient in their use of titania as a pro-

moter, even though coprecipitation should yield considerable titania in the bulk. Does this signify then that coprecipitated samples also contain mainly surface titania? Or perhaps the reverse, that a surface coating tunnels into the interior during calcination? In either case, why did coprecipitation and not surface coverage promote sintering?

Comparison of Ti coverage by extraction and XPS. To examine this point an attempt was made to extract the titania from the support by washing in acidic H₂O₂ solution. Two catalysts were studied, both containing 3.3 wt% titania and both calcined at 600°C. In one case the sample had been coprecipitated, in the other a surface layer had been applied. In the latter experiment over 90% of the titania was easily removed, but only about 58% was dissolved from the coprecipitated sample. Thus much of the titania probably was in the bulk on the coprecipitated sample. That so much was easily extracted probably reflects the small ultimate particle size (~30 Å).

Results from X-ray photoelectron spectroscopy (XPS) confirmed this view. In Table 2 three pairs of silica-titania samples were compared. Each pair consisted of one coprecipitated sample and another sample prepared to contain the same composition but as a surface titania layer. After activation at 600°C X-ray photoelectron spectra were taken and the intensities of the Ti 2p peaks compared. In each case the coprecipitated sample yielded a considerably lower

TABLE 2

XPS Intensities Show a Lower Coverage by Ti on Coprecipitated Silica-Titania than when Silica Is Coated with a Titania Surface Layer (All Catalysts Activated at 600°C)

Overall Ti/Si ratio	Ti/Si Ratio by XPS	
	Coprecipitated	Surface layer
.006	.0056	.0136
.022	.0167	.0338
.050	.0340	.0510

TABLE 3

In Coprecipitated Samples Sintering May Cause a Migration of the Titania toward the Surface

Ti/Si ratio by XPS	
Coprecipitated	Surface layer
0.0338 (600°C)	0.0461 (450°C)
0.0389 (800°C)	0.0437 (750°C)
0.0411 (870°C)	0.0465 (900°C)

contribution to the Ti intensity. Since XPS is a surface technique, with penetration down to about 20 Å, these results indicate what would be expected—a lower surface concentration of titania on the coprecipitated samples.

One other point was also revealed by XPS intensities. This is shown in Table 3. During the sintering process the surface concentration of titania increased on coprecipitated samples, suggesting a migration from the interior. Such a change would not be possible on samples containing only a surface layer of titania. No development of crystallinity was detectable by X-ray diffraction on either sample, even up to 950°C.

II. Experiments Involving Two Activation Steps

Order of attachment. Since the coprecipitated samples had a lower surface concentration of titania, why were they equally effective at promoting melt index? Many experiments suggest that the formation of Ti–O–Cr links, which is rather difficult, is very dependent on subtle variations in the preparation of the catalyst. For example some titanium compounds were completely ineffective, while others did promote activity and RMIP. The valence of the chromium, on treatment with titanium, also seems to make a difference. And even the method and order of impregnation could conceivably be important, because in the first case, where the titania was coprecipitated as part of the support, the chromium

was impregnated onto the titania. Conversely in the second case the chromium was impregnated before the titania rather than onto it, and both components probably attached to the silica. So the chances of forming Ti–O–Cr links may have been increased by the first procedure.

That the order of impregnation is important is particularly evident in Table 4, where two series of samples were impregnated with titanium isopropoxide. In the first case it was added to Cr/silica which had been calcined in O₂ at 800°C, thus anchoring the Cr to the silica before deposition of Ti. Organics were then oxidized away at the various temperatures listed. Although the Cr(VI) was reduced by the titanium ester, apparently the formation of Ti–O–Cr links did not occur because in Table 4(a) almost no promotion of melt index was observed. Analysis indicated that the titanium did stick to the surface.

In the second series of samples in Table 4, shown in column (b), only the order of impregnation was reversed. Titanium ester

TABLE 4

The Promotional Effect of Titania Depends on How It Is Attached

Temperature	Relative melt index potential	
	Cr first ^a	Ti first ^b
300°C	<1	~500
400°C	<1	180
500°C	<1	65
600°C	~1	12
700°C	1.5	4.5
800°C	1.0	2.2

^a CrO₃ was first anchored to silica by calcination in O₂ at 800°C. Then the catalyst was impregnated with a pentane solution of titanium isopropoxide, dried, and calcined in O₂ at the temperature listed (2.0 Ti/nm²).

^b Titanium isopropoxide was first impregnated onto the virgin silica and calcined in O₂ at 800°C. Then CrO₃ in CH₃CN was impregnated and after being dried, the catalyst was calcined in O₂ at the temperature listed (2.3 Ti/nm²).

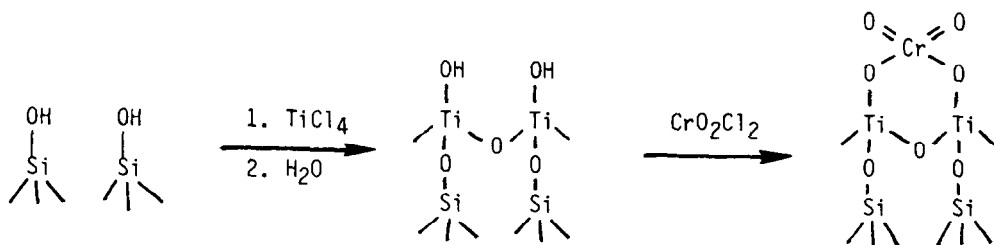
was reacted in the same amount as before with virgin silica which was then calcined at 800°C to convert the Ti into titania. Then CrO₃ was impregnated anhydrously to avoid rehydrating the surface, and afterward the catalyst was calcined in O₂ at the temperatures listed. Here the chromium must have attached to the titania rather than silica even though ingredients and temperatures were the same as in the first series of samples, because a large promotional effect was observed.

In yet another series of experiments the procedure in Table 4(b) was repeated, but starting with a silica calcined at 800°C instead of virgin silica. This more nearly reproduces the conditions of procedure (a) where the titanium ester reacts with a dehydroxylated surface. Again a large promotional effect was observed like that in Table 4(b). So the lack of a promotional effect in Table 4(a) must indicate that the chromium was already fixed to the silica when the titanium was added, and that this did not change during later calcination. Conversely in procedure (b) the chromium probably attached in large part to the titania. In fact, Cr/silica did adsorb slightly less titanium than pure silica activated at the same temperature, probably due to the prior attachment of chromium to the surface.

However large the promotional effect of procedure (b), it always decreased as the temperature was increased, as is evident in

Table 4. This could be interpreted as a migration of the chromium away from the titania, or as the conversion of Cr_B centers into Cr_A which we know also occurs even in the absence of titania. Whatever the cause, this rearrangement at higher temperatures could be partly reversed. Another sample like that in Table 4 (procedure (b), 800°C, RMIP = 2.2) was slurried in dry hexane, to which a small amount of t-butanol was added. The chromium dissolved into the hexane as the ester, then redeposited onto the support as the hexane was evaporated. After being calcined again, this time at a lower temperature, 300°C, RMIP increased tenfold. Thus the high melt index form of chromium was recreated from the low melt index form.

The results in Table 4 make it fairly clear that titania acts as a promoter through direct links to the chromium, and not by just being nearby as a "feeder site" or some other possibility. However, the following experiment adds to the certainty of this interpretation. Virgin silica was exposed to TiCl₄ vapor at 150 through 300°C, completely dehydroxylating the surface and saturating it with Ti. Residual chloride groups were hydrolyzed with water vapor at 200°C, and then CrO₂Cl₂ vapor was added at 200°C. This catalyst, without any high temperature activation, polymerized ethylene to yield relatively high melt index polymer (RMIP = 5) and even oligomers.



Since extensive rearrangement was unlikely at 200°C, it seems reasonable that the chromium actually attached to the titania.

Hydroxyls as part of the active site. The

use of TiCl₄ offers another experimental opportunity. Recently Schuit and coworkers have postulated (10) from isotopic experiments that surface hydroxyls might actually

be a necessary part of the active site, furnishing the initiating proton. Since all hy-



droxyls can be easily removed by reaction with TiCl_4 (9), one can test this idea. Virgin silica was first calcined at 600°C to remove internal hydroxyls, then rehydrated in liquid water overnight. After being dried at 150°C the surface was dehydroxylated by reaction with TiCl_4 vapor at 150°C through 300°C . Chloride residue was partially burned away by O_2 at 800°C and afterward CrO_3 was impregnated from dry CH_3CN , leaving a dry orange powder. Finally samples were calcined in O_2 between 300 and 800°C . These catalysts were highly active like those in Table 4(b) and exhibited a similar promotional effect on RMIP from the titania. Thus hydroxyls are apparently not necessary.

Although unlikely, one could still argue that some hydroxyls were replenished by oxidation of the organic solvent (unlikely because the solvent was removed at 200°C under flowing argon, there was no visible decomposition of the CrO_3 , and other chromium compounds yielded the same results). To answer this objection one further experiment was done. Cr/silica was activated at 600°C in air, then reduced in CO at 300°C . TiCl_4 vapor at 200°C removed hydroxyls, and a final treatment in O_2 at 800°C removed chloride and reoxidized the chromium (the reduction was necessary because Cr(VI) is stripped off by TiCl_4 as CrO_2Cl_2 vapor). This catalyst was again highly active (in fact more active than had the TiCl_4 not been employed due to the promotional effect of titania) although no organics were used.

Cr_B behavior. Whether formed by anhydrous impregnation of chromium, as in Ta-

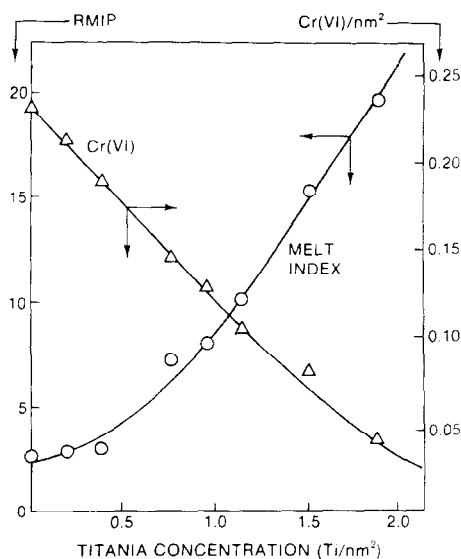


FIG. 6. Samples of silica were impregnated with an alcoholic solution of titanium isopropoxide to various levels of Ti, followed by 1% Cr as the acetate, and R/R activation (CO at 870°C , air at 600°C). Afterward the amount of hexavalent Cr was determined and each sample was allowed to polymerize ethylene.

ble 4, or by R/R activation, Cr_B -type sites seemed to be more sensitive to promotion by titania than Cr_A sites. This is demonstrated in Fig. 6 which plots the RMIP obtained after R/R activation (CO 870°C , air 650°C) of a series of samples varying in titania concentration. The more titania, the higher the RMIP, with the slope much greater than in Fig. 2 where Cr_A sites were examined.

Although titania promoted activity, Fig. 6 also shows that it destabilized Cr(VI), at least in the R/R procedure. That is, as the titania level increased the concentration of Cr(VI) found after reoxidation was decreased. The decreased stability of Cr(VI) may be the cause of the increased activity, and it emphasizes that only a fraction of the chromium need be active. In some cases only $0.04 \text{ Cr}/\text{nm}^2$ was hexavalent (0.1%) yet the catalyst exhibited good activity. Increasing the total chromium did not result in more Cr(VI), or more activity, but did often lower the RMIP.

CONCLUSIONS

The presence of a small amount of titania on the Phillips Cr/silica polymerization catalyst can be a powerful promoter, enhancing both activity and especially melt index response. The promotional effect probably derives from the creation of Ti–O–Cr links which change the electronic environment on the Cr active center. The proportion of Ti–O–Cr links formed, relative to Si–O–Cr links, is extremely sensitive to subtle variations in the preparation of the catalyst, and determines the magnitude of the promotional effect.

We have found no optimum Ti/Cr stoichiometry such as that reported by Pullukat and Shida (4) and Pullukat *et al.* (5, 6) at Ti/Cr = 3. Even if all Cr really were attached to Ti at this stoichiometry, it is not clear why the promotional effect should decline when Ti/Cr > 3 as they report. Furthermore, in this report we have noted promotional effects many times greater than the optimum observed by Pullukat and Shida and Pullukat *et al.* at Ti/Cr = 3. This was achieved through special preparations in which the chromium was anhydrously impregnated *onto* the titania rather than *with* it. Thus it is likely that in most straightforward preparations, such as that described by Pullukat and co-workers or that described here as Cr_A, only a fraction of the chromium is actually attached to titania.

We did find an optimum titania concentration on coprecipitated samples activated at high temperatures (>800°C), but it was not related to Ti/Cr stoichiometry. Rather it was caused by sintering. The more titania present, the lower the sintering temperature, and both activity and melt index declined with the onset of sintering. This was observed only on coprecipitated silica–titania and not on silica containing a surface layer of titania. The effect was pronounced in air, but retarded in carbon monoxide.

In the promotion of Cr_A centers by titania, coprecipitated samples were more effi-

cient than silicas containing a surface layer of titania. This was possibly caused by subtle differences in the preparation, that is impregnating the Cr onto the titania rather than with it. Since coprecipitated samples contained much of their titania in the bulk, this increased efficiency may have compensated for the lower concentration of titania on the surface.

In the promotion of Cr_B centers by titania, these subtle differences in preparation no longer exist. Consequently, coprecipitated silica–titania was less effective than surface layer samples owing to the lower Ti concentration on the surface. Not only were lower melt index values obtained, but higher temperatures were needed to bind the chromium. This may imply a greater level of strain in the surface layer samples.

The notion that each active Cr center must be associated with a hydroxyl group to provide the initiating proton can be disproved by reacting these hydroxyls with TiCl₄. After residual chloride is burned away in dry O₂, these catalysts are highly active, exhibiting the usual promotion by titania.

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