JOURNAL OF CATALYSIS 35, 345-352 (1974)

Supported Chromium Oxide Catalysts for Olefin Polymerization

IX. The Nature of the Narrow γ-Phase ESR Signal and its Correlation with Catalytic Activity

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Received March 16, 1973

A new examination of the numerous results concerned with the γ-phase ESR signal leads to a coherent theory taking in account both ESR and activity measurements. The signal is associated with a three-chromium-atom center with mixed valency and the average oxidation degree is 5. The qualitative correlation between signal intensity and catalytic activity is explained.

INTRODUCTION

In the preceding paper (1) a new model for the active centers of the Phillips catalyst was proposed. The active centers are considered to comprise three chromium ions with mixed valencies, Cr^{3+}, Cr^{6+}, Cr^{3+}, bound to the carrier (the silica alumina co-oxide zone) at the borderline between the bare carrier and the zones covered with chromium oxide. This model gives a good account of the kinetic data obtained with these catalysts for the polymerization of ethylene and propylene, and also allows a more accurate determination of the dispersion state of the chromium upon the surface of the carrier. On the other hand, several ESR observations seem to indicate that there exists some correlation between the sharp ESR so-called γ-phase signal and the catalytic activity. It was interesting to make a new examination of the ESR signals in order to explain their changes with new ideas in relation with this model for active sites.

THE γ-PHASE SIGNAL

In spite of the great number of workers who have studied the narrow resonance line of the ESR pattern of chromia–alumina or chromia–silica–alumina catalysts since 1960, no convincing explanation of the correlation between the species giving rise to the sharp signal (called the γ-phase chromium) and the catalytic activity versus ethylene polymerization has emerged. Data on the γ-phase peak are very numerous. It was observed on catalysts supported on silica, silica–alumina, but not with pure chromia gels. The signal is well characterized. The g factor lies at about $g = 1.97$. The width has a value of 50 G and is generally not very dependent on the catalyst composition.

The majority of the studies have essentially been concerned with the catalyst obtained by the activation heating treatment, mostly without contact with monomer. A large bibliographic review for chromia–alumina solids has been made by Poole and MacIver (2). Pecherskaya and Kanzanskii (3) have determined the variation of the intensity of the sharp ESR peak with temperature between −196 and 300°C and found that the susceptibility varies according to a Curie–Weiss law with a Weiss temperature of +25°K. This indicates that it is not a very dilute state. The effect of oxygen chemisorption shows that the γ-phase lies on the surface of the catalyst. As the width does not vary with the chromium content, the signal seems to arise from a definite state. Many species could be supposed to give rise to the signal. As early as 1960, O'Reilly (*4*) proposed to attribute it to single electrons captured by surface Cr^{6+}. An examination of the corresponding spin-hamiltonian shows that only the $(3d)^1$ configuration can explain the symmetrical shape of the peak at X band and the slight dissymmetry at K band.

This hypothesis was adopted by Cossee and van Reijen (*5*) on the basis of magnetic susceptibility measurements, then also by most authors.

Bukaneva *et al.* (*6*), following the work of Rode *et al.* (*7*), showed that the spectra do not correspond to any of the intermediate states observed during the thermal decomposition of CrO_3 and that it may only originate from a species bonded to the carrier, but not from agglomerated chromium oxide. This is the starting point of the theory developed by Kazanskii and Turkevich (*8*) and by Pecherskaya and Kazanskii (*9*). This theory concludes that there are Cr^{5+} ions incorporated in the carrier network, on its surface. The Cr^{5+} ions exist in a different symmetry environment on different supports, namely tetrahedral on silica, tetrahedral, or distorted octahedral on alumina or silica–alumina. The variations of the g factor when adsorbing water or oxygen are those which can be calculated on the basis of the theoretical assumptions.

Van Reijen and Cossee (*10*) have reached nearly the same conclusions, but with slightly different methods. They studied the γ-phase signal at liquid hydrogen temperature (20°K) and concluded that Cr^{5+} was present in tetrahedral or square pyramidal symmetry. Only the signal corresponding to the square pyramid would be seen at high temperature. This was confirmed by the observation at 20°K of the hyperfine structure resulting from enrichment with ^{53}Cr.

It was noticed by Poole and MacIver (*2*) that the γ-phase chromium seems to be at least partially associated to the β-phase chromium (the chromium clusters on the surface of the catalyst) but not the δ-phase chromium, even though the latter comprises the isolated atoms. It seems that there is no reducing treatment which can lead from isolated Cr^{5+} ions to isolated Cr^{3+} ions.

CORRELATION BETWEEN THE SIGNAL INTENSITY AND THE CATALYTIC ACTIVITY

Some correlation between the γ-phase signal and the activity has been noticed for a long time. Kazanskii (*8*) observed that when one plots the signal intensity and the activity versus ethylene polymerization as a function of the chromium content of the catalyst one obtains curves showing some parallelism, especially at low content, and the maxima of the two curves lie at about 2% Cr, for a silica support.

Ayscough, Eden, and Steiner (*11*) have found a relation between the increase of the signal of a catalyst which has polymerized, after contact with water vapor, and the activity.

Durrieu (*12*), for a catalyst supported on silica–alumina, found the same kind of correlation as Kazanskii (but between signal intensity and activity versus propylene polymerization), and he showed that some refinement could be brought when considering only the part of the signal which disappears after extraction of the soluble chromium of the catalyst by boiling water, but the maximum lay at about 5–6% Cr.

A more detailed examination shows that these correlations are not entirely convincing. There is never proportionality between intensity and activity; the relation is only qualitative. Treatments which give an increase of the activity at low temperature (reducing pretreatments) may correspond to a diminution of the signal intensity. In the same way, the signal decreases during the polymerization reaction and even becomes zero under certain conditions (*6*).

In order to take into account these observations, Kazanskii (*8, 9*) proposed that, during the formation of the active center by reaction of ethylene with the Cr^{5+} ion, there was no variation of the oxidation state but a change of symmetry; the coordination became that of a square pyramid. In that environment no signal would be observed at liquid nitrogen or at higher temperatures. This could explain why the more active catalysts give rise to only a little peak at these temperatures.

However, the test of that hypothesis by Karra and Turkevich (*13*) down to 1.6°K brought no positive conclusion; no new signal was observed. In the same way van Reijen *et al.* (*10*) have noticed two kinds of γ-phase signal but these were not related to activity. As no more precise experiments at low temperature were done, the question remained unanswered.

NEW MODEL FOR THE STRUCTURES ASSOCIATED WITH THE SIGNAL

All these observations have led us to conclude that the signal and the activity may have only an indirect relation and are bound together through an independent parameter. Following the new model proposed previously (*1*) for the active center we propose now a new model for the sites responsible for the γ-phase ESR signal.

If one considers the variations of the signal intensity as a function of the chromium content or the increase of the signal referred to chromium at low content, as observed by Matsumoto, Tanaka, and Goto (*14*) and by Deren, Haber, and Kosek (*15*), the relation sought is easily found if one supposes that the active centers and the γ-phase are located at the same place on the catalyst surface, i.e., as supposed for the active centers, on the borderline of the flat domains of chromium spread on the carrier surface.

The whole length of the border would then be the parameter which binds together the two kinds of measurements. The observed differences result from the fact that the species do not have the same oxidation degree.

This hypothesis gives a better agreement with the complementarity between γ- and β-phase than the ones assuming isolated chromium.

The oxidation degree of the species giving rise to the γ-phase ESR signal is higher than that of the β-phase (+3) and higher even than that of the active centers (*1*) as seen when reducing the catalyst. According to the theory proposed for the active center, we suppose that the γ-phase is composed by a set of three chromium atoms of the borderline as

$$Cr^{6+}–Cr^{3+}–Cr^{6+}.$$

The average oxidation degree of the γ-phase is then 5.

This agrees with the hypothesis suggested by Ellison and Sing (*16*) as early as 1966 and detailed further since that time. These authors suppose that the signal comes from the electron excess of the Cr^{3+} on structures of the type $Cr^{6+}–O_2^-–Cr^{3+}–O_2^-–Cr^{6+}$ which show a double exchange ferromagnetism of the Zener type.

When varying the oxidation degree of the catalyst, there will then result two well-separated curves for the activity and the intensity of the ESR signal, the latter corresponding to the less reduced state.

EXPERIMENTAL RESULTS AND DISCUSSION

The kinetic measurements concerning the ethylene polymerization have been made using an integral dynamic reactor according to the process described previously (*18*). The ESR spectra have been registered using a Brucker B-ER 400S spectrometer operating at X band. The shapes of the pattern are in most cases identical, so that it is good enough to use the height of the peak as a measure for the relative intensity.

Variation of the γ-Phase Signal During the Thermal Treatment

The catalyst was treated *in situ* in the ESR cavity using a thermal regulation unit, but the spectra were recorded at a fixed temperature (20°C) in order to avoid correcting calculations. The activation gas flow (nitrogen) was introduced by a capillary leading down to the bottom of the tube containing the catalyst sample, and the flow was calculated so as to maintain a fluid bed.

None of the recorded spectra corresponds

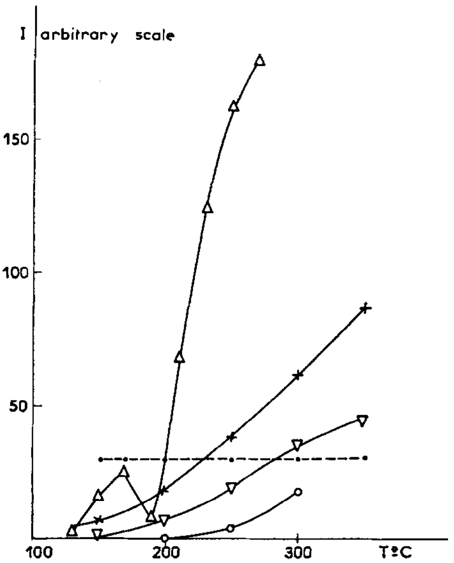

FIG. 1. Variation of the intensity of the γ-phase signal with thermal treatment for various catalysts with silica–alumina (87–13%) carrier. ×—impregnated with 3.6% CrO_3; ∇—impregnated with 3% sodium dichromate; ○—impregnated with 3% chromium nitrate; ●—impregnated with 3.6% CrO_3, activated 550°C, soluble chromium extracted by boiling water; △—impregnated with 18% CrO_3.

to a treatment at a temperature lower than 130°C. This avoids the presence of too great an amount of water on the catalyst. Successive treatments with 2 min duration at temperatures increasing by steps of 20 or 30°C followed a first drying at the lowest temperature (130°C). The results are reported in Fig. 1.

The intensity of the signal is approximately zero for the fresh impregnated catalyst after the drying treatment (silica–alumina support with 3.6% chromium content impregnated by an aqueous solution of Cr(VI) oxide). The signal increases regularly with the temperature. The same observation can be made with catalyst impregnated with sodium bichromate but the increasing rate is lowered. For a catalyst impregnated with Cr(III) nitrate, the signal appears only at 200°C, at the temperature of the nitrate decomposition. At this temperature all the chromium is quickly oxidized to +6. It is a confirmation of the fact that the γ-phase signal is observed only when +6 chromium is present.

The signal of a catalyst with high chromium content (18%) has a slightly different behavior. After a first decrease at about 170°C, which is associated with an important loss of water at this temperature, it increases to a very high value. For the other samples, there is no noticeable loss of water above 130°C.

A special sample is obtained upon activation of the usual catalyst at 550°C and extraction of the soluble chromium with boiling water. Its signal does not vary, in spite of the fact that it includes initially a great excess of water. The water has effect only if soluble chromium is present on the catalyst.

The appearance of the γ-phase signal at low drying temperature has been observed by many authors. Ellison and Sing report it for a catalyst with 11.3% Cr, dried at 50°C. It is unlikely that stable Cr^{5+} ions bound to the carrier can appear at that temperature, because their formation needs a strong interaction. The fact that the signal appears easier with a great chromium content led them to the assumption that the signal arose from the surface of the chromium.

We do not agree with that view; the signal is not observed with pure chromia gels and there is essentially chromium in multilayers on a 11.3% catalyst. It seems better to suppose that before a high temperature treatment which permits the ultimate chromia–carrier interaction, the chromium is poorly organized and for a high content the whole length of the borderline of the chromium domains will greatly depend on the preparation and on the treatments, permitting in some cases a very high signal. Then most of the first Cr^{3+} ions appearing on these catalysts contribute to the γ-phase formation.

Effect of a Reducing Pretreatment

The effect of a reducing pretreatment by ethylene or by hydrogen has been examined in the same conditions as the activity measurements reported in the previous

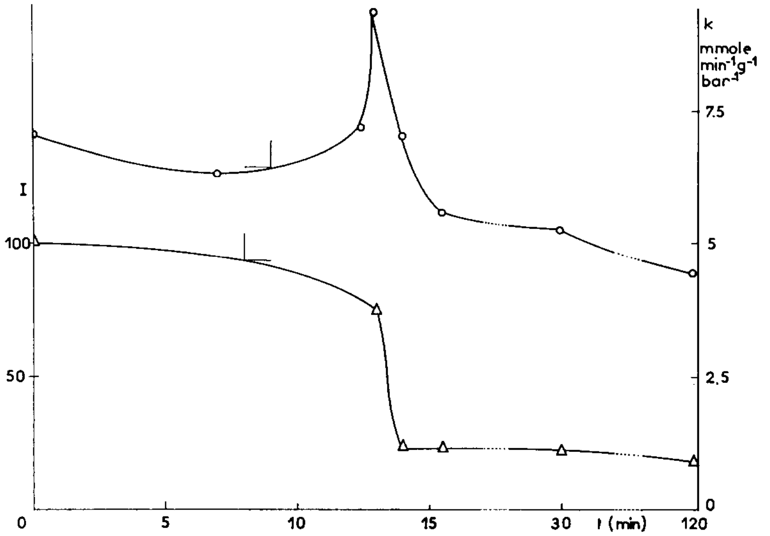

FIG. 2. Variation of the signal intensity (△) and activity (○) with the duration of the reduction by hydrogen at 295°C.

papers (*1*). As shown in Figs. 2 and 3, the treatments which give maximum activity and maximum signal intensity are different, and the maximum of the signal intensity does correspond to a moderately reduced catalyst. The signal intensity decreases very strongly after the maximum in the case of the hydrogen pretreatment, and it has been suggested that at this point the reduction is very fast (*18*).

For the hydrogen pretreatment, the signal is recorded after contact with ethylene, and for this reason the oxidation degree is always below 5. The same observations have been noticed by some authors, but were not explained. Kazanskii and Pecherskaya (*19*) reported that moderate reductions increase the signal intensity, which is decreased by further reduction.

Ermakov *et al.* (*20*) have observed that a moderate reduction during 15 hr (H_2 at 150 or 200°C, ethylene at 100°C) increases the signal. It disappears after a stronger reduction (ethylene at 200 or 300°C, hy-

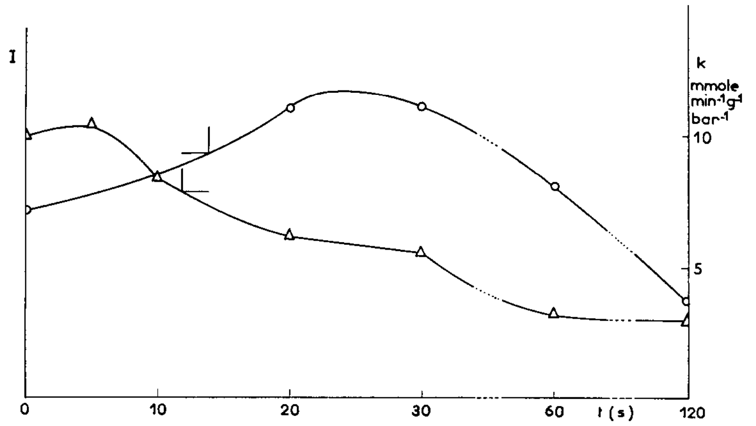

FIG. 3. Variation of the signal intensity (△) and activity (○) with the duration of the pretreatment by ethylene.

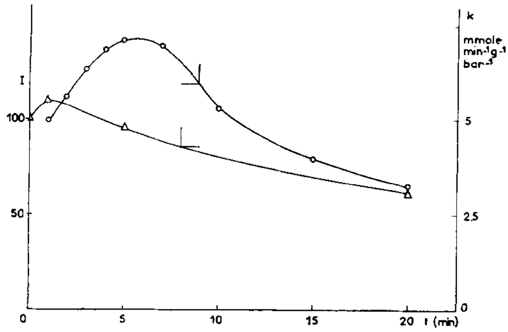

FIG. 4. Variation of the signal intensity (△) and of the polymerization rate (○) during ethylene polymerization (145°C, 0.1 bar).

drogen at 350°C) but may eventually appear again after air exposure.

Ayscough, Eden, and Steiner (*11*) obtain the same kind of curve for the activity and the signal intensity as a function of the temperature of the first contact with ethylene, according to our theoretical curves.

Variation of the Signal During the Ethylene Polymerization

During the polymerization of ethylene at 145°C the signal intensity reaches a maximum value and then decreases continuously. The maximum is observed during the induction period which precedes the maximum rate. The variations of the rate and signal intensity are reported in Fig. 4. The two curves have the character expected according to our model.

In their experiments at high pressure, Bukaneva *et al.* (*6*) have observed the same phenomenon, but the signal disappears gradually during the reaction. In a further paper, Kazanskii (*9*) gives some details concerning the shape of the kinetic curve and also points out the shift between maximum signal and maximum activity.

Influence of the Ethylene Pressure

For a catalyst which has a first contact with ethylene at a fixed temperature (145°C) and at a pressure varying from 0.01 to 0.2 atm the variations of the signal intensity and activity are opposite (Fig. 5). In the domain where the apparent reaction order is greater than unity, the signal decreases continually with increasing pressure. It becomes constant when the reaction order becomes constant. This demonstrates that, as we have supposed previously (*1*), the number of the active centers increases with the ethylene pressure below 0.1 atm, and at higher pressure, no new active centers are formed. This points out the fact that γ-phase and active center concentration are linked, although their variation can be parallel or opposite according to the range of the oxidation degree.

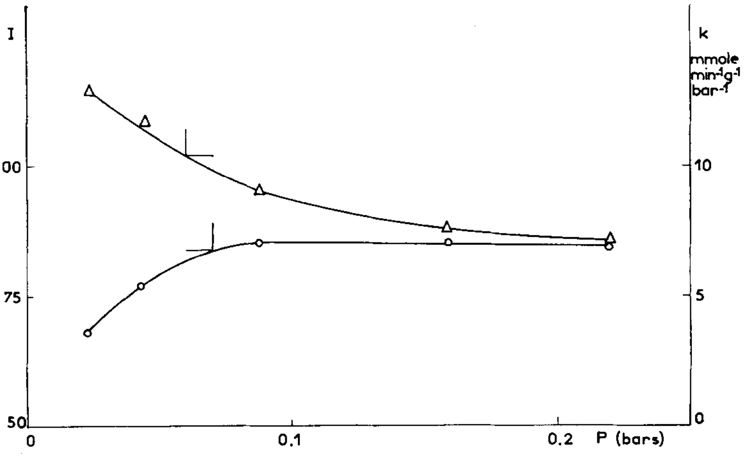

FIG. 5. Variation of the signal intensity (△) and of the activity (○) with varying ethylene pressure.

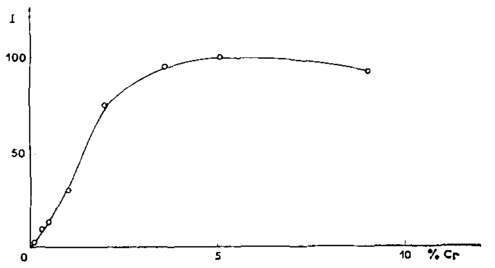

FIG. 6. Variation of the signal intensity at activity maximum (145°C, 0.1 bar) with chromium content.

Influence of the Chromium Content

In Fig. 6 are reported the variations of the γ-phase signal at maximum activity without pretreatment as a function of the chromium content. As might be expected, the maximum of the signal intensity is found at higher chromium content (5% Cr) than the maximum of the activity (2% Cr).

It is to be noted that these maximum activities are generally lower than the maximum activities after a reducing pretreatment in optimum conditions. According to our model the number of sets of the type Cr^{3+}-Cr^{6+}-Cr^{3+} or Cr^{6+}-Cr^{3+}-Cr^{6+} depends on the mean oxidation degree d of the active part of the catalyst. Then starting from the values of signal intensity and activity without pretreatment for catalyst with varying chromium content, and from the maximum activity after pretreatment (at $d = 4$), it is possible to calculate the maximum of the signal intensity (at $d = 5$) for the same catalysts. The results of these calculations are plotted in Fig. 7. The curves of activity and signal intensity corresponding to fixed oxidation degrees (4 and 5, respectively) show a good parallelism, and it is then possible to explain why many authors have observed parallel variations for catalysts in a limited range of d.

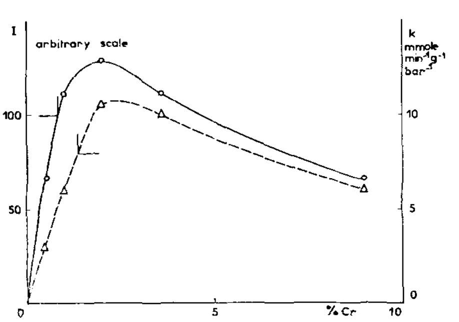

FIG. 7. Variation of the corrected intensity (△) of the γ-phase signal and of the activity (○) with chromium content (for nature of the correction, see the text).

CONCLUSION

The study of the ESR sharp line of the Phillips catalyst made in relation with activity measurements has led to a coherent theory which was verified by studying many parameters of the activation or polymerization process. It permits us to explain the many observations which show a correlation between the active centers and the so-called γ-phase and brings a new confirmation for our theory of the active centers as a set of three Cr atoms located at the borderline of the chromium domains spread on the carrier surface.

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