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The Activation of the Phillips Polymerization Catalyst

II. Activation by Reduction/Reoxidation

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A procedure for activating Cr/silica or Cr/silica–titania polymerization catalysts is described which boosts activity and especially melt index potential. It consists of reducing the chromium at 700–900°C with carbon monoxide or an organic sulfide, followed by reoxidation in dry air at a lower temperature. The reduction step also dehydroxylates the support surface while simultaneously promoting an aggregation of the chromium. During reoxidation the chromium is then redistributed onto the surface in a new form by reaction with oxide bridges. The process is chemically analogous to the anhydrous impregnation of chromium onto a calcined support.

INTRODUCTION

In Part I of this series the control of the molecular weight (MW) of polyethylene from Cr/silica and Cr/silica–titania catalysts was greatly extended by utilizing two principles. First, both MW and activity were found to be inversely related to the hydroxyl population on the support. And this, we discovered, could be additionally lowered by calcining the support in reducing agents like carbon monoxide. Second, two types of active polymerization centers were proposed to exist, one producing low MW polymer, the other high. The low MW center, called Cr_B, would be preferred for certain applications. It was favored by impregnating the Cr anhydrously onto a highly dehydrated support so that the Cr reacted with oxide bridges rather than hydroxyls. Unfortunately, this two-step procedure is rather complicated even though high quality polyethylene of the desired MW is produced. Instead we introduce in this paper a simpler procedure which also takes advantage of these two principles. The new procedure requires only one activation step and does not resort to anhydrous impregnation.

We call this simplified procedure "R/R activation" after the two processes it entails—first a high temperature reduction of the Cr, followed by its reoxidation at a lower temperature (*1–3*). During reduction, not only is the support chemically dehydroxylated as described in Part I, but the bonding of the Cr to the support is also disrupted, destroying the normal Cr_A centers. We believe that this deactivation results from an aggregation of the Cr into CrO or Cr_2O_3 clumps on the surface. Reoxidation then breaks up these aggregates, redistributing individual Cr(VI) atoms over the surface again. However, because the surface has been dehydrated the new bonding occurs mainly with siloxanes or other oxide bridges, favoring low MW, or Cr_B, centers. In this way the anhydrous impregnation described in Part I is simulated in one activation step.

Pullukat *et al.* (*4–6*) have simultaneously developed another activation procedure which also involves a reduction followed by a reoxidation. In their case Cr(VI) was reduced by a titanium ester, $Ti(OR)_4$, to form what was believed to be a chromium III titanate, $Cr(OTi(OR)_3)_3$. This material was then heated in a nonoxidizing atmosphere and later reoxidized, during which some Ti–O–Cr links were thought to remain intact. We too have found that both Cr_A and Cr_B type catalysts are responsive to titania

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promoter (see Part III of this series); however, we have found the R/R effect to be independent of titanation. In this paper we introduce and define some of the principles of R/R activation. These apply to both Cr/silica and Cr/silica–titania catalysts.

EXPERIMENTAL

Activation and polymerization conditions have already been described in Part I of this series, as well as the definition of the relative melt index potential (RMIP). In these experiments the anhydrous impregnation technique was not used. Consequently all catalysts contained 1 wt% Cr before activation; silicas A and B were impregnated with an aqueous solution of either CrO_3 or chromium III acetate, as specified in each experiment.

RESULTS AND DISCUSSION

Reduction to Active Cr(II)

After activation in air by the usual one-step procedure discussed in Part I, the Phillips polymerization catalyst contains hexavalent chromium monodispersed on a silica or silica–titania surface. Each Cr is probably individually attached to the support (*7*). On contact with ethylene in the reactor near 100°C a reduction to the active lower valent form occurs. However, it is also possible to perform this reduction during activation with carbon monoxide at 300–400°C. This reaction has been well studied by Krauss (*8–11*) and others (*12, 13*) who concluded that most or even all of the Cr is cleanly reduced to a highly coordinatively unsaturated Cr(II) species. We too have confirmed this point by pulsed titration. The result is a catalyst even more active for polymerization than the hexavalent form because it no longer requires a reduction by ethylene (*14*).

This is shown in Fig. 1 where Cr/silica was calcined in O_2 at 850°C. The polymerization rate is plotted against reaction time after exposure to ethylene. Cr(VI)/silica did not initiate polymerization immediately but only after an induction period which corresponds to the reduction of Cr(VI) by ethylene to the lower valent active form (*14, 15*). Afterward the rate gradually increased during the next hour or two. In Fig. 1-B the same sample is shown after it had been reduced in carbon monoxide at 350°C to Cr(II). The kinetics (that is the rate of increase) are almost identical to Cr(VI)/silica except that there was no induction time. The reduced catalyst began polymerizing ethylene at a significant rate immediately after being introduced into the reactor, making it more active than Cr(VI)/silica. The increasing rate is not completely understood, but it might indicate a slow initiation step, that is, that the first ethylene is added more slowly than succeeding ones.

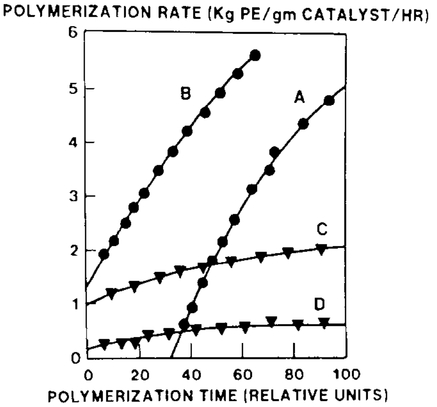


FIG. 1. Samples of Cr/silica were calcined in O_2 at 850°C, then as follows: (A) no reduction; (B) CO at 350°C; (C) CO at 500°C; (D) CO at 700°C. Afterward each was allowed to polymerize ethylene in a high pressure autoclave. The rate of ethylene consumption is plotted against time for each.

Thermal Deactivation of Cr(II)

However, when the temperature of reduction in carbon monoxide was increased to 500°C in Fig. 1-C, and again to 700°C in Fig. 1-D, the polymerization rate gradually declined until by 850°C almost no activity remained. This was not due to overreduction because the average oxidation state (determined by pulsed titrations with O_2 back to the hexavalent state) remained at

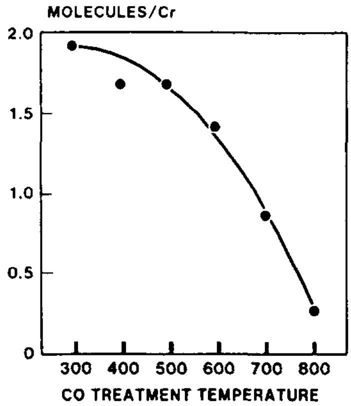


FIG. 2. Cr/silica was calcined in O_2 at 850°C, then in CO at the temperature shown, before being cooled to −78°C in He. Pulses of CO were passed through the catalyst and the amount chemisorbed is plotted.

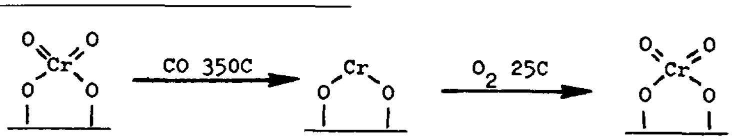
2.0. Instead it must have been due to some change in the bonding of the Cr(II) to the surface, lowering its coordinative unsaturation. This same deactivation effect could also be achieved by heating Cr(II) in N_2 instead of CO.

The lost coordinative unsaturation was confirmed by chemisorption experiments. In Fig. 2 the catalyst was again calcined in O_2 at 850°C, and then reduced in CO 1 h at the temperature indicated before being cooled to −78°C in helium. Then pulses of carbon monoxide were injected through the catalyst bed until no further adsorption was noticed. Plotted is the amount of carbon monoxide chemisorbed, which reflects the coordinative unsaturation. After reduction at 300°C nearly two molecules of CO were chemisorbed per Cr atom. Thus almost all of the chromium must have been exposed. As the reduction temperature was increased, however, chemisorption fell off until by 800°C it was less than 0.3 CO/Cr. This loss of coordinative unsaturation has also been observed by several previous researchers under static, rather than flow, conditions. Most notably, Krauss (*8–11*) studied the chemisorption of CO, N_2, and O_2 on Cr(II)/silica, and also the heats of adsorption, and the reflectance spectra. The Turin group has also observed this inactive form of Cr(II) (*12, 13*).

The nature of this deactivated form of Cr(II) is unknown. Its low level of coordinative unsaturation might indicate that it has burrowed into the surface, coordinating with surface oxides. Another possibility, which we favor for reasons to be discussed, is that the higher temperatures promote an aggregation of the Cr(II). However, these aggregates must not be very large or crystalline because no X-ray diffraction lines were detected, even from samples reduced in CO at 870°C for several hours.

Reoxidation of Active Cr(II)

When exposed to oxygen at 25°C, the active form of Cr(II) produced a brilliant yellow chemiluminescence (*15*) adsorbing exactly one O_2 per Cr(II). The easiest catalysts to completely reoxidize were those reduced at only 300–400°C, where little thermal deactivation had occurred and coordinative unsaturation was still high. These completely reverted back to the orange Cr(VI) form. The reoxidized catalyst was identical in activity and relative melt index potential (RMIP) to the original parent catalyst before reduction. This is summarized below. Apparently the bonding of Cr_A centers to the surface did not change too drastically during reduction.



Reoxidation of Deactivated Cr(II)

Samples containing the deactivated form of Cr(II), that is those reduced several hours at 800–900°C, were sometimes more difficult to completely reoxidize. Some-

TABLE 1

Treatment sequence	Color	Valence	Induction time	RMIP
1. Activation: O_2–870°C	Orange	Cr(VI)	Yes	1.0
2. Reduction: CO–350°C	Pale green	Cr(II)	No	0.7[a]
3. Reoxidation: O_2–25°C	Orange	Cr(VI)	Yes	1.0

[a] The minor drop in RMIP caused by reduction in CO was always found. It probably results from bringing to life early in the run certain high MW centers which otherwise would not become active until much later. The first centers to come alive always yield a slightly lower MW than those coming on stream later.

times exposure to oxygen at 25°C did not convert all of the Cr back to the hexavalent form; instead higher temperatures were required, depending on the severity of the reduction. This probably indicates a rearrangement or aggregation of the Cr during reduction. Unlike the example in Table I, reoxidation of this deactivated Cr(II) did not lead to the original hexavalent parent. Instead a Cr_B hexavalent catalyst was obtained with improved activity and RMIP.

This, of course, is in good agreement with the principles discussed in Part I. There Cr_B centers, which yield a higher RMIP, were formed by the attachment of chromium at a low temperature to a highly dehydrated support in which mainly strained oxide bridges, rather than hydroxyls, reacted. In the R/R treatment the original Cr_A type attachment was probably disrupted by the reduction at 800–900°C, which also dehydrated the surface of the silica or silica–titania support. Then during reoxidation at a lower temperature the chromium was reattached as Cr(VI) by reaction mainly with oxide bridges, giving Cr_B type centers like those of Part I.

Simple R/R Activation in CO

Actually the initial oxidation step, which left the catalyst hexavalent before reduction, was unnecessary. Simply heating the virgin Cr/silica or Cr/silica–titania, whatever the starting valence, to 800–900°C in CO yielded deactivated Cr(II) and Cr(III) species. In some cases, which will be discussed later, this deactivated Cr was known to be aggregated. Reoxidation at a lower temperature then yielded Cr_B behavior.

This is illustrated in Fig. 3. In 3-A the RMIP of the parent Cr_A catalyst is plotted after activation in dry air at various temperatures. In 3-B the virgin Cr(III)/silica–titania catalyst was heated in CO to the temperature shown, and after a 3-h hold it was reoxidized in air at the same temperature. Above about 650°C these samples had a higher RMIP than those in 3-A. This probably reflects the decreased surface hydroxyl population which results from treating the support in CO instead of air, discussed in Part I. However, in 3-C the catalyst was again reduced at 760–925°C but reoxidized at a lower temperature, 760°C, and the RMIP increased even further. This cannot reflect increased dehydroxylation because 3-B and 3-C had the same reducing treat-

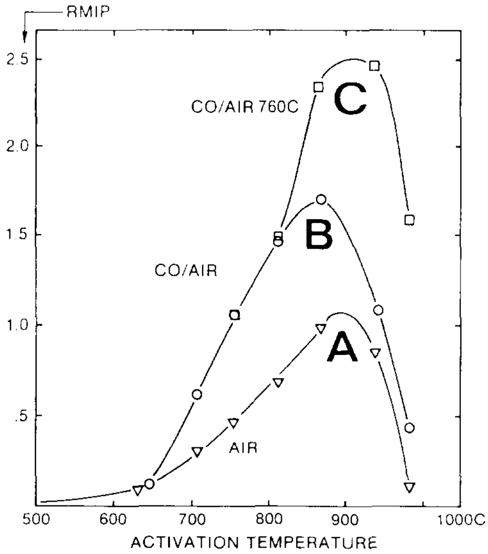


FIG. 3. Samples of Cr/silica–titania were calcined as follows: (A) in dry air 5 h at the temperature shown; (B) in CO 3 h, then air 2 h both at the temperature shown; (C) in CO 3 h at the temperature shown, then air 2 h at 760°C. Afterward each sample was allowed to polymerize ethylene.

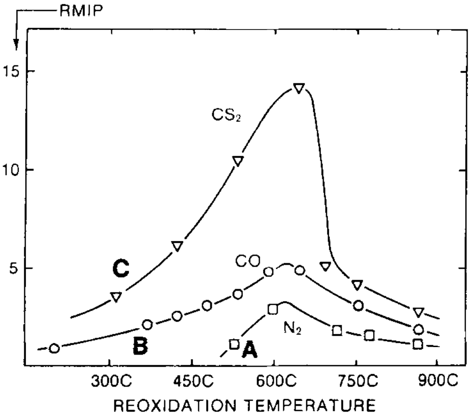


FIG. 4. Samples of Cr/silica–titania were calcined at 870°C in (A) N_2, (B) CO, or (C) N_2 with CS_2 vapor. Then each was reoxidized in dry air at the temperature shown, before being allowed to polymerize ethylene.

ment. Instead it can only result from a change in the bonding of the Cr to the surface, that is, to Cr_B centers.

Figure 4-B shows the optimum reoxidation temperature. In these experiments Cr/silica–titania was reduced at 870°C and then reoxidized at the temperature indicated. RMIP passed through a maximum at about 600°C. Both the position and height of this maximum were similar to that found in Part I (Fig. 5) when the chromium was impregnated anhydrously. In both cases RMIP was increased about sixfold over that attainable by simple one-step activation in air, further evidence of a common underlying cause.

R/R Effect From Nitrogen

Figure 4-A shows the R/R effect with no contribution from additional dehydroxylation by CO. In these experiments virgin silica–titania was impregnated with an aqueous solution of chromic III acetate. This does not lead to monomeric Cr(III) on the surface but, as Coronet and Burwell (*16*) have demonstrated, to a hydrated amorphous Cr_2O_3 aggregate. The choice of chromium III compound is not particularly important. The chloride or nitrate can also be used, and in one series of experiments Cr_2O_3 was even coprecipitated with the silica–titania. These samples were then heated in N_2 to 870°C where the support was thermally dehydroxylated only, and where aggregates of Cr_2O_3 remained or perhaps even grew. Afterward they were reoxidized to Cr(VI) in dry air at the temperatures shown in Fig. 4-A.

Again a maximum RMIP was obtained after reoxidation around 600°C and, in the absence of chemical dehydroxylation, this value was about twice that attainable from the one-step activation at 870°C. This agrees well with results from anhydrous impregnation (Part I, Fig. 5), and again it demonstrates that the particular species of reduced inactive Cr, in this case Cr_2O_3, is unimportant so long as it can reoxidize at about 600°C to hexavalent Cr_B centers. Comparison of 4-A with 4-B shows the effect of dehydroxylation by CO, about a twofold improvement in RMIP, again in agreement with anhydrous impregnation.

Other Reducing Treatments

Reducing the catalysts in H_2 instead of CO probably created both Cr(II) and Cr(III) species on the surface (*14, 15*). However, no improvement over that seen in 4-A by N_2 was noticed, probably because H_2 does not dehydroxylate the support. Similarly NH_3 gas performed no better.

In contrast, reduction by a mixture of CO and CS_2 vapor, shown in 4-C, was an extremely effective dehydroxylation treatment. Thus RMIP was greatly improved over reduction by CO alone. Although sulfur was rarely retained by the support alone, it was retained when Cr was present, in the amount of S/Cr = 1–1.5, indicating the formation of a chromium sulfide. The black color of the reduced catalyst also suggested this. Catalysts reduced by CS_2 did not chemiluminesce when exposed to air at 25°C, but did release H_2S in the presence of moisture. This surface sulfide species was easily reoxidized to Cr(VI) when heated in dry air and by 650°C no more sulfur could be detected on the catalyst. However, an

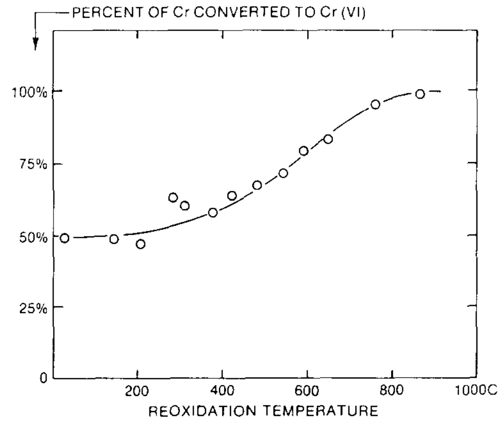


FIG. 5. Samples of virgin Cr(III)/silica–titania were heated in CO to 870°C, held 3 h, then oxidized 2 h in dry air at the temperature shown. The percent of Cr converted to Cr(VI) has been plotted.

unusual deep red color often developed instead of the expected orange, and these catalysts were extremely active.

Attempts to use R/R activation in combination with haliding treatments, such as those used in Part I, were unsuccessful. In some cases, judging from the violet color, $CrCl_3$ was formed. However, reoxidation was always very difficult and little improvement in RMIP was obtained.

Ease of Reoxidation

Exactly why the optimum reoxidation temperature was often around 600°C, as in Fig. 4, is not clear. Two processes must occur during the reoxidation step: (1) oxidation to Cr(VI), and (2) attachment to the support by reaction with oxide bridges. The minimum temperature needed for the second of these, the attachment, may have been fairly constant in these experiments since the type of support and the 870°C reduction temperature were not varied.

The minimum temperature needed for the other process, the actual oxidation to Cr(VI), was of course dependent on the state of the chromium after reduction. The easiest catalysts to reoxidize were those such as in Fig. 2 where only Cr(II) was formed. Oxidation and then reduction at 870°C yielded a gray material, amorphous to X-ray diffraction, which still chemiluminesced on contact with air at 25°C, but did not completely revert back to Cr(VI). Instead only a yellow tint developed. By 600°C, however, these samples were almost entirely reoxidized to Cr(VI). While isolated Cr(II) passes directly to Cr(VI) on contact with O_2, the deactivated Cr(II) may perhaps pass through Cr(III) especially if it is aggregated, making the reoxidation a little more difficult.

Catalysts containing mainly Cr(II), but also some Cr(III), could be prepared by directly heating virgin Cr(III) catalysts in CO. These samples, also amorphous to XRD, chemiluminesced like pure Cr(II)/silica, and the maximum RMIP was not greatly affected. However, they may have been slightly more difficult to reoxidize. In Fig. 5 the percent conversion to Cr(VI) is plotted against reoxidation temperature for a series of Cr(III)/silica–titania samples heated to 870°C in N_2 and then reduced the usual 3 h in CO. About half of the chromium reoxidized immediately on contact with O_2 at room temperature, suggesting perhaps a low order of aggregation. However, the rest was more difficult to convert to Cr(VI). At 600°C, where peak RMIP fell, about 75% of the chromium had been reoxidized, and only by about 800°C did all of it become Cr(VI).

Crystalline Cr_2O_3

Most difficult to reoxidize were samples containing only Cr(III), particularly the crystalline alpha Cr_2O_3. It is known that in the absence of the silica support amorphous Cr_2O_3 (chromia) remains amorphous when heated in an inert atmosphere to nearly 600°C (*17–19*), but in oxygen an exothermic crystallization to alpha chromia occurs at as low as 250°C (*18, 20, 21*). The transition is catalyzed by even a trace of Cr(VI), which perhaps acts as a flux (*22*). The crystalline material has a lower surface area and is extremely resistant to attack by acids or bases, or to oxidation.

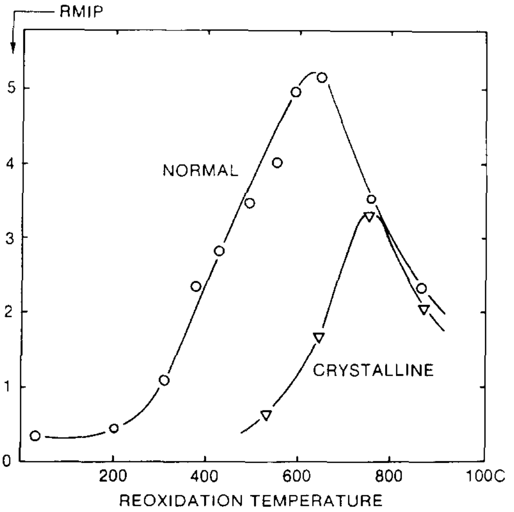


FIG. 6. Samples of Cr/silica–titania were heated to 870°C in two ways: (A) O_2 to 650°C, N_2 to 870°C, which promotes the formation of large crystallites of alpha Cr_2O_3; and (B) N_2 to 870°C, which does not promote crystallization. All samples were then held 3 h in CO, followed by oxidation in dry air 2 h at the temperature shown.

We have observed a similar behavior on silica and silica–titania, although displaced to higher temperatures. Catalysts containing amorphous Cr_2O_3, heated in flowing dry N_2 to 870°C, remained amorphous and fairly easy to reoxidize. This is evident in Fig. 4-A, where the maximum RMIP of the N_2 treated samples was found to be around 600°C, like the Cr(II) samples. However, when heated in N_2 in the presence of some Cr(VI) to act as flux, this same catalyst developed large crystallites (X-ray diffraction indicated 200 Å diam) of alpha Cr_2O_3. The crystalline material was much more difficult to reoxidize, and the maximum RMIP was always shifted to higher reoxidation temperatures.

This effect is evident in Fig. 6, where two series of samples were both reduced in CO at 870°C and then reoxidized in dry air at the temperatures plotted. Only the method of initially heating to 870°C was different. In 6-A, which encouraged the formation of large crystallites of alpha Cr_2O_3, the catalyst was first heated to 650°C in O_2 forming monodispersed Cr(VI). Then the O_2 was replaced by N_2 and the heating was continued to 870°C. Since Cr(VI) is not stable in the absence of O_2 at these temperatures, over 90% of it slowly decomposed to Cr_2O_3 in the presence of the remaining Cr(VI) which catalyzed the formation of crystallites. These crystallites, detected by XRD, probably survived reduction in CO at 870°C and then were very difficult to reoxidize later, requiring higher temperatures for equivalent conversion to Cr(VI).

In contrast, the samples in Fig. 6-B, which were initially trivalent (from impregnation of Cr(III) acetate), were simply heated in N_2 to 870°C. Thus the product was still Cr_2O_3 before reduction in CO but there was no chance for the growth of large crystallites here, because Cr(VI) was not present to act as a flux. Hence no XRD pattern was detected. In 6-B the optimum reoxidation temperature was about 600°C, compared to almost 800°C in 6-A.

Figure 7 provides further evidence that the temperature of peak RMIP depends on the ease of reoxidation. Here the reduced

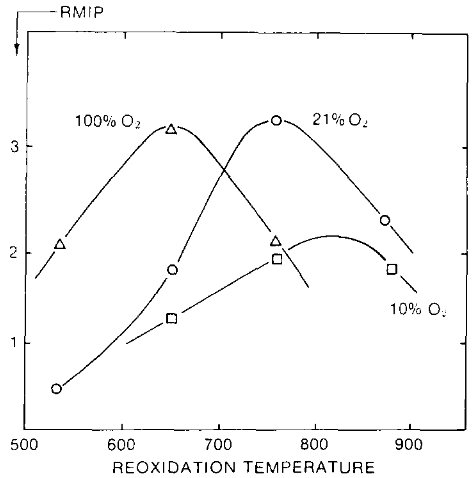


FIG. 7. Samples of Cr/silica–titania were heated to 650°C in air, then to 870°C in N_2, followed by a 3 h hold in CO. Afterward they were reoxidized at the temperature shown in either pure O_2, air, or a mixture of air and N_2, and then each was allowed to polymerize ethylene.

crystalline catalyst was reoxidized in three different gasses varying in oxidative potency, 7-A in pure oxygen, 7-B in dry air, and 7-C in half air and half N_2. As the oxygen concentration declined the optimum reoxidation temperature increased. Usually, though not always, as the optimum temperature increased for whatever reason, the peak RMIP value also decreased since Cr_B centers revert back into Cr_A as the temperature is increased.

CONCLUSIONS

The R/R effect of increased chain termination is completely analogous to the anhydrous impregnation technique discussed in Part I. During reduction the support becomes dehydroxylated while the chromium is immobilized as aggregates of Cr(II) or Cr(III). Then during reoxidation at a lower temperature hexavalent chromium reattaches by reaction with oxide bridges. The new type of active centers, which we call Cr_B, produces lower MW polyethylene than is ordinarily obtained. The optimum reoxidation temperature is determined in part by the crystallinity of the aggregates, but even when easily reoxidized the chromium probably requires a certain minimum temperature to react with the surface.

A wide variety of compounds besides CO can be used as reducing agents, such as hydrocarbons, H_2, SO_2, or NH_3. Even inert gasses like N_2 or argon will work, because Cr(VI) also thermally decomposes into Cr_2O_3 crystallites at 700–900°C. However, the most effective reducing agents are those which also enhance the dehydroxylation of the support, in particular CO and the organic sulfides. This dehydroxylation mechanism is not completely understood but is thought to be related to the water gas shift reaction.

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