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Supported Chromium Oxide Catalysts for Propene Polymerization

I. Relationship between the Catalytic Activity and the Dispersion State of the Chromium Supported on a Silica Gel with 13.5% Alumina

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The impregnation of a silica-alumina catalyst by chromic acid and the activation of the resulting catalyst causes an important change in the texture which may be explained by a chemical interaction between the carrier and the chromium oxide. The area covered by the chromium oxide, measured by oxygen chemisorption, is always a low fraction of the total available area. It goes through a maximum with chromium content, and decreases with the average of oxidation number. Linear relations between catalytic activity and area are observed to hold only in limited ranges, and the quality of the coverage seems to be as important as the value of the area covered.

INTRODUCTION

One of the industrial processes for olefin polymerization, the Phillips process, uses as catalysts chromium oxide deposited on silica-alumina, this carrier itself being used in the industrial transformation of hydrocarbons. The exact nature of the active centers, and even the respective roles of chromium and carrier are not known satisfactorily. Even in the apparently more simple case of a supported metal, the effect of the carrier, difficult to define, is not merely a physical one (*1*). Here, the carrier is impregnated with chromic acid and the subsequent thermal treatment plays an important part in the creation of active centers; chromium oxide is stabilized by the carrier, and the chromium is thus kept at a high valency. The importance of this property in polymerization activity has been recognized for a long time (*2*) and it is of interest to know how it might be related to the degree of dispersion of the oxide on the carrier surface. Indeed a high coverage might simultaneously favor the formation of a great number of polymerization sites and the inhibition of other sites of the carrier responsible for secondary reactions, particularly in the case of propene.

Among the possible methods, the measurement of the selective oxygen chemisorption on the trivalent oxide was chosen to evaluate the degree of dispersion.

In a first study, silica-alumina with 13.5% alumina, impregnated to give different chromium contents, and activated in various ways, was examined.

EXPERIMENTAL

Materials. Propene (CFR) and propane (Antar) were commercial products, used after purification through molecular sieves (Union Carbide 5 Å). Silica-alumina was a product of the Ketjen firm.

Catalysts. They were obtained by impregnating the carrier, at room temperature, with the amount of an aqueous solution of chromic acid calculated to give total absorption. They were dried 15 hr at 300°C under nitrogen, and then activated 4 hr, generally at 550°C in an air stream. The resulting catalysts were stored under vacuum in sealed glass bulbs. Solids without hexavalent chromium have been prepared by extraction with water of several of the preceding catalysts.

Catalytic activity and chemical analysis. The determination of the chromium contents and of the specific rate of propene polymerization have been described in a previous paper (*3*).

Textural studies. The textures of the solids were obtained from their nitrogen adsorption–desorption isotherms, at —196°C. Measurements were carried out after outgassing 15 hr at 300°C, under a residual pressure of 10^{-5} torr. Results of specific area determinations are expressed in terms of weight of outgassed products. The average pore radius was calculated either by the formula $\bar{r}_p = 2V/S$, where V is the volume adsorbed at saturation, or by Kelvin's formula, which gave about the same result for the carrier and a typical catalyst with 3% Cr.

Oxygen chemisorption. The principle and the volumetric application were described by Bridges, McIver, and Tobin (*4*) for a hydrogenation catalyst chromia-alumina. These authors assumed that the amount of chemisorbed oxygen may be deduced from the difference between the adsorption isotherms of this gas at —196°C, obtained before and after outgassing 1 hr at —78°C. Here, gravimetric measurements were preferred, which are related more directly to the required value. Hydrogen treatment was carried out for 13 hr at 500 torr and at 450°C. It was preceded and followed by an outgassing for 3 hr at 10^{-5} torr. The sample was then cooled to —78°C under an argon pressure of about 10 torr. The argon was then removed and oxygen admitted up to a pressure of 100 torr. A weight equilibrium is reached in less than 30 min. A vacuum is once again obtained, the physically adsorbed oxygen desorbs, and a new equilibrium is reached after 15 min, this corresponding to chemisorbed oxygen. The resulting value does not depend on the oxygen pressure if it is kept between 50 and 150 torr. Theoretically the maximum coverage would mean that a two-dimensional film of chromium oxide was deposited on the carrier. Making this assumption and using the crystalline structure of α-chromia, calculations show that a 1% chromium content gives an area of 12 m^2 (*4, 5*). The actual coverage S_{Cr} is obtained assuming that for the same area, the same quantity of oxygen is chemisorbed by chromia either pure or deposited on a carrier. A sample of chromia prepared via the thermal decomposition of ammonium bichromate followed by a treatment at 700°C under air was therefore used for the described measurements. For 1 g, the area was 23 m^2 and the chemisorbed oxygen was 3.293 mg. Thus 1 mg of chemisorbed oxygen corresponds to an area of 6.98 m^2 of chromia. This value is in excellent agreement with the value obtained by volumetric measurements.

The ratio of the experimental area S_{Cr} to the theoretical area so defined is the dispersion ratio of the chromium oxide on its support.

The determination of the active surface of a supported catalyst by the measurement of selectively chemisorbed gas on the deposited element has often been applied to metals, chiefly platinium and nickel, but seldom to oxides. In all cases, it is supposed that the carrier does not chemisorb the gas and that the coverage ratio is the same for the active species whether it is pure or supported. The first assumption is fully verified and the second appears to be also. Indeed, if the amounts of oxygen chemisorbed were different on the supported oxide and on the pure oxide of the same area, a value of 1 should never be obtained for the dispersion ratio. In fact, this value has been obtained several times in the whole study.

The reduction by hydrogen before the chemisorption does not seem to modify the dispersion. Indeed, different results have been obtained on catalysts of various average oxidation numbers (Table 2). Furthermore, a reduced catalyst has the same texture ($S = 398$ m^2/g, $\bar{r}_p = 20.5$ Å) as the activated solid ($S = 400$ m^2/g, $\bar{r}_p = 21.3$ Å). Finally, the monomer itself reduces the catalyst at the early stages of the reaction. Consequently the measured dispersion is doubtless that of the chromium oxide for the polymerization.

The use of a very precise balance, a Sartorius balance, has enabled us to establish a measurement technique which is very direct. Since it is possible to detect a weight change of one 1 μg for a maximum load of 1 g, it has been possible to obtain sufficient accuracy (about 2%) even in the case of the lowest coverages (1.3 m²/g).

RESULTS

Catalysts with different chromium contents. The results obtained with these catalysts are presented in Table 1. For low chromium concentrations, the catalytic activity shown in the last column was corrected for reaction to form oligomers on the support. The correction may be made at the end of the reaction by weighing the high polymer formed, but it seemed better to use the complete chromatogram to determine the velocity of propene consumption and of oligomer formation. More details will be soon published (*6*).

TABLE 1
CATALYSTS WITH DIFFERENT CHROMIUM CONTENTS

% Cr[a]	d[a]	S[b] (m²/g)	$\bar{r}_p$[b]	S_{Cr}[c] (m²/g)	t[c]	$k \times 10^5$[d] (sec^{-1} g^{-1})
0	—	622	22.1	0	—	0
0.14	3.3	590	22.0	1.3	0.77	0
0.51	4	545	21.5	4.1	0.67	0.5
1.06	5.35	514	23.4	8.3	0.65	2.5
1.77	5.2	465	22.0	12	0.57	4
2.9	5.2	415	19.4	14	0.40	6.0
5.01	5.41	422	19.9	24.3	0.40	12.0
6.84	5.39	384	18.5	27.2	0.33	16.0
8.97	5.39	313	17.2	21.8	0.2	5.2
12.65	4.98	256	16.8	20.4	0.13	0.1

[a] Chromium contents and average oxidation number d.

[b] Specific area S and average pore radius $\bar{r}_p$ of the catalyst.

[c] Area S_{Cr} covered by chromium oxide, and dispersion ratio t (ratio of S_{Cr} to the theoretical area of a bidimensional film).

[d] Catalytic activity for high polymerization.

Catalysts with 3% Cr at various average oxidation numbers. The activation was done in nitrogen for the first catalyst (average oxidation degree $d = 3.2$), in oxygen for the last ($d = 5.88$), and in air at various HSV. The results are reported in Table 2 and results for solids without hexavalent chromium are shown in Table 3.

TABLE 2
CATALYSTS WITH 3% CR AND DIFFERENT AVERAGE OXIDATION NUMBER

d[a]	S (m²/g)	$\bar{r}_p$ (Å)	S_{Cr} (m²/g)	t	$k \times 10^5$ (sec^{-1}g^{-1})
3.2	381	20.6	5.9	0.16	0
4.4	395	20.5	11.5	0.32	3.5
4.6	414	20.5	12.5	0.35	4.2
5.15	400	21.3	14	0.39	6
5.4	425	21.5	18.1	0.50	10
5.6	444	22.0	22.7	0.63	14
5.88	465	22.3	22	0.61	13

[a] The signification of symbols is the same as in Table 1.

Different activation temperatures for catalysts with 3% Cr. Table 4 gives the results obtained in this series. The preceding Tables show that the area of the catalyst and the pore radius are modified by the presence of chromium. They decrease when chromium content increases, or at constant chromium content, they decrease with average oxidation number.

The chromium oxide surface is generally low, less than 27 m²/g, and the dispersion t is less than 1. The surface reaches a maximum with about 7% chromium and then

TABLE 3
Catalysts after Water Removal of Hexavalent Chromium

d_i[a]	t_i[a]	% Cr	d	S (m²/g)	$\bar{r}_p$ (Å)	S_{Cr} (m²/g)	t	$k \times 10^5$ (sec⁻¹ g⁻¹)
4.7	0.35	1.3	3.0	—	—	2.06	0.13	0
5.15	0.39	0.85	3.0	395	23.3	1.87	0.18	0
5.6	0.63	0.4	3.0	—	—	3	0.63	0

[a] Average oxidation number and dispersion ratio of the catalyst before extraction.

TABLE 4
Catalysts with 3% Cr Activated at Different Temperatures

T (°C)[a]	d	$S_{support}$[b] (m²/g)	S (m²/g)	$\bar{r}_p$ (Å)	S_{Cr} (m²/g)	t	$k \times 10^5$ (sec⁻¹ g⁻¹)
550°	5.15	622	400	21.3	14	0.39	6
620°	4.8	610	404	21	11.7	0.33	5
700°	4.5	560	342	20.5	24.2	0.67	4.5

[a] Temperature of activation.
[b] Specific area of the carrier after a thermal treatment similar to that of the catalyst.

decreases, indicating agglomeration of the chromium oxide. The agglomeration is more important when the average oxidation number is lower, all the other conditions being the same. After extracting the hexavalent chromium, the remaining trivalent chromium oxide is not as accessible as the initial deposit. Finally, the catalytic activity increases with the average oxidation number. It goes through a maximum with the chromium content but here the maximum is observed for a higher value (7%) than that (3%) which is generally indicated (*2*).

Discussion

Texture

As a consequence of its chemical composition, the BET area of the catalyst is necessarily different from that of the carrier even if impregnation and activation are without effect on the texture. The theoretical area of the carrier per gram of activated catalyst is calculated. This value is always higher than the measured area, as shown in Fig. 1, where the difference is plotted versus the chromium content (curve I) and versus the average oxidation number for 3% Cr (curve II).

The cause of this difference might be the corking of the smallest pores by the chromium oxide, which closes their entrances. In this case, the average pore radius would increase more and more with the chromium content; in fact this does not occur.

A similar study was made by Deren (*7*) for chromia-alumina catalysts. The total area decreased only for chromium content greater than 2% and the decrease in area for chromium content more than 4% was less rapid. He postulated a purely physical obstruction, perhaps reversible, the agglomeration of chromium oxide under the effect of temperature progressively freeing the blocked pores.

Our observations are quite different since an important diminution of area appears at low chromium content. Besides, the extraction of water-soluble chromium would open any pores filled with chromium; in fact the area is unaffected. These results indicate that the decrease of area is caused chiefly by chemical interaction between chromium oxide or chromic acid and the silica-alumina carrier. In another study, more proof will be given (*8*), but it is known that the chemical reactivity of silica-alumina towards hydrochloric acid, for instance, is far greater than that of pure alumina. For a given chromium content and various activation treatments, the parallel decrease of area and hexavalent chromium content shows that the reduction of the

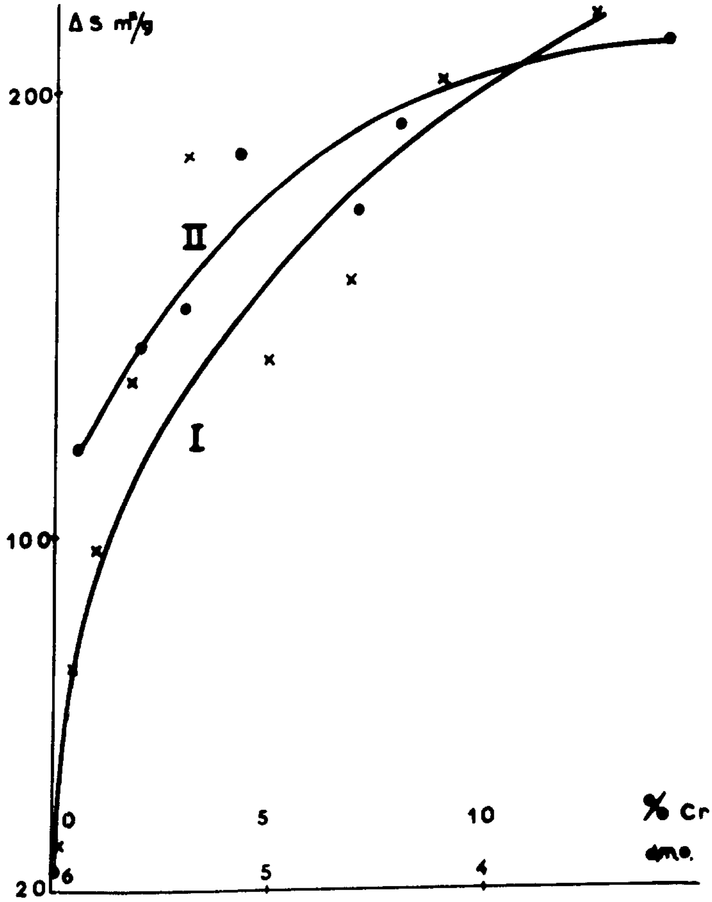

FIG. 1. Difference between areas of carrier and of catalyst, versus chromium content (×, curve I) or average oxidation number, with 3% Cr (●, curve II).

chromium oxide is closely linked to its reaction with the carrier surface. As for the modification of texture brought on by an activation at 700°C, the explanation is that, under the same conditions, the texture of the carrier is also changed.

Dispersion of Chromium on the Carrier

It is to be noted that the dispersion ratio (ratio of covered area to area of an equal amount of chromium oxide in a two-dimensional film) is never 1, even when the average oxidation number is near to its highest value 6. There is always a certain agglomeration of the oxide. Perhaps there are only a limited number of active sites on the carrier which can fix the chromium oxide. The activity of these sites towards fixation might be variable so that the agglomeration of chromium on the more active centers would precede its fixation on the others. The existence of chemical interactions during the impregnation tends to limit the coverage. This conclusion is supported by consideration of the coverage ratio, defined in its classical meaning for impregnated silica-alumina catalysts, which is inferior to that of impregnated alumina (*4*) or coprecipitated alumina (*9*), as shown in Fig. 2.

When the conditions of activation involve a decrease of the average oxidation number, the important chemical interaction is accompanied by an agglomeration of the reduced chromium oxide since in the same time the dispersion ratio, the coverage ratio, and the total area decrease. It is possible also that the shrinking of the carrier en-

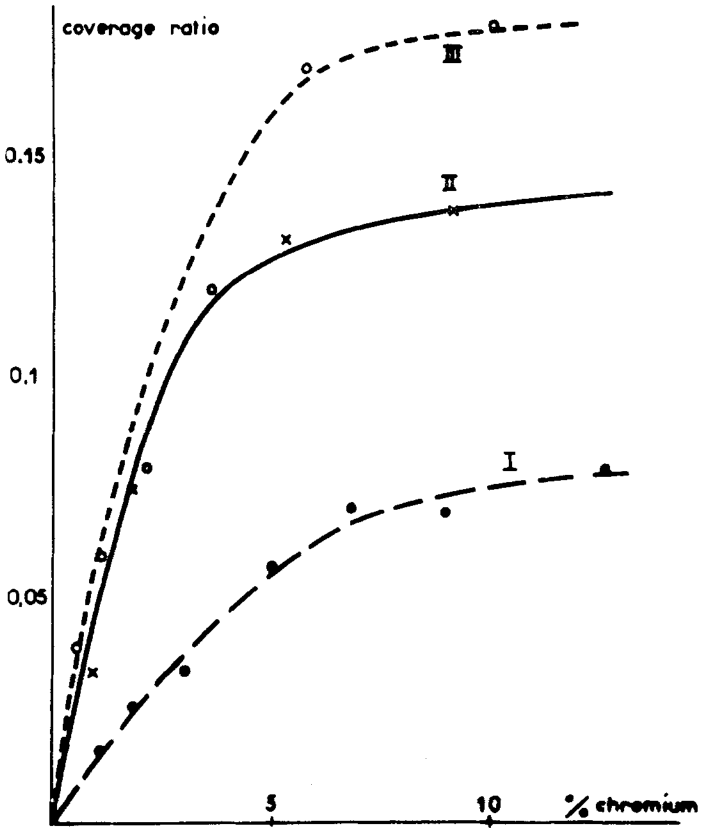

FIG. 2. Variation of the coverage ratio versus chromium content on silica-alumina (●, curve I), for coprecipitated chromia-alumina (×, curve II), and on alumina (○, curve III).

closes a fraction of the oxide in its pores. However, this is not a large fraction since after removal of water-soluble chromium, the measured area covered by the remaining oxide is significant. Furthermore, the activation at 700°C involving an important decrease of the area and average oxidation number gives a high value for the coverage and dispersion ratios.

The comparison of initial and extracted catalysts gives an indication about the relative dispersions of trivalent and hexavalent oxides, except for the catalyst activated in nitrogen, which contains superficial trivalent oxide. Assuming that hexavalent chromium oxide is superficial, its coverage ratio may be calculated. It is surprising that this value may be as low as 0.2 for high chromium content. Therefore, the effect of dispersion is not the major cause of certain high values of the average oxidation number of the deposited chromium oxide. Perhaps the vigorous agitation of the particles by the air favors the dispersion of chromic anhydride by movement in the adsorbed phase or even via gaseous phase. The melting point of chromic anhydride is 190°C and its vapor pressure could be important at 550°C, but its high density stabilizes it around the fluidized powder.

Coverage and Activity

A linear relation is found when the average oxidation number varies, for catalysts with 3% Cr (Fig. 3, curve I). A minimal area of 7 m^2/g, according to $d = 3.5$, is critical for activity. An activation leading to a lower value of d agglomerates the chromium oxide in clusters, the structure of which is like that of massive oxide, completely inactive. The activity of the catalyst activated under oxygen ($d = 5.88$) is

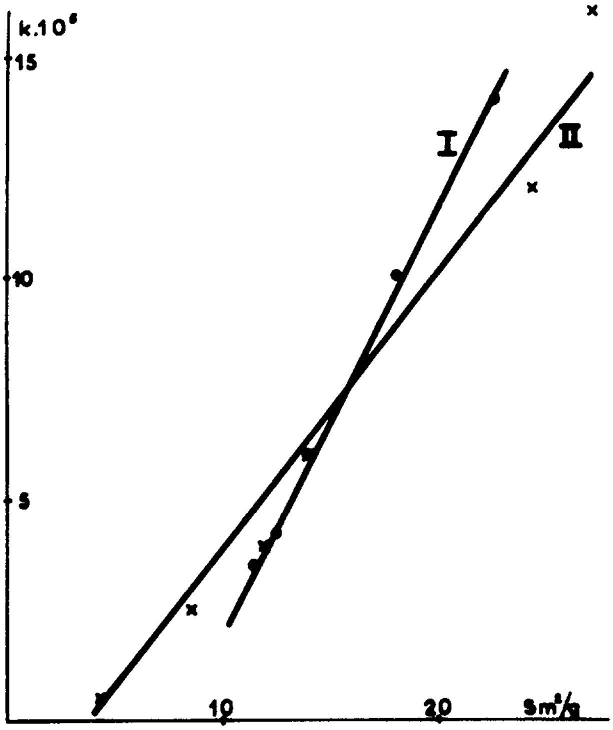

FIG. 3. Catalytic activity versus covered area with 3% Cr and different average oxidation number (●, curve I), at different chromium contents (×, curve II).

slightly lower than that of the catalyst with $d = 5.6$ which contains three times more trivalent chromium; the relationship between activity and hexavalent chromium content is then accidental.

The inactivity of catalysts with high chromium content may also be explained by the agglomeration of oxide to form massive oxide. Consequently, the validity of the linear law between k and S_{Cr} with different chromium contents (Fig. 3, curve II) is limited to 7% Cr. Besides, a critical value of the coverage is found again, but explained differently. Here, the coverage is low, since the chromium content is low; then, the propene is preferentially transformed to oligomers by the acid sites of the carrier, still in great number, rather than to polymer by the few chromium sites.

The variation of two parameters involving these linear relations suggests a general relation between activity and coverage. Since the two curves are not identical and apply to a limited field of chromium contents, the unique measure of S_{Cr} is not sufficient to predict the activity of the catalyst. Catalysts with high chromium content have a high coverage but no activity, so the quality of the surface must also be considered. In this connection, two factors might influence the activity of the polymerization sites: chemical linkings between chromium oxide and carrier (in relation with the large change of texture resulting from the impregnation) and the state of agglomeration of deposited chromium oxide. The next articles of this series (following paper) will be able to strengthen these conclusions.

REFERENCES

1. CARTER, J. L., AND SINFELT, J. H., *J. Phys. Chem.* **70**, 3003 (1966).
2. HOGAN, J. L., AND BANKS, R. L., U. S. Patent 2,825,721, March 4, 1958.
3. GUYOT, A., AND DANIEL, J. C., *J. Polymer Sci.* **A1**, 2989 (1963).
4. BRIDGES, J. M., MCIVER, D. S., AND TOBIN, H. H., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **2**, 2161 (1961).

5. SELWOOD, P. W., *Bull. Soc. Chim.*, D489 (1949).
6. REVILLON, A., Thesis, Lyon, France, 1967.
7. DEREN, J., HABER, J. H., AND SIECHOWSKI, J., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 993 (1965).
8. CHARCOSSET, H., REVILLON, A., AND GUYOT, A., *J. Catalysis* **8**, 334 (1967) (Part II of this series; following paper).
9. POOLE, JR., C. P., KEHL, W. L., AND MCIVER, D. S., *J. Catalysis* **1**, 407 (1962).