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Supported Chromium Oxide Catalyst for Olefin Polymerization

IV. Physico-Chemical Study of the Activation Process*

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Both magnetic susceptibility and oxygen chemisorption measurements on chromium oxide supported on silica-alumina catalyst show a limited evolution of the dispersion state of the chromium oxide during the time of the activation treatment in air at 550°C. The Cr(III) domains tend to be more isotropic, and the reverse is true for the Cr(VI) domains. However, the activity for ethylene polymerization is only slightly stabilized by a longer activation time.

INTRODUCTION

In the first papers of this series (*1*, *2*), a relationship was found between the activity of the supported chromium-oxide catalysts for propene polymerization and the dispersion state of the chromium oxide. The rate constant goes through a maximum for an average number of chromium oxide layers between two and three. The dispersion state is fixed by the conditions of the chemical interaction between the chromium oxide and the support of silica-alumina, and it has been shown that this interaction, which begins at room temperature during the impregnation process, undergoes an important exothermic step around 300°C during the drying process itself. It may be expected that the actual conditions of the activation process (temperature and duration) are very important for the development of the active sites. In the earlier patents of the Phillips Petroleum Co. (*3*), it is quoted that the optimal conditions of activation are 550°C, 4–6 hr, in an air stream. These conditions are used by most authors, but very few studies have been carried out on the activation process (*4*). It may be mentioned that Daniel (*5*) has found a strong effect of activation air velocity on the hexavalent chromium content, which increases with increasing air velocity and levels off above 200 v/v/hr. Moreover, we obtained a few data on the influence of the temperature on the dispersion state of the chromium oxide (*1*).

The purpose of the present paper is to describe a rather detailed study of the effect of the duration of the activation process in air (high v/v/hr) at 550°C on the texture of the catalyst, the dispersion state of the chromium oxide, and the activity of the catalysts for ethylene polymerization.

EXPERIMENTAL

The catalyst contains 3.5% Cr supported on a silica-alumina carrier. It is dried for 15 hr at 300°C under a stream of nitrogen. A first sampling is operated; then the temperature is raised to 550°C, and a second sample is picked up. The activation process begins at this time by replacing nitrogen by air. Samples are then picked up at various times. The following measurements have been carried out at each sample: solu-

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ble Cr(VI) and residual Cr(III) chromium titration, specific surface area, oxygen chemisorption after reduction with H_2 at 450°C, both on the raw catalyst and the solid residue after aqueous extraction, and finally magnetic susceptibility between 4 and 77° K on the catalyst and after reduction with H_2. The experimental methods have been described elsewhere (*1–6*).

The activity of the catalysts for ethylene polymerization at 145°C is measured at low ethylene pressure (0.1 atm), using a dynamic method similar to that described by Clark *et al.* (*9*). The samples of catalysts picked up during the activation process are poisoned by air or water and have to be reactivated a few hours at 350°C in a stream of helium in the cell used for the activity measurements. It has been found that such treatment does not change the activity of catalysts activated in situ in the measuring cell. The ethylene diluted in helium goes through a fluid bed of catalyst to a catharometer as a detector: Its deviation is a continuous measurement of the instantaneous rate of ethylene consumption. The curves giving this polymerization rate R vs. time show a maximum $R_{\max}$, which for reasons discussed in another paper (*8*), and after proper correction, is characteristic of the catalytic activity. This activity is expressed for 1 g by the rate $R_{\max}$ = maximum instantaneous monomer conversion x flow rate. The reproducibility of measurements is excellent.

Results and Discussion

There is a strong interaction between the chromium oxide and the carrier during impregnation and the drying process, as shown by the decrease of the surface area from 585 to 520 m^2/g. The fast heating from 300 to 550°C does not change this value very much. But during the first 2 hr of the activation process, there is the essential step of an important decrease of the surface area. On the other hand, the heating treatment induces a reduction of the chromium oxide limited by the activation in air. After 2 hr, the effects level off and an average oxidation degree of 5.4 is reached (Fig. 1).

The results of the chemisorption measurements are illustrated in Fig. 2. The area covered by the trivalent chromium oxide decreases continuously, and the dispersion ratio (ratio of the actual area covered to the calculated one assuming maximum dispersion) comes from 0.38 to 0.28 during the first 6 hr of the activation process. The behavior is not very different for the hexavalent chromium, except that the initial oxidation treatment causes a slight increase of the area covered and that the change of the dispersion ratio is more limited (from 0.53 to 0.48).

Concerning the magnetic susceptibility

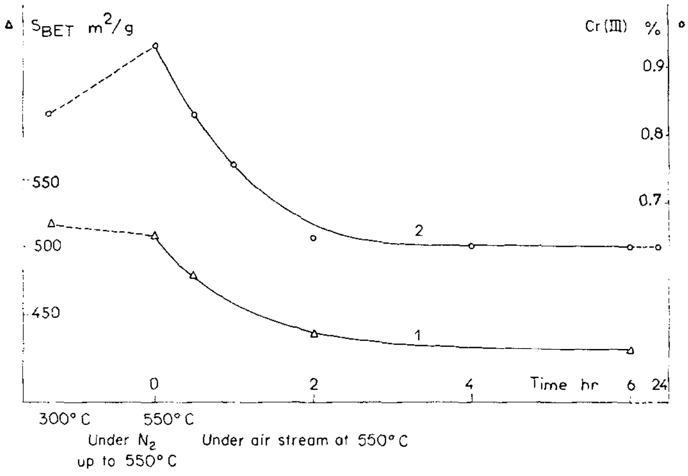

Fig. 1. Specific area (1) and percentage of trivalent chromium content (2) vs the time of activation.

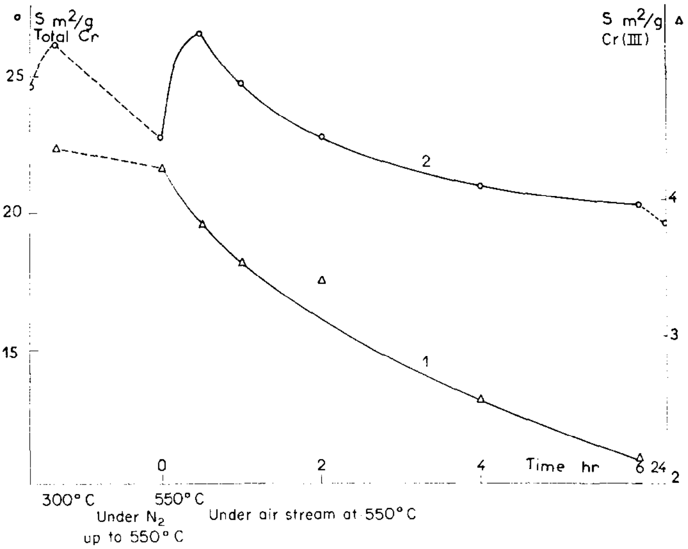

FIG. 2. Oxygen chemisorption results: area covered with trivalent (1) and to Al-chromium (2).

measurements, it has been observed at first that the Curie–Weiss law is obeyed down to 4 and even 2°K; thus there is no thermal blocking of the spins, and it may be concluded that all the chromium is dispersed in very small magnetic domains, and the size is less than 50 Å. Also, chemisorption of oxygen does not noticeably change the magnetic susceptibility: Thus there is no oxidation of the Cr(III) when the catalyst is exposed to air. Another result is that there is practically no difference between the raw catalyst and the solid residue after aqueous extraction. Then, as previously explained and justified (*9*),* the magnetic susceptibility is actually due to the Cr(III), and there is no soluble Cr(III).

Concerning the value of p^2/N where p is the difference in the population of the two sublattices of antiparallel spins, and N is the total number of spins, the results shown in Fig. 3 indicate a different behavior of the Cr(III) domains and total Cr domains. In all the cases, the values are larger than one, and according to Neel's theory (*10*), that means that the domains are anisotropic, with the larger dimension being in the direction of the spins. The data about the structure of α-Cr_2O_3 indicate that the direction of the paired spins are parallel to the "principal face" of the hexagonal structure (*11*). One may suppose that the unpaired spins are located exclusively on the lateral faces of the microcrystals, and that p^2/N is proportional to the area of the lateral faces. Assuming the same parallelepipedic shape for these x microcrystals, for a given number of layers n and a total area S_{Cr}, the area of their lateral faces is $2n(xS_{Cr})^{1/2}(1+\alpha)/\alpha^{1/2}$, i.e., is proportional to $\alpha^{1/2}+\alpha^{-1/2}$, where α is the ratio of the length to the width of the parallelepiped. Assuming further that for $\alpha = 1$, one has $p^2/N = 1$, it is possible to calculate the relationship between the change of p^2/N and the change of the average value of α for the magnetic domains. This relationship indicates a decrease of α by a factor

* With further reference to the possibility of oxidation states other than Cr^{3+} and Cr^{6+}, it may be added that actually no ferromagnetism, which would be induced by the presence of even minor amounts of Cr^{4+}, has been detected. On the other hand, an estimate of the intensity of the ESR signal of the γ phase indicate that Cr^{5+} might contribute to a maximum of 4% of the paramagnetism observed, but the actual existence of Cr^{5+} in these catalysts remains to be proved and has been challenged recently by Ellison *et al.* (*Trans. Faraday Soc.* **66** (4), 1004 (1970) who "interpret the γ phase in terms of a mixed valency of the Zener-double-exchange ferromagnetic type–Cr^{+3}-O^{2}-Cr^{6+}-."

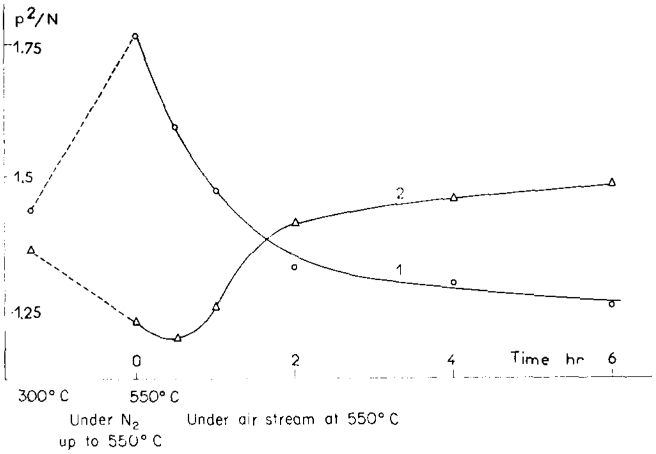

FIG. 3. Magnetic measurements results values of p^2/N for trivalent (1) and total chromium (2) domains.

of 2 for the Cr(III) domains during the activation process. This is in excellent agreement with the decrease of the surface area covered by Cr(III). Thus it may be concluded that the oxidation of the Cr(III) oxide during the activation process shortens its elongated microcrystals which become more isotropic. The interpretation for the total Cr is more difficult. The increase of p^2/N shows that the domains become more anisotropic and the decrease of the area covered tends to indicate that there is a small decrease in the average width of the domains. However, although the values of the dispersion ratio indicate a higher broadening of the chromium oxide, the values of Weiss' constants (which are around —3°K for total Cr and around 0 for Cr(III), show that the total chromium is dispersed in larger domains than the trivalent. We have already suggested that the hexavalent chromium is more mobile, possibly, as shown recently by Holm and Clark (*12*), it tends to come from the alumina part of the carrier to be fixed on the silica part. Then the values of p^2/N and the values of the dispersion ratio reflect only the average situation of the hexavalent chromium.

As shown on Fig. 4, these changes in the dispersion state of the chromium have practically no effect on the activity, as measured by the value of the maximum instantaneous rate R_{max}. It may be seen only

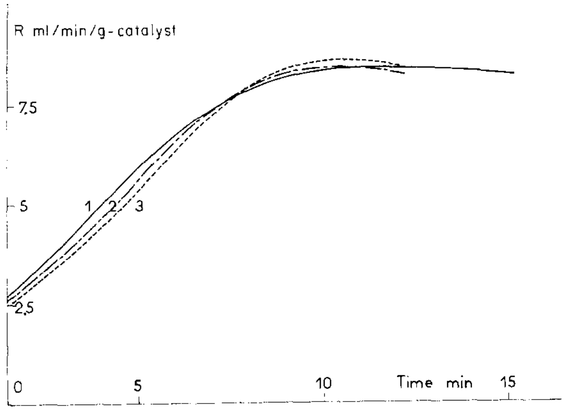

FIG. 4. Instantaneous rate of ethylene polymerization at 145°C/g-catalyst activated (1) 4 hr, (2) 1 hr, and (3) 0.5 hr.

TABLE 1

EVOLUTION OF THE PROPERTIES OF A CATALYST ACTIVATED IMMEDIATELY AFTER ITS IMPREGNATION

Sample N	Temperature	Atmosphere	Time of activation	CrIII	SCr	Maximum rate of ethylene polymerization
	(°C)		hr	(%)	m²/g	(ml/min/g-catalyst)
(1)	300	N_2	—	0.81	20.3	1.5
(2)	500	N_2	—	0.86	13.8	8.0
(3)	550	Air	0.5	0.81	18.8	9.0
(4)	550	Air	1.0	0.83	16.6	8.9
(5)	550	Air	2.0	0.80	18.3	9.0
(6)	550	Air	4.0	0.70	18.7	8.5
(7)	550	Air	6.0	0.725	19.3	8.4

that the rate begins to decrease later for a longer activation process so that the maximum rate is more stabilized.

The results quoted above refer to a catalyst which has been dried and activated a few weeks after impregnation. Another sample has been activated immediately, and in this case, there are some differences in the evolution of the physical and chemical properties as shown in the table. The major differences are observed in the area covered by total Cr, which is lower in any case, probably because the complete diffusion of the chromic acid in the pores of the catalyst has not been allowed, so this area increases during the activation process. However, the limit is practically the same as in the preceding case. Again the catalytic activity remains practically unchanged.

CONCLUSION

The above results show that the duration of the activation process is not an important factor for determining the activity in the polymerization of ethylene, although a slight evolution of the coverage with chromium oxide is observed. It may only be said that a longer time of activation improves the reproducibility of the properties of the catalyst. As shown by Matsuda *et al.* (*13*), the heating rate up to 550°C is more important. This is in agreement with our preceding statement that the base of the active centers is formed by an exothermic reaction around 300°C which fixes the Cr(III) layer by a chromosiloxane bond.*

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