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Supported Chromium Oxide Catalysts for Propene Polymerization

II. Catalytic Activity and Dispersion State of the Chromium on Various Carriers—General Relationship

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Measurements of the activity in the propene polymerization of the area covered by chromium oxide, and of the specific area of several activated catalysts prepared by impregnation of various materials such as silica, alumina, or aluminum silicate with chromic acid were carried out. They confirm the existence of chemical interactions between the supporting material and the deposited oxide, which govern the dispersion of the chromium and the activity of the catalysts. The results suggest a distribution of sites which have different activities and are characterized by the number of hexavalent chromium oxide layers.

INTRODUCTION

The purpose of the present work was to test the validity and the general character of the results obtained in the preceding paper (*1*) about the occurrence of chemical interactions between chromium oxide and silica-alumina (13.5% Al_2O_3) used as a supporting material, and also about the correlations between the catalytic activity in propene polymerization and the coverage of the area with the chromium oxide.

Several carriers were used, silica, alumina, silica-alumina of various compositions, and also silica-alumina treated with sodium compounds. The data confirm the importance of the chemical interaction in the enhancement of the activity and indicate that the activity of a particular site may be governed by the number of layers of chromium oxide deposited.

MATERIALS AND METHODS

We describe here only the catalysts prepared specially for this work and also a few changes in the experimental methods described in the preceding paper.

Supporting materials. Using the same Ketjen silica-alumina (13.5% Al_2O_3) as previously, different carriers were prepared; alumina was removed by attack with hydrochloric acid at different acid concentration (*2*). Sodium was added by means of either carbonate or acetate solutions. Chromium and sodium were also deposited simultaneously using sodium bichromate. In addition, the following carriers were used: another Ketjen silica-alumina (24.8% Al_2O_3), a commercial alumina (DeGussa), a commercial silica (BDH), and a silica prepared by ionic exchange from sodium silicate on a resin. Finally a chromed catalyst (2.9% Cr) normally activated (average oxidation number: $d = 5.15$) was extracted with water and the material obtained was used as a new carrier.

Chemical analysis. Aluminum after dissolution by acid extraction was titrated either by complexing with EDTA or by colorimetry with Aluminon. Sodium was estimated by flame spectroscopy.

Oxygen chemisorption. In some cases, the catalysts were treated with hydrogen at 550°C instead of 450°C to assure complete reduction to trivalent chromium.

RESULTS

1. *Pure Carriers and Chromia*

a. Texture. For the materials derived from the Ketjen silica-alumina, the nitrogen adsorption–desorption isotherms are of type IV. Pore-size distribution was calculated following the method given by Pierce (*3*). The total area of the materials, the mean cylindrical pore radius, and the areas contributed by pores of different sizes are given in Table 1. All these data correspond to 1 g of solid desorbed at 300°C.

The alumina is composed of small nonporous spherical particles. For the BDH silica and that obtained by exchange, most of the value of the area corresponds to micropores of less than 15 Å.

TABLE 1
TEXTURE OF THE CARRIERS

	Contribution of pores to the area						
Carrier $\bar{r}_p$(Å):	>55	55–36	36–28.6	28.6–20.7	<20.7	$\bar{r}_p{}^a$	S^b (m²/g)
Al_2O_3	90	—	—	—	—	—	90
Gel at 24.8% Al_2O_3	10	130	230	135	0	32.6	505
Gel at 13.5% Al_2O_3	6	40	109	282	185	22.1	622
Gel at 11% Al_2O_3	6	26	89	321	208	21.3	650
Gel at 7.4% Al_2O_3	—	—	—	—	—	22	665
Gel at 1.9% Al_2O_3	—	—	—	—	—	15.1	669
Gel at 0.6% Al_2O_3	13	99	156	268	109	25.6	645
Gel at 0.015% Al_2O_3	190	145	43	32	49	46.3	459
Gel at 0.015% $Al_2O_3{}^c$	—	—	—	—	—	—	416
Gel at 0.25% Na	6	17.5	75.5	308	194	21.4	601
Gel at 0.46% Na	—	—	—	—	—	22.5	590
Gel at 4% Na	7	32	104	247	75	24.2	465
SiO_2 by exchange	—	—	—	—	—	—	596
SiO_2 BDH	—	—	—	—	—	—	120

[a] Average pore radius calculated with the formula $r_p = 2V/S$.
[b] Total area.
[c] Activated at 700°C.

For silica-alumina carriers, removal of alumina down to 2% does not greatly change the area or the average pore radius. Stronger treatment increases the pore radius and greatly decreases the area, indicating a collapse of the solid structure. When sodium is added, the area slightly decreases at first and then markedly.

b. Chemisorption and activity. For all the carriers used which do not contain chromium, the amounts of oxygen chemisorbed are less than a few micrograms per gram. Their role in the chemisorption process is thus negligible.

The pure chromia, the solid containing sodium, the silica, and the alumina do not transform the propene. The Ketjen silica-alumina, however, has a high activity for oligomerization, which decreases slightly with partial removal of the alumina, and becomes nil if all the alumina is removed.

2. *Catalysts*

The results for the catalysts with different aluminum contents and 3% chromium are given in Table 2.

For catalysts containing sodium (Table 3) the carrier (13.5% Al_2O_3) was impregnated with chromic acid after sodation, except for the catalyst with 1.55% of sodium (bichromate). Finally, some data concerning the catalysts prepared from pure alumina, pure silica, or by total removal of Al_2O_3 from the Ketjen gel, are gathered in Table 4.

When the alumina content of the carrier decreases, the specific area of the catalyst goes through a maximum. The proportion of hexavalent chromium increases together with the dispersion ratio of the chromium oxide which reaches unity, but the catalytic activity decreases. However, for catalysts

TABLE 2
GELS WITH ABOUT 3% Cr AND VARIOUS ALUMINA CONTENTS

% Al_2O_3[a]	% Cr[a]	d[a]	S[b] (m^2/g)	$\bar{r}_p$[b] (Å)	S_{Cr}[c] (m^2/g)	t[c]	$k \times 10^6$[d] ($sec^{-1}\ g^{-1}$)
24.8	3.17	4.31	374	21.3	14.9	0.39	4
13.5	3	5.4	425	21.5	18.1	0.50	10
11	2.97	5.42	465	20.6	22.5	0.63	3.1
7.4	2.85	5.8	490	18.5	26.7	0.70	9
1.9[e]	3	5.8	535	14.6	32.8	0.91	3.5
0.6[e]	3	6	550	27	27.8	0.77	3
0.3[e]	2.26	5.92	535	18.6	27.1	1	2.8
0.015[e]	2.35	5.85	438	46	28.2	1	1
13.5[f]	2.9	5.15	410	21	13.8	0.4	5.5

[a] Alumina content of the carrier. Total chromium content in the catalyst 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 theoretical area of a bidimensional film).

[d] Catalytic activity for high polymerization.

[e] Hydrogen treatments at 550°C, before determination of S_{Cr}.

[f] Catalyst resulting of the impregnation of an extracted catalyst.

TABLE 3
CHROMED GELS WITH VARIOUS Na CONTENT

% Na[a]	% Cr	d	S (m^2/g)	$\bar{r}_p$ (Å)	S_{Cr} (m^2/g)	t	$k \times 10^6$ ($sec^{-1}\ g^{-1}$)
0.008	2.9	5.2	4.5	19.4	14	0.40	6
0.25	2.4	5.63	420	21	19	0.66	7
0.46	2.14	5.25	400	22	13.5	0.52	2.5
1.55[b]	3.26	5.52	430	23.5	20	0.51	7.5
4	1.47	4.8	344	31.3	5.1	0.29	1.2

[a] Sodium content of the carrier.

[b] Carrier impregnated with sodium bichromate.

TABLE 4
PURE CHROMED SILICA AND ALUMINA

Carrier	% Cr	d	S (m^2/g)	S_{Cr} (m^2/g)	t	$k \times 10^6$ ($sec^{-1}\ g^{-1}$)
Al_2O_3 Degussa	2.87	3.95	—	20.3	0.59	0
SiO_2 BDH	2.46	4.21	—	13.9	0.47	0
SiO_2 by exchange	2.7	5.64	350	23.1	0.71	0
SiO_2 (0.015% Al_2O_3)	2.35	5.85	435	28.2	1	1
SiO_2 (0.015% Al_2O_3)	6.04	5.59	392	27.2	0.37	1.5
SiO_2 (0.015% Al_2O_3)[a]	2.35	4.8	366	—	—	6

[a] Catalyst activated at 700°C.

containing different amounts of sodium, the activity and the covered area do vary in the same way. The case of the catalyst prepared using sodium bichromate is special: The sodium has no effect and the behavior of the bichromate ion is similar to that of the chromic anhydride.

The catalyst prepared with alumina as

carrier is totally inactive; if silica is used, the activity is noticeable only if the activation treatment is carried out at 700°C.

DISCUSSION

1. Texture and Dispersion

The difference ΔS between the calculated area of the carrier and the specific area of the catalyst is shown in Fig. 1 versus the alumina content ($\leqslant 13.5\%$). With the gel at 25% Al_2O_3, a large value of ΔS was also observed. These results confirm the occurrence of a chemical interaction between the chromium oxide and the carrier, in particular the aluminated part of this, since the decrease in area becomes nil when most of the alumina has been extracted. A significant decrease in S is observed also with the silica "by exchange"; but in this case, there are only small pores ($\bar{r}_p < 15$ Å) in the carrier, and the extraction of soluble chromium oxide causes an increase in area up to 520 m^2/g. Here a process of colmatation (closing of pores by deposition of material) occurs which is partly reversible. Such a process might account, at least partly, for the observed difference with the dealuminated gels; indeed, a part of their area, generally greater than the observed decrease of area, is contributed by small pores, the radius of which is less than 20 Å. Also, in the case of gel with 25% alumina, which does not contain such small pores, the difference is only 108 m^2/g. However, after a total dealumination of the gel with 13.5% Al_2O_3, the area of these small pores (<20 Å) represents yet 10% of the total area and the value of ΔS in nil. Perhaps, deposition of the chromium oxide occurs preferentially on the larger pores in all cases where the carriers are issued from a Ketjen gel. The area covered is less than the area contributed by pores with a radius greater than 36 Å. Then the difference would be a consequence of chemical interactions.

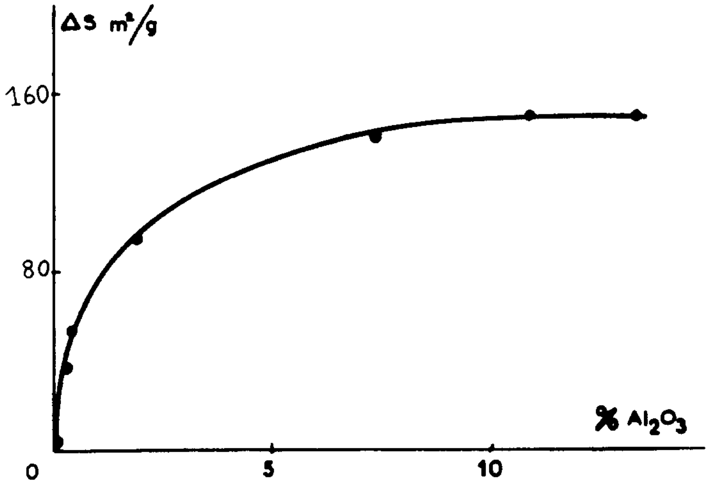

FIG. 1. Difference between the area of carrier contained in 1 g of catalyst and specific area of this catalyst, versus the alumina content of the carrier.

Obviously these interactions involve primarily the Si–O–Al bonds, but they seem to be possible also with pure silica. For instance, the difference observed with the silica "by exchange" after removal of hexavalent chromium seems too important to be accounted for by the low residual chromium content (0.16%) which might correspond with a covered area of only 2 m^2/g. Also for the catalyst using the totally dealuminated solid and activated at 700°C, the decrease of area, from 550° to 700°C (72 m^2) is clearly greater than that which is caused by the corresponding thermal treatment of the carrier (43 m^2).

A treatment of the Ketjen gel with a sodium compound also causes a strong decrease of the area; this fact is easily explained by the action of the sodium ions, which leads to the opening and the redistribution of siloxane bonds and, *a fortiori*, of the aluminosiloxane bonds; such an action suppresses the smaller pores. Nevertheless, after impregnation and activation a new and large decrease of the area is observed, but it is difficult to distinguish the action of chromium oxide and that of the sodium ions.

Finally, a catalyst obtained after extraction, reimpregnation, and reactivation of a typical catalyst possesses exactly the same texture and the same coverage of chromium oxide as the initial catalyst; clearly, the chemical interaction is limited to the first treatment and also, the chromium oxide tends to be deposited, fixed, and agglomerated onto a limited number of special sites of the supporting material.

In similar conditions of activation and with equal chromium contents, the dispersion of the chromium will be higher when the number of these sites is low, because their role is to reduce the mobility of the chromium oxide. Thus the coverage and dispersion ratios are maxima on a carrier totally dealuminated, and as a general rule they decrease when the aluminum content increases. The same conclusion holds also for the average degree of oxidation.

It seems therefore confirmed that the reduction of the chromium oxide is accompanied by its reaction with the supporting material. This finding may be explained easily by considering the relative volatility of chromic anhydride and the relationship found between hexavalent chromium content and the degree of dispersion. CrO_3 will be reduced more easily if it is deposited on a site already chromed, because at the working temperature, the reduction of bulk chromic oxide is spontaneous. The superficial layer of the oxide clusters so formed may be reoxidized by the air into volatile chromic anhydride, stable in its hexavalent state in the presence of oxygen and in the vapor phase; the high density of the anhydride causes its deposition again so that an equilibrium is reached which depends upon a number of factors. High values of the working temperature, of the number of interaction sites, and of the chromium content favor the reduction on the one hand, and on the other hand a good stirring by the gas stream and a high oxygen content favor the maintenance of a high oxidation degree of the chromium.

2. Dispersion and Activity

Catalysts prepared with silica do not possess high activity for propene polymerization although they are known to be active for ethylene polymerization (*4*). In our case the activity becomes high enough only if the activation treatment is carried out at a very high temperature, in order to allow any chemical interaction between the deposited oxide and the carrier to occur.

The linear relationships previously found (*1*) between the catalytic activity k and the area S_{Cr} covered with chromium oxide are not satisfied here. The specific activity—which is the ratio of k to S_{Cr}, i.e., the activity for the unit area covered with chromium oxide—and the average number n of layers of chromium oxide, defined as the reciprocal of the dispersion ratio t, are considered in order to find a general relationship. The values so obtained in our two studies are reported in Fig. 2.

Even though the catalysts possess different origins or have undergone various treatments, an average curve accounts quite satisfactorily for the results. Figure 2 shows that the activity is low and tends to be nil when n becomes great as well as when it approaches unity; also, the activity is maximum when the value of n is about 2 or 3. When the number of layers increases, the chromium oxide is deposited as clusters more and more like bulk chromium oxide which is totally inactive. When the dispersion is maximum ($n = 1$), the chemical interactions do not occur, which might be the reason for the very low activity of the corresponding solids. In the intermediate range where the activity goes through its maximum values the experimental points are somewhat dispersed, but this is easy to understand: The average number of layers does not define completely the dispersion state of the chromium oxide; in order to fit more closely the actual situa-

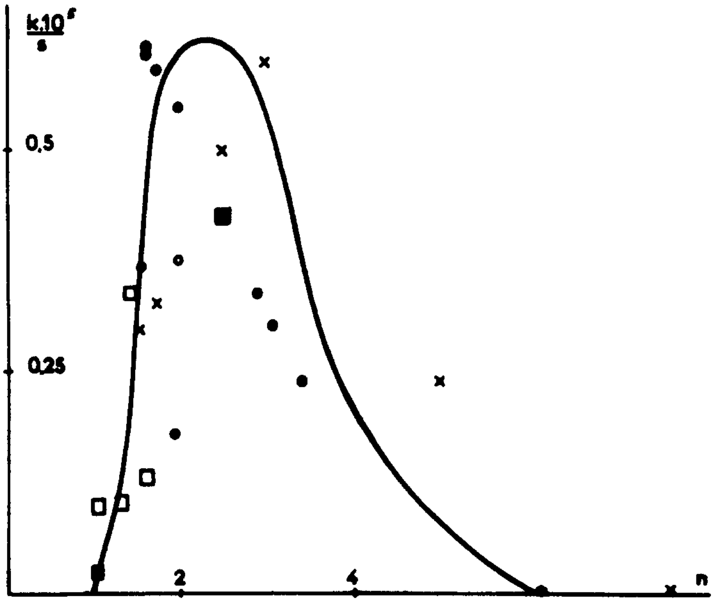

FIG. 2. Specific activity versus number of layers of chromium oxide for all the catalysts of the two studies.

tion it is necessary to know the distribution of the number of layers. In this connection, our measurements show only that the trivalent oxide is generally more closely packed than the hexavalent oxide.

In all likelihood, the catalysts contain several kinds of sites with different activities. Such a situation has already been postulated by Clark and Bailey (*5*) in order to explain the very broad molecular weight distribution observed for typical polyethylenes; for polypropylene some measurements obtained in our laboratory (*6*) also indicate a broad distribution. An active site might involve a layer of trivalent oxide chemically bonded with the carrier and covered with one, two, or more layers of hexavalent oxide. Depending on the number of these layers the activity of a particular site does vary and probably decreases when the number of layers increases. When the activation conditions have allowed the reduction of a greater amount of oxide, the trivalent oxide is agglomerated, covering the bonded layer and thus destroying the active site.

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