

The Oxidation State of Chromium in Silica-Alumina-Supported Polymerization Catalysts

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A polymerization catalyst consisting of chromium oxide supported on silica-alumina was modified by reduction with controlled amounts of ethylene and by oxidation with controlled amounts of oxygen. Addition of ethylene at up to 300° increased catalyst activity but decreased the Cr^V content (as determined by ESR measurements.) At 400° ethylene caused a sharp decrease in both activity and Cr^V content. Addition of small amounts of oxygen to a catalyst inactivated by reduction increased activity without significant change in Cr^V content. Further addition of oxygen caused inactivation and increase in Cr^V content. The results can be explained by assuming that the presence of chromium in an oxidation state IV is essential for catalytic activity.

It has frequently been attempted to correlate the ability of chromium oxide on silica-alumina to catalyze the polymerization of ethylene with some oxidation state of chromium (1-8). Most of the work has been done in hydrocarbon solvents which are liable to modify the catalyst. In this study we have attempted to elucidate the problem by polymerizing gaseous ethylene (9, 10) on catalysts which have previously been selectively reduced or oxidized.

EXPERIMENTAL

Catalyst preparation. The support used was Davison F-1-13 silica-alumina Fluid Cracking Catalyst; it was impregnated with aqueous chromic acid solution, heated under stirring, and dried overnight in an oven at 130°. This preparation containing 30 mg of CrO₃ per gram of catalyst was fluidized by a dry air current and heated gradually to 600°; the air was replaced by argon and, after cooling, the catalyst was kept in a closed glass container under argon at virtually atmospheric pressure.

Pretreatment. In the first stage the catalyst was transferred under argon to the reaction vessel which was then evacuated

and heated to 300°. Evacuation was continued for 30 min yielding an ultimate vacuum of 10⁻⁴ mm Hg.

The second stage of the pretreatment consisted of the addition of ethylene or oxygen in controlled amounts to the catalyst at definite temperatures. The catalyst was kept in contact with these gases and was then used for the determination of activity either after further evacuation or straightaway.

Activity measurement. Exploratory runs showed that the isothermal rate of polymerization of ethylene changed rapidly and did not follow a pure order law. It was therefore decided to take as a measure of catalytic activity the decrease in the pressure of ethylene between the 2nd and 7th min of contact under the following fixed conditions: gas volume, 540 ml; temperature, -24° (melting point of CCl₄); initial pressure, 180 mm Hg. The pressure did not fall by more than 20 mm Hg during this period even at maximum activity. The catalyst covered the flat bottom of the reaction vessel in a sufficiently thin layer to maintain constant temperature during polymerization. The activity was expressed as milligrams of ethylene disappearing

from the gas phase per gram of catalyst per minute.

Measurement of electron spin resonance. Electron spin resonance measurements were carried out with a Varian V 4502-12 X-band spectrometer equipped with a 9-inch magnet. A 100-kc/sec modulation frequency was used, the amplitude of which was kept smaller than the line-width. All spectra were taken at room temperature and recorded as the first derivative of the absorption curve. The intensity I of the resonance was calculated by the approximation suggested by Varian (11)

$$I = KW^2H$$

where W is peak separation of the derivative and H is height of the resonance. The constant K was fixed by setting the resonance intensity of a standard sample of the catalyst to one. The catalyst sample in the cavity was contained in a thin-walled quartz tube. The catalyst sample could be directly transferred from the reaction vessel to this tube and sealed off.

RESULTS

After the first stage of pretreatment (evacuation at 300°) the catalyst was cooled. For the second stage of the pretreatment about 500 μ moles of ethylene per gram of catalyst was introduced and the reaction vessel was kept at the desired temperature until all ethylene disappeared from the gas phase. The activity was then determined at -24° (Table 1). It is known that at temperatures above 250° no polymerization takes place (12); during pre-

TABLE 1
ACTIVITY OF CATALYST AFTER PRETREATMENT
WITH ETHYLENE

Maximum temperature of first contact with ethylene	Activity (mg ethylene/g catalyst min)	Pretreatment
-24°	3.0	No pretreatment
100°	5.0	10 min at 100°
300°	8.0	10 min at 100° and 30 min at 300°
400°	0.0	10 min at 100° and 30 min at 400°

TABLE 2
INFLUENCE OF EVACUATION ON ACTIVITY
OF CATALYST

Temperature	Activity with evacuation	Activity without evacuation
200°	8.0	6.8 (by interpolation)
300°	12.0	8.0
400°	0.6	0.0

treatment below that temperature a little ethylene was polymerized to polyethylene which clogged somewhat the pores of the catalyst.

It can be seen from Table 1 that the activity rose with increasing temperature of pretreatment up to about 300°; a similar effect has been observed before (10). The increase in activity was not due to some specific reaction of ethylene. It has been shown that pretreatment with carbon monoxide (13) and some organic compounds (14) also raised the activity of the catalyst. It has therefore been accepted that reduction of some Cr^{VI} is essential to achieve activity. Inspection showed that the catalyst had turned yellow-green or dark green (according to the intensity of the pretreatment), indicating that reduction had in fact taken place.

Reduction of supported Cr^{VI} was accompanied by oxidation of ethylene which yielded oxidation products. It has been shown elsewhere (15, 16) that small amounts of foreign gases adsorbed on the surface lowered the activity considerably. In order to gauge the true improvement in activity, the catalyst was evacuated for 30 min at different temperatures after first having been pretreated with ethylene at 100° for 10 min. Table 2 shows the activity of the catalyst after heating to the indicated temperature with and without evacuation. The activity was indeed raised by evacuation, particularly at high temperatures.

Inspection of Tables 1 and 2 also shows that heating the catalyst to 400° in the presence of organic material destroys activity. Apparently, the more drastic reduction causes inactivation. This behavior indicates that the catalyst has to contain

Cr in an *intermediate* oxidation state in order to be active. Cr^{III} or Cr^{II} (17) cannot, therefore, be accepted as an active species. This conclusion is in line with previous observations that complete reduction of the catalyst renders it inactive (10).

Turning now to the low-temperature data of Table 1; it will be noted that the catalyst showed some activity at -24° even without pretreatment. The activity could be observed on the first instance of contact with ethylene; no incubation period was encountered. This should not be taken as proof that the unreduced catalyst was active; it has been shown that during the first stage of pretreatment (heating to 300° in vacuum) reduction took place, apparently due to organic impurities like grease vapor (10, 12). When such a catalyst was reoxidized *in situ*, its catalytic activity was destroyed: the catalyst was contacted with oxygen at 350° or 400° , evacuated in order to eliminate adsorbed oxidation products, again contacted with oxygen, and cooled to 100° . After renewed evacuation, the catalyst was cooled to -24° . The activity was zero. This is a further indication that the presence of Cr

in an oxidation state less than VI is essential.

To this oxidized catalyst ethylene was added in small controlled amounts at 100° ; no polymerization could be observed. If this seemingly dead catalyst was heated together with small amounts of ethylene to 300° , kept at this temperature for 10 min, evacuated for 2 min and the activity then determined at -24° , activity was partly or completely restored depending on the amounts of ethylene used (Fig. 1). The ethylene was not added cumulatively; each point represents a separate experiment starting from the same batch of fluidized catalyst.

Whereas an over-oxidized catalyst could be reactivated by reduction, an over-reduced catalyst regained activity on treatment with oxygen: The catalyst was at first reduced by contact with ethylene at 400° for 30 min. This treatment destroyed nearly all the activity (Table 1). The inactivated catalyst was then contacted at room temperature with a little oxygen (~ 10 mm Hg), evacuated, and heated under continued evacuation at 300° for 30 min. The activity after this treat-

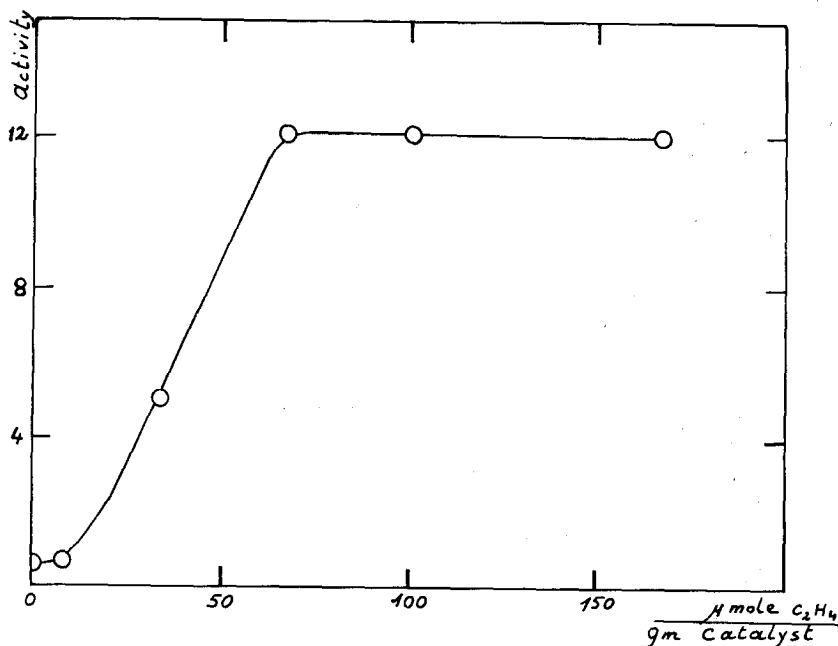


FIG. 1. Activity after addition of ethylene to oxidized catalyst.

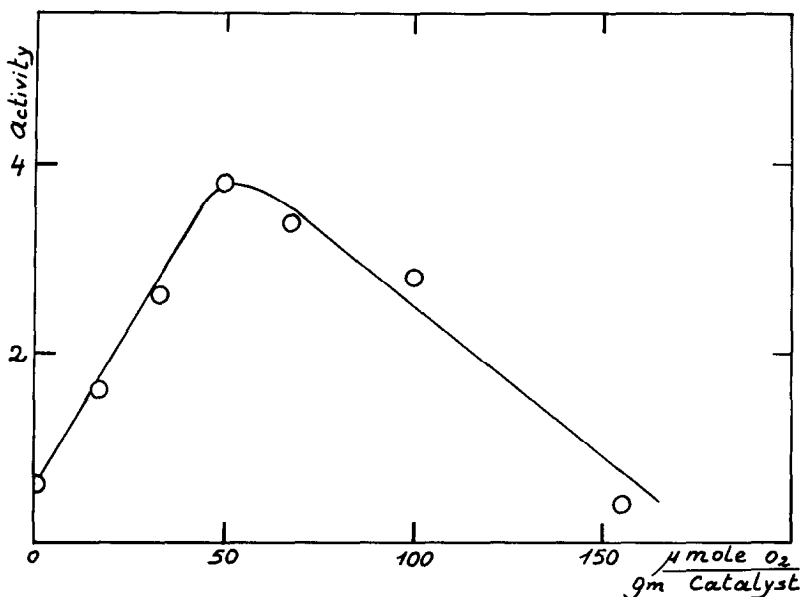


Fig. 2. Activity after addition of oxygen to over-reduced catalyst.

ment was found to be 12 mg of ethylene per gram of catalyst per minute.

The oxidation of the reduced, inactive catalyst was also carried out with controlled amounts of oxygen. In this case the catalyst was not evacuated after contact with oxygen. The results of this set of experiments are shown in Fig. 2. It is apparent that small amounts of oxygen restore some measure of activity. It is shown elsewhere (16) that addition of oxygen effects adversely the activity of the fully activated catalyst. This effect opposes the full reactivation by oxygen of the over-reduced catalyst.

Since a catalyst containing only supported trivalent or hexavalent chromium did not prove to be active, it was attempted to associate the catalytic properties with tetra- or pentavalent chromium. It has been shown by O'Reilly and MacIver (18) that an ESR signal at about $g = 1.97$, termed γ -phase signal, was due to supported Cr^{V} . Kazanskii *et al.* (3) studied the intensity of the signal before polymerization and found it to correlate well with the activity of the catalyst. However, as has been pointed out before (10), their own results showed that the signal intensity was greatly reduced on polymerization

without affecting the activity of the catalyst.

The results of the following experiment are further evidence that the chromium species giving rise to the γ -phase signal cannot be essential for catalytic activity. From the same batch samples were taken and given different pretreatments; their γ -phase ESR signal intensity and activity were determined (Table 3). It can be seen that the signal had its maximum intensity after fluidization; the signal decreased on raising the temperature of contact with ethylene. The activity, on the other hand, passed through a maximum at a pretreatment temperature of 300° . It follows that if the γ -phase signal

TABLE 3
ACTIVITY AND ESR SIGNAL OF THE CATALYST

Treatment	ESR signal intensity	Activity
Before fluidization	0.15	0
After fluidization	2.2	3.0
After first contact with ethylene at room temp.	1.9	—
at 100°	1.7	5.2
at 300°	1.00	12.0
at 400°	0.08	0.6

intensity is a true measure of Cr^{V} concentration, activity is not caused by Cr^{V} .

The influence of oxygen on the γ -phase signal intensity was also investigated. The experiments were carried out with a fully activated catalyst and with one which was inactivated by treatment with ethylene at 400° (Fig. 3). The amount of oxygen appearing on the abscissa of the graph was that of oxygen added less that remaining in the gas phase. With the activated catalyst a measurable amount of oxygen remained in the gas phase only when more than $50 \mu\text{moles}$ of oxygen per gram of catalyst were introduced into the reaction vessel. With the inactivated catalyst the

pressure remained negligible up to $100 \mu\text{moles}$ of oxygen per gram of catalyst.

It will be noted that both the intensities and their first derivative increase with increasing amounts of oxygen taken up and that the inactivated catalyst consumed far more oxygen than the activated one for the same increment in signal intensity. Possibly a minimum concentration of oxygen at the surface is necessary in order to oxidize Cr^{III} or Cr^{IV} to Cr^{V} . On evacuation at 300° the ESR signals of both catalysts returned to their respective original intensities. It will be remembered that the activity of the activated catalyst decreased on addition of oxygen. This effect proved

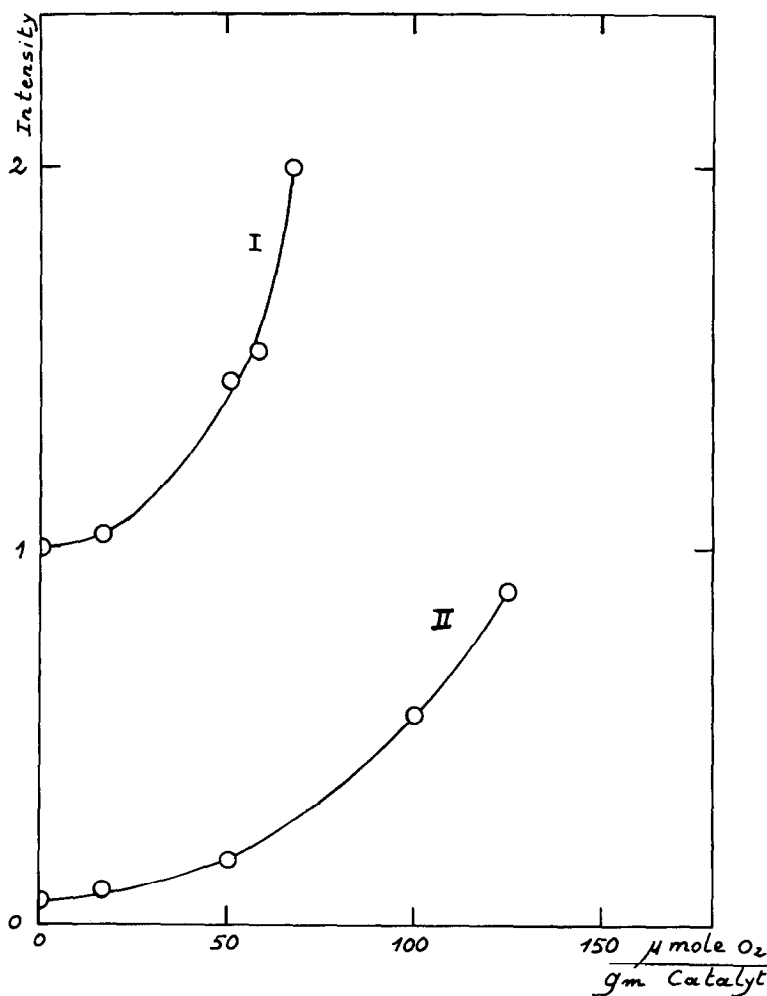


Fig. 3. ESR signal intensity after addition of oxygen to I, activated catalyst; II, over-reduced catalyst.

to be reversible (16). Apparently the increase in ESR signal intensity was also reversible. On the other hand the activity of a previously inactivated catalyst increased on addition of small amounts of oxygen (Fig. 2); but on evacuation the activity not only failed to decrease, it even increased and, when sufficient oxygen had been used, the activity after evacuation reached the same value as that of a catalyst which had not previously been inactivated. Thus the oxygen causing the ESR signal increase could be reversibly removed, yielding in both cases a catalyst with the maximum inherent activity of about 12.

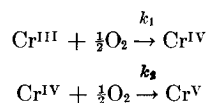
It was attempted to oxidize the catalyst fully by contact with oxygen (500 mm Hg) at temperatures varying from 25° to 400°. This treatment did not decrease the ESR signal intensity below the value of an active catalyst.

DISCUSSION

The above results allow the following interpretation. In order to be active some chromium must be in an intermediate oxidation state. When chromium on silica-alumina is present only in oxidation states III or VI, no catalytic activity towards the polymerization of ethylene is observed. It has also been shown that the species which gives rise to the γ -phase ESR signal is not active. It is generally accepted that this signal is due to Cr^{V} ; it is possible, however, that there exists another type of Cr^{V} on silica-alumina, the ESR signal of which does not appear at room temperature. Such a Cr^{V} could be responsible for activity since it was only shown that there was no correlation between the γ -phase ESR signal and the activity. In that case the active species may be the square pyramidal form the ESR signal of which is observed only at -253° (8). However, no study of the correlation of this low-temperature signal with catalytic activity has been reported. Steiner (19) suggested that the growing polyethylene chain attached to chromium destroyed some symmetry property with consequent disappearance of the γ -phase signal; on treatment with

water, the polyethylene chain was liberated, the symmetry being restored; this hypothesis was advanced in order to explain the correlation of activity with increase of γ -phase signal on treatment with water (10). After the water treatment, the catalyst was inactive. It is shown elsewhere (16) that on withdrawing the water by evacuation at 300° , activity is restored. At first sight this effect would contradict Steiner's suggestion; but it is possible that at the high temperature at which the system was evacuated, polyethylene on the catalyst reattached itself to the chromium which will then be again active towards polymerization; for, evacuation at room temperature did not suffice to restore the activity. Alternatively, the addition of water may cause a reversible change in coordination of the active Cr^{V} species which passes over into the inactive γ -phase.

Since it has been established that there is no direct correlation between the γ -phase signal and the activity, there remains no necessity to stipulate that the active center contains Cr^{V} . Indeed, the results of the experiments point in the direction that Cr^{IV} is an essential ingredient of the catalytic system. The reduced catalyst which has lost most of its original activity regains activity on addition of minute amounts of oxygen. The curve showing the dependence of activity on the amount of oxygen added (Fig. 2) does not indicate an intermediate between Cr^{III} and the active species; the oxidation of Cr^{III} to Cr^{IV} would be a possible explanation for this behavior. In that case the following reaction scheme may be proposed



Starting from pure Cr^{III} and assuming complete consumption of the added oxygen, the fractions of Cr^{III} , Cr^{IV} and Cr^{V} can be calculated; this was done for the case $10k_1 = k_2$ (Fig. 4). The assumption of equilibrium being attained between the different oxidation states leads to similar curves. From comparison with Fig. 2, it is apparent that the experimentally determined

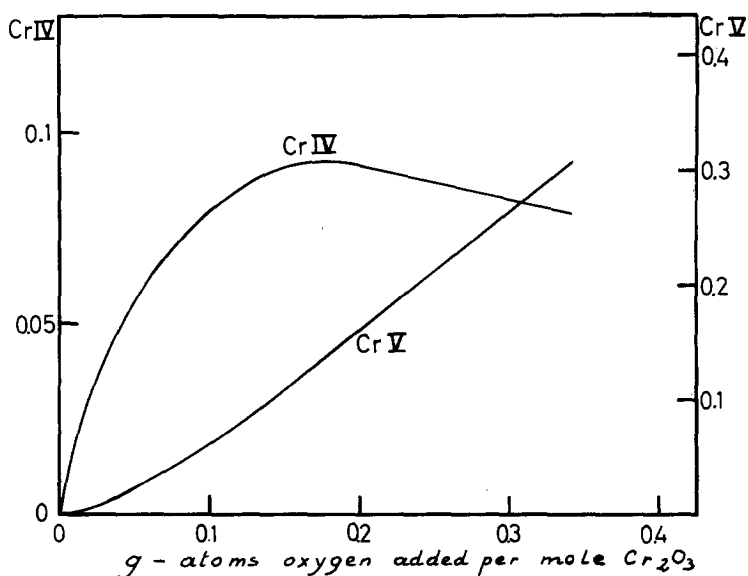


Fig. 4. Fractions of Cr^{III} oxidized to Cr^{IV} and Cr^V as calculated on the assumption $10k_1 = k_2$ (see text).

activity curve has the same shape as the theoretical curve for Cr^{IV} while comparison with Fig. 3 shows that the experimentally determined ESR signal intensity curve corresponds to the theoretical curve for Cr^V. On the other hand, when the overoxidized catalyst is reduced with minute amounts of ethylene, activity does not rise for the smallest amounts but only after more ethylene is added. There is, therefore, evidence that the reduction of Cr^{VI} to the active state passes through an intermediate, possibly Cr^V, strengthening the case that Cr^{IV} is the active state of chromium.

If Cr^{IV} is assumed to be essential for catalysis, the correlation between activity and increase of ESR signal on addition of water (10) can be explained as follows: the added water destroys the stability of the Cr^{IV} sites, which thereupon pass over into Cr^V through oxidation by Cr^{VI} or by disproportionation. In both cases the increase of the ESR signal would be proportional to the amount of Cr^{IV} originally present and indirectly to the activity as observed by Ayscough, Eden, and Steiner (10). On evacuation at 300°, water is lost, the stabilizing power of the site restored and the amount of organic material on the catalyst easily reduces some chromium to

Cr^{IV}. In such a way activity may be restored.

As in the case of Cr^V, which is unstable by itself but extremely stable on proper supports, it is quite reasonable to suppose that Cr^{IV} can be stabilized on suitable sites. It could be shown that supported Cr^V resisted oxidation by oxygen even when heated to 400°; the γ -phase ESR signal was not affected. Unfortunately, it was not possible to determine Cr^{IV} directly and thereby to prove its existence and stability in the catalyst.

The following model can therefore be proposed only tentatively to explain the experimental results. During fluidization, potentially active sites are formed which are able to stabilize Cr^{IV} atoms. However, since fluidization is carried out with air, the chromium in the potentially active sites is mainly Cr^V and Cr^{VI}. The ESR signal intensity is therefore high after fluidization and the activity low. On heating with ethylene, Cr^{IV} is formed from Cr^V with the result that signal intensity decreases and activity increases. At low temperatures, only the most accessible Cr^V is attacked; as the temperature is raised, chromium in the better protected sites is also reduced. At about 300°, maximum

activity is reached. On heating to 400°, Cr^{IV} and Cr^V form Cr^{III}; both the activity and the ESR decrease to a small fraction of their value at 300°.

Treatment with oxygen oxidizes Cr^{III} and Cr^{IV}. When oxygen is added to a fully active catalyst Cr^{IV} is oxidized, activity falls, and the ESR signal increases. When oxygen is added to a reduced, inactivated catalyst in which little Cr^{IV} is present, Cr^{III} is oxidized to Cr^{IV} and eventually to Cr^V, activity rises and the ESR signal intensity increases. On further additions of oxygen, the activity falls either because of oxidation to Cr^V or because of the inhibiting effect of oxygen and oxidation products. On evacuation at 300°, the newly formed Cr^V is reduced to Cr^{IV}; activity rises further and the ESR signal intensity falls. The easy reversibility of the increase of ESR signal is thought to be due to the accessibility of the sites oxidized under mild conditions, these are exactly those sites which are also most easily reduced. Ethylene treatment at 300° decreases the ESR due to Cr^V in the bulk only slightly, but the same treatment cancelled all the ESR increase obtained on mild oxidation.

The results are therefore in accord with the view that it is Cr^{IV} which confers activity to specific sites of silica-alumina and similar supports.

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