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Interaction between Chromium Oxide and Its Silica – Alumina Support and Activity of the Resulting Polymerization Catalyst

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Summary

Differential thermal analysis and composition, texture, and coverage measurements were carried out and gave evidences for chemical interaction between chromium oxide and the silica–alumina support of an olefin polymerization catalyst. Such interactions are related to the activity vs. propene polymerization and these relations allow to suggest that the active centers involve a layer of trivalent chromium oxide linked to the support by chromosiloxan bonds and covered with one or more layers of hexavalent chromium oxide.

Inasmuch as a great number of studies are now published about the chromium oxide–silica–alumina catalysts discovered by the Phillips Company [1] and their activity in the olefin polymerization, little is known about the exact influence of one of the two major components of the catalytic system: the support. Attention has been paid chiefly to the chromium oxide. It has been very well established that a high average oxidation degree of the supported chromium oxide of a fresh activated catalyst is related to a high activity, and it is well known, but not clearly explained that during the activation treatment the support allows the chromium oxide to be reduced only to a limited extent. Also it is known, but not explained, that the best catalysts are supported on silica–alumina or even silica but not on pure alumina. In recent papers [2] we have studied the dispersion state of the chromium oxide and its relationship with the activity of various catalysts and we have shown that important and irreversible modifications of the texture of the solid occurred during the catalyst preparation. These modifications are more important with silica–alumina than with pure silica and their magnitude is related to the alumina content of the silica-alumina. Such facts indicate that chemical interactions occurred between the chromium oxide and the support.

The purpose of the present study is to make precise the mechanism of these interactions and to give a better knowledge of the possible structure of the active sites involved in the polymerization.

The study was focused chiefly on the first steps of the catalyst preparation—impregnation and activation—and also on the part played in the activity of the catalyst vs. propene polymerization by the various products of these interactions.

EXPERIMENTAL

Catalysts

The supports used are two Ketjen silica-aluminas, containing, respectively, 13.5 and 24.8% Al_2O_3, and their derivatives resulting from partial dealumination with hydrochloric acid. They have been impregnated, at room temperature, with the amount of an aqueous solution of chromic acid calculated to give total absorption; the concentration of the solution is adjusted so that to obtain the desired chromium content.

The impregnated support is dried 15 hr at 300°C under nitrogen, and then activated 4 hr generally at 500°C, in an air stream. The activated catalyst is then stored under vacuum in sealed glass bulbs. The surface area of the solids were obtained using the BET method and the area covered with chromium from oxygen chemisorption measurements [2].

The determination of the catalyst's activity vs. propene polymerization, using chromatographic methods, has been published [3].

DTA Measurements

The apparatus has been described elsewhere [4]. It uses a differential thermocouple platinum, rhodium-platinum (10% Rh). The apparatus is swept by a stream of gas (generally dry air with a flow of 3 liter/hr). About 150 mg of sample is placed in a cell 4 mm deep, 4 mm large, and 17 mm long. Such a disposal allows a good contact between the sample and the flowing gas. Kieselguhr calcined at 1000°C is used as reference. The heating rate is 10°C/min.

ESR Measurements

They were carried out in quartz ampoules, at room temperature, in a Varian Model 4502-02 spectrometer (X-band).

RESULTS AND DISCUSSION

Interactions during the Impregnation

It was observed that the extraction of the water-soluble part of the chromium oxide–activated catalyst also causes extraction of a part of the alumina, and then a more systematic study of the solubilization of this compound by chromic compounds was undertaken. The results are presented in the Table 1. It appears that the washing of the support does not dissolve any alumina, even if it has been partially dealuminated by means of an hydrochloric acid treatment; moreover a noticeable quantity of silica is extracted.

TABLE 1. Solubility of Alumina and Silica by Water Extraction of the Catalysts

Al_2O_3 %	Chromic compound	Cr, %	Activation temp., °C	Cr (VI), %	Al_2O_3 dissolved[a]	SiO_2 dissolved[a]
13.5	None	0	550	—	0.03	120
11.0[b]	None	0	550	—	0.03	n.d.[c]
0.6[b]	None	0	550	—	0.10	n.d.
13.5	$Cr_2O_7K_2$	3.26	550	2.74	0	n.d.
13.5	$Cr(NO_3)_3$	1.77	550	1.31	2.2	140
13.5	CrO_3	3	550	1.4	5.7	n.d.
—	—	3	550	2.15	10	90
—	—	3	550	2.6	13	170
—	—	3	700	1.5	7	n.d.
1.9[b]	—	3	No	3	7	85
0.6[b]	—	3	No	3	2	n.d.
13.5	—	5	550	4.0	14	90
13.5	—	6.85	No	6.85	20	n.d.
13.5	—	6.85	130	6.85	21	n.d.
13.5	—	6.85	550	5.5	22	n.d.
		9.0	550	7.2	31	210

[a] Expressed in milligrams of oxide dissolved per gram of catalyst.
[b] Support partially dealuminated using hydrochloric acid.
[c] n.d., not determined.

When the support is impregnated and activated, the amount of Al_2O_3 which may be dissolved depends (a) on the acidity of the chromic compounds, (b) on the amount of chromium and more precisely of hexavalent chromium, and (c) on the amount of residual Al_2O_3.

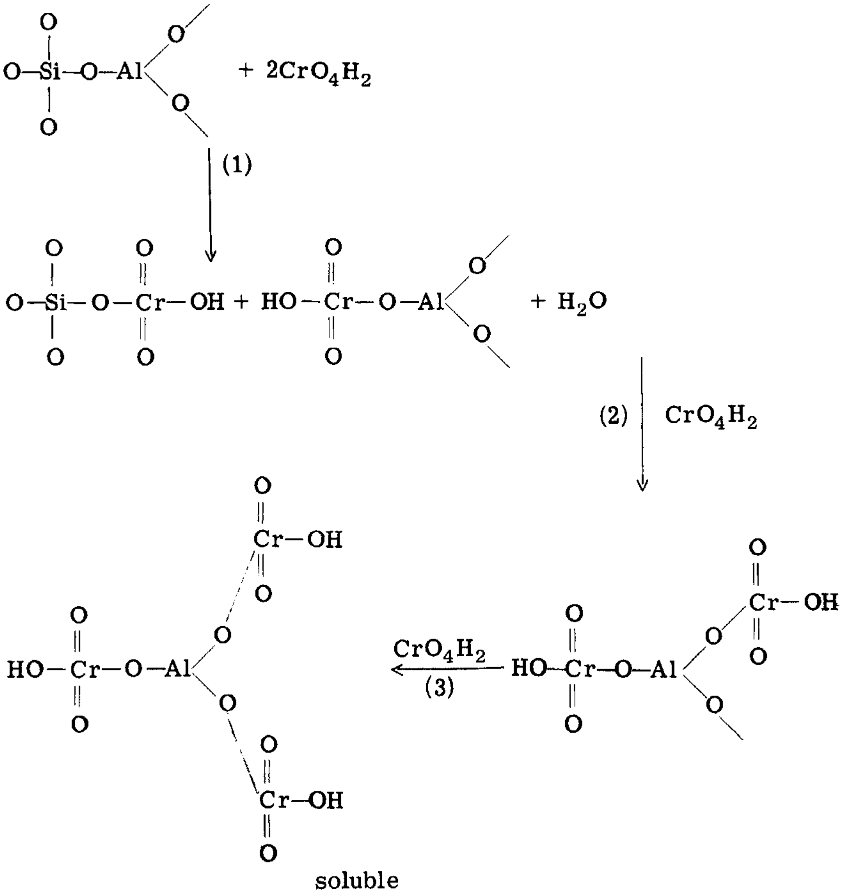
Roughly, the atomic ratio between the aluminum dissolved and the chromium engaged is 1:3 and is consistent with the fact that three protons necessary for the exchange with Al(III+) are given by three molecules of chromic acid. Such a ratio is also obeyed when the dealumination is carried out step by step, directly by attack of the silica–alumina with chromic acid without any thermal treatment of the solid. However, when the aluminum content decreases, the extraction becomes more difficult. Also during such a treatment, silica is extracted essentially during the first step but not during the following ones.

Such features are exactly parallel with those observed when the silica–alumina is dealuminated by any other acid such as hydrochloric acid. Another similarity is shown by the slight increase of specific area caused by the partial dealumination of the silica–alumina, illustrated in Table 2. Obviously the acid attack of the silica–alumina involves the aluminosiloxan bonds, as neither pure silica nor pure alumina can be solubilized by acids. According to Topchieva et al.[5], these bonds are located on limited parts of the solid surface at the boundaries of particles of pure silica and particles of pure alumina.

TABLE 2. Specific Area of Silica-alumina Partially Dealuminated

Dealuminating acid	Al_2O_3 residual, %	Specific area[a]
None	13.5	622
$H_2Cr_2O_7$	12.4	674
HCl	11	650
HCl	7.4	665
HCl	1.9	669
HCl	0.6	645
HCl	0.015	459

[a] Square meters per gram of solid desorbed at 300°C.



Then the acid dissolves, first, the mixed oxide region (step 1) and further attacks essentially the alumina particles (step 2 and 3); the aluminoxan bonds can be broken after one of the aluminum atoms bears as substituant an anion Cl^- or CrO_4H^-. New pores are created by the attack essentially in the alumina part of the solid, and finally the porous alumina particles disappear totally, causing a drop of the specific area of the solid.

The above statement proves that the interactions between the chromium oxide and the silica–alumina support, which via adequate treatment will drive to an active polymerization catalyst, begin as soon as the two components of the catalytic system have been contacted.

Attempts have been made to know the possible modification of the texture caused by the impregnation itself. The surface area has been measured after a limited desorption treatment at 200°C under vacuum. The value obtained was 534 m^2/g, in place of a value of 585 m^2/g calculated for the support (initially 622 m^2/g) after correction for the chromium content: then a decrease of 50 m^2/g is observed. After this treatment the chromium oxide is totally extractible with water, and after that the area is 643 m^2/g. Thus it appears that the limited thermal treatment caused a drop of the area of about 30 m^2/g and that another drop of 20 m^2/g is reversible and caused by the closing of pores by the chromium oxide. We have tried also to measure the area covered with chromium oxide just after impregnation, using oxygen chemisorption. These measurements normally involve treatment under hydrogen at a temperature of 450°C, which are without effect on a catalyst activated at higher temperatures, but which would modify seriously an impregnated but inactivated catalyst. We thought that the difficulty could be avoided if the chromium oxide was rapidly reduced before the measurements. This was done in two ways: first, rapid heating at 450°C under hydrogen, and, second, reduction at 250°C under hydrogen and subsequent heating under hydrogen. The two methods give, respectively, 15.9 and 15.4 m^2/g. The excellent agreement between them incline us to admit that the value of 15.5 m^2/g is representative of the area covered by the chromium oxide after the impregnation, at a 3% chromium level. It is interesting to note that the oxide is not fully spread on the surface of the support but in some way agglomerated, probably into specific places. The maximum area which could be covered by a complete spreading should be 36 m^2/g.

Differential Thermal Analysis

Figure 1 illustrates typical thermograms of some impregnated silica–alumina together with that of pure chromic anhydride. All the catalysts show a great endothermic phenomenon between 100 and 300°C, which corresponds most probably to a desorption of the absorbed water. Some of them show also an exotherm between 250 and 420°C. It has been easily recognized that this exotherm, although not presented by any silica–alumina used, is dependent more on the silica-alumina support than on the chromium content. In the case of the support with 13.5% Al_2O_3, as the chromium content increases from 0.29 to 12.85% the area under the peak increases slightly, and the temperature of the maximum decreases correspondingly from 420 to 275°C. But the area under the peak is much higher in the case of a support with 24.8% Al_2O_3. Partial dealumination of this support, before impregnation, causes a large drop in the intensity of the peak. Using a silica–alumina with 13.5% Al_2O_3, the peak disappears totally after dealumination either with hydrochloric acid or with chromic acid.

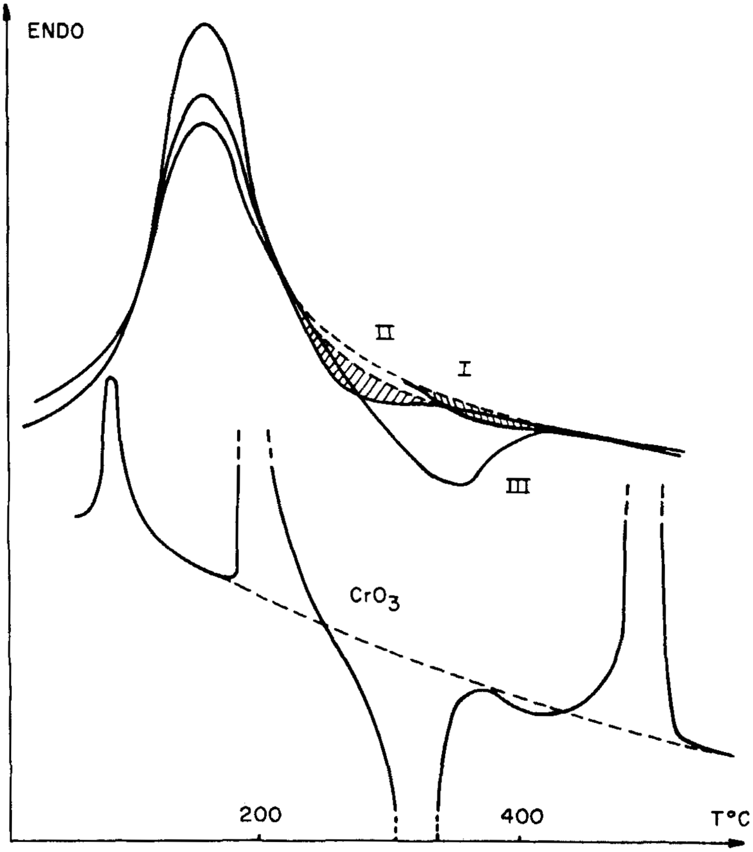


FIG. 1. DTA diagrams of CrO_3 and three typical catalysts: I, Al_2O_3 13.5%, CrO_3 2%; II, Al_2O_3 13.5%, CrO_3 24%; III, Al_2O_3 24.8%, CrO_3 6%.

However, the intensity of the peak increases slightly if the impregnated solid is allowed to stand at room temperature for several months. Also, it was observed that a small peak was visible with a partially dealuminated 13.5% Al_2O_3 catalyst, after 6 months standing. This is due probably to a very slow diffusion of the chromic anhydrid in the narrowest pores of the support.

The intensity of the peak does not change if the sweeping gas is air, notrogen, or helium. Using hydrogen, some complex effects observed are probably caused by a reduction of the chromium oxide. If the air stream is wet, another exotherm is observed at 550°C. It corresponds to a well-established phenomenon of rehydration of the silica–alumina [6].

The peak, associated with the chromium oxide, is not observed if the catalyst has been activated, even if a second impregnation is carried out. It seems to be characteristic of an interaction between the chromium oxide and a specific aluminated part of the silica-alumina. However, there is no peak with impregnated silica. It has been shown that the soluble product of dealumination of a fresh silica–alumina by chromic acid is not responsible for the exothermic peak; at first, the impregnation of a fresh silica–alumina with a solution of this product does not cause any increase of the peak area and, second, if a silica–alumina sample has been extracted with a chromic acid solution, the impregnation of the solid residue using the extraction solution does not allow us to observe the peak. Finally, the extraction solution may be evaporated; the thermogram of the solid residue is then very close to that of the pure CrO_3 which is shown in the lower part of Fig. 1. This thermogram is in agreement with those already published by Lorthioir and Michel [7]; it shows three endotherms at 70 (weak), 190 (strong), and 470°C (strong), corresponding to an unknown phenomenon, the melting, and the reduction to Cr_2O_3, respectively, and two exotherms, a strong one at 330°C corresponding to a partial reduction to $Cr_2[(Cr_2O_7)_3]$ and a weak one at 410°C which would correspond to a polychromate formation $[Cr_4(Cr_7O_{27})]$.

It must be noted that we have never observed the exothermic peak at 108°C reported by Topchiev et al. [8] and attributed by them to the formation of an aluminum chromate.

Obviously a certain correlation does exist between the occurrence and the magnitude of the exothermic peak and the activity of a catalyst, activated in a convenient way, vs. propene polymerization. Some results reported in Table 3 support this statement. It may be suggested that the magnitude of the peak corresponds to a 'potential' activity of the catalyst which could be developed only by means of an adequate activation treatment. However, it must be noted that the absence of the peak does not exclude any activity, and thus the exothermic peak reflects something related to the formation of the more active sites only. Other sites might possibly exist; on the other hand, it is possible also that when a very limited number of active sites can be formed, the exothermic phenomenon associated with a primary step of their formation is too weak to be detected by the apparatus used. The appearance of a very small peak for the partially dealuminated silica–alumina after 6 months supports the second hypothesis.

The question arises now as the nature of the phenomenon reflected by the exothermic peak. Simultaneous thermogravimetric analysis indicate that no significant accident in the rate of the loss of weight could be associated with it.

TABLE 3. Activity and DTA Peak Area of Catalysts Based on Various Supports of Silica

Al_2O_3, %	Cr, %	AOD[a]	$k \times 10^5$, sec^{-1}	DTA area[b]
0	3	5.85	2.5	0
13.5	3	5.6	17	1
11	3	5.4	3	0 (0.2)[c]
24.8	3	5.8	6	7
16.4	3.3	4.8	<1	0.8

[a] AOD, average oxidation degree.
[b] Arbitrary units.
[c] After 6 months.

Although the behavior of the supported chromium oxide is definitely different from that of the bulk oxide, the occurrence of an exothermic partial reduction at 330°C for the last suggests the same possibility for the first. Against such an hypothesis, the position and the magnitude of the peak do not depend on the oxidizing power of the surrounding atmosphere.

However, titrations made on powders heated at the normal rate in the DTA apparatus up to the beginning, the top, and the end of the exothermic peak, respectively, definitely prove the occurrence of a partial reduction of the chromium oxide. The results of these titrations are reported in Table 4. Discrepancies of the titration are ascribed to a partial rehydration of the hydroscopic solid during handling. The rapid reduction which takes place during the few minutes of the exothermic phenomenon stops after it. The amount of chromium reduced is much lower when the support has been partially dealuminated before impregnation. It is also in semiquantitative relation with the areas under the DTA peak, and, finally, it depends essentially on the type of support used, but, at least in the case of the support with 13.5% Al_2O_3, it is practically independent of the amount of chromium oxide engaged. If one admits that the DTA peak is related to the active sites, this observation could provide a way to know the number of these sites. Using the support mentioned (13.5% Al_2O_3) the number of potential sites should be about $3 \times 6 \times 10^{23}/52 \times 10^3$, i.e. 3.5×10^{19} sites per gram of support. In an earlier study in our laboratory [9] using catalyst obtained by impregnation of the same support, inhibition experiments allowed us

TABLE 4. Chromium Oxide Reduction and ESR Signal Formation during DTA Experiments

Catalyst			DTA peak						
Al_2O_3 in support, %	Dealumination	Cr impreganted, %	Position, °C	Area[a]	End of heating, °C	Cr(VI) residual, %	Cr(III), %	Amount Cr reduced[b]	ESR[a] signal
13.5	No	3	335	1	260	2.34	0.153	2.8	6.6
—	—	3			330	2.16	0.436		36.3
—	—	5	315	1	260	4.55	0.094	3.1	6.0
—	—	5			330	4.27	0.404		28.4
—	—	6.85	300	1.1	200	5.69	0.072	2.9	3.0
—	—	6.85			300	5.37	0.366		12.5
10	Yes	3	—	0	260	2.64	0.052	0.9	4.4
—	Yes	3	—	0	335	2.57	0.140		9.9
24.8	No	3	345	7	200	2.52	0.109	12.2	7.15
—	—	3			345	1.16	1.33		9.45
—	—	3			410	—	1.50	13.9	13.0
—	—	6	315	7	220	6.05	0.209	20.4	13
—	—	6			310	4.07	2.25		10
16.4	Yes	3.3	325	0.8	220	3.03	0.117	1.8	6.9
	Yes	3.3			350	3.08	0.297		28.7

[a] Arbitrary units.

[b] The amount of Cr reduced corresponds to the reduction associated with the exothermic phenomena and is calculated from the Cr(III) titrations which are expected to be more reliable. It is calculated in milligrams of Cr reduced per gram of catalyst.

to estimate the maximum number of active sites of a typical catalyst as being 3×10^{19} per gram.

In the case of the catalyst with 24.8% Al_2O_3, the potential number of sites seems to be much higher and 3% chromium is possibly not sufficient to cover all these sites by the impregnating chromium oxide. However, the activation of the catalysts based on this support is more difficult to carry out in good conditions.

An ESR signal of the γ-phase has been often associated with the active centers in olefin polymerization [10]. The results reported on the last column of Table 4 show that the development of the ESR signal becomes important at the temperature of the exothermic peak.

However, the units used are expressed in per cent of the intensity of the signal of a typical catalyst activated at 550°C.

Thus it may be seen that the intensity of the signal obtained after heating in the DTA apparatus is only a fraction smaller than the final signal. Furthermore, its increase does not stop when thermal treatment is pursued beyond the DTA peaks, and there is no relationship between intensity and the area of the DTA peak. Most probably there exist different structures responsible for the ESR signal; this fact was proved recently in the case of silica–chromium oxide catalyst by Vanreijen and Cossee [11]. Only a part of these structures are to be associated with the active sites. In our case it is probable that structures other than those associated with the DTA peak are responsible for the ESR signal.

Furthermore, it has been observed that, in the conditions of thermal treatment used in the DTA experiment, the exotherm is not associated with any change, either of the specific area or of the area covered with chromium oxide. It is likely that changes of these parameters involve longer thermal treatments. The fact that the position of the DTA peak depends on the amount of the chromium oxide remains to be explained. We suggest the following. It is not obvious that after the impregnation the chromium oxide would be in a position to react with the structures of the support associated with the DTA peak; either some attack of the solid is necessary before these structures are made accessible, or the chromium oxide must be mobile on the surface in order to come in contact with these structures. In the first hypothesis, one may remark that the thermal treatment carried out at 200°C before surface-area measurements of the impregnated solid has caused some modifications of the texture. Obviously these modifications are deeper if the temperature is higher or if the amount of chromium engaged is higher, and then the DTA peak could be observed only at higher temperatures if the chromium content is lower. In the second hypothesis when the chromium content is high, sufficient chromium oxide is in contact with the reactive structures to permit the reaction to be observed at rather low temperatures. On the other hand, if the chromium is in low amount it must be moved on the surface to come into contact.

Obviously the mobility of the chromium oxide is higher at higher temperature, and if the chromium content is low, higher temperature is necessary for observing a reaction rapid enough to cause an exothermic phenomenon.

Activation Treatment

We have already suggested [2] a mechanism based on the mobility of the chromium for the correlation between the intensity of the air stream in the activation treatment and the maintenance of a high content of hexavalent chromium. According to this mechanism, the chromium anhydride, the melting point of which is 190°C, does have a noticeable vapor pressure in the temperature range used for the activation treatment. Then it can be vaporized partly, but its high density causes it to be deposited quickly. In contact with the solid, the chromic acid may be reduced, chiefly when the temperature is higher than 470°C (DTA peak of CrO_3), but also the surface layer may be reoxidized by the air and then becomes volatile again. Thus by successive jumps through the vapor phase, any molecule of chromic anhydride may be moved on the surface of the solid. The mobility of the chromic anhydride is better when the powdered solid is more dispersed and fluidized by the air stream in the activation cell. It depends also on the temperature and results from an equilibrium between the volatilization of the chromic anhydrid, its deposition upon the surface, its interaction with the support, its thermal decomposition, and the agglomeration of the trivalent oxide. The data reported in Table 5 illustrate the above considerations quite well. It may be seen that, depending on the activation conditions, the area covered with chromium may be greater or lower than that of the impregnated support; for catalysts activated at 550°C under air close relationships between the change in area, the oxidation degree of chromium, and the activity vs. the propene polymerization are observed. At other temperatures the equilibria are deplaced, so that although the area covered may be increased (700°C), the chromium oxide is more reduced on the average and the activity is lowered. These last results show that a higher dispersion state of the chromium oxide is not necessarily related to a higher activity. On the contrary, the activation at 700°C causes a drop of the activity and also of the average oxidation degree of the chromium. As indicated by the results of the first lines of Table 5 such drops are probably related to a process of agglomeration of the trivalent chromium oxide. Then it may be supposed that the agglomeration of the oxide has occurred on the trivalent base of some of the active sites, covering them and destroying their activity. On the other hand, a great amount of chromium hexavalent oxide has been spreaded over the surface, owing to a higher volatilization rate, but this kind of chromium oxide is not responsible for a high activity. The simultaneous occurrence of these two types of chromium oxide, the spread

TABLE 5. Changes in Area Covered by Chromium Oxide with Activation Condition Silica-Alumina, 13.5% Al_2O_3, 3% Cr (area covered after impregnation 15.5 m^2/g)

Activation temp., °C	Gas	VSH[a]	AOD[b]	Change in area covered	Activity[c], $sec^{-1} \times 10^5$
550	N_2		3.2	−9.8	0
—	Air	40	4.4	−4.0	3.5
—	Air	50	4.6	−3.0	4.2
—	Air	100	5.15	−1.5	6
—	Air	200	5.4	2.6	10
—	Air	400	5.6	7.2	14
—	O_2	400	5.72	6.5	13
620	Air	400	4.8	−3.8	5
700	Air	400	4.5	9.7	4.5

[a] Volume gas per volume of solid, per hour.
[b] AOD, average oxidation degree of the chromium.
[c] Activity vs. propene polymerization (high polymers only).

and the agglomerated ones, has been already qualitatively proved by magnetic measurements, which give evidence for a character of "superantiferromagnetism" of this supported antiferromagnetic material [12].

At 620°C the effect of reduction and agglomeration overcomes the spreading by volatilization.

However, in the above equilibria, the reversibility of one of the processes, the reduction, is limited. Trivalent chromium oxide shows a strong tendency to be agglomerated, thus reducing the area of the surface layer; and only this last one is possibly reoxidized. Even if one uses the better activation conditions, it is quite impossible to improve the activity or to increase noticeably the average oxidation degree of a catalyst which has been previously badly activated. After the first treatment under N_2 at 300°C, the AOD of a 3% chromium catalyst is generally of about 5.5. It may be decreased greatly if the activation conditions do not maintain the major part of the chromium anhydride in or near the vapor phase, but it may be increased only up to about 5.6 under an air stream, and 5.7 under oxygen. Then it seems that a part of the chromium cannot be reoxidized. We suggest that this part might correspond to the amount involved in the reduction process associated with the DTA peak. As has been indicated previously, this amount would correspond to about 0.3 g of chromium per gram of catalyst, when the support contains 13.5% Al_2O_3. This suggestion is supported by the data reported in Table 6. The catalysts concerned in this table have been activated in the same conditions of temperature and air stream. When the chromium content is very low, there is not a sufficient amount of oxide to react with the available sites of the support, and then the DTA peak is smaller. But as soon as the chromium content is 0.5%, the DTA peak is quite fully developed and the amount of chromium reduced is close to the limiting value.

With greater amounts of chromium, extra reduction take place, as in the bulk oxide, because the average number of chromium oxide layers increases.

Active Centers

The activity data in the last column of Table 6 show that the reaction of the chromium oxide with the adequate structures of the support is not a sufficient condition to develop the activity. It seems that an active center must involve not only a trivalent chromium atom linked to the support but also hexavelent chromium deposited on it. As has been shown from magnetic measurements [12], a part of the hexavalent chromium is always spread in a monolayer on the surface. So, if the chromium content is too low, there is not hexava-

TABLE 6. Influence of Chromium Content on Properties of Activated Catalysts (support 13.5% Al_2O_3, activation temperature 550°C, air stream of 400 VSH)

			DTA peak			
Cr, %	Cr(VI), %	Amount Cr reduced	Area	Position, °C	No. of Cr layers	Activity
0.140	0.014	0.126	0.5	420	1.3	0
0.51	0.27	0.24	1	385	1.5	0.5
1.06	0.83	0.23	1	365	1.55	2.5
3.0	2.6	0.40	1	335	1.60	14
9.0	7.12	1.88	1.1	300	5.0	5.2
12.6	8.4	4.2	1.1	275	7.7	0.1

lent oxide enough to cover the trivalent oxide sites, and the active sites are not complete. The necessity of the coverage of the support-reduced chromium sites with hexavalent chromium is in agreement with the results already published [2], which show that for a great variety of catalysts differing by the nature of the support, the chromium content, the oxidation degree, and the sodium content, polymerization activity is very low when the average number of chromium oxide layers is close to 1 and goes through a maximum when this average number is between 2 and 3.

All the data presented before support the view that, at least with a catalyst supported by a silica–alumina, an active site is formed by a particular site of the silica-alumina reacted with a chromium oxide molecular which is then reduced to the trivalent state and covered with one or several layers of hexavalent chromium oxide.

The question arises as to the precise nature of the site of the silica–alumina. Obviously these sites are eliminated by a dealumination treatment. We have verified that the product of the water extraction of a silica–alumina impregnated by chromic acid, which has been shown to be not related to the DTA peak, is also not responsible for the polymerization activity.

It is not active by itself, even if it has undergone the activation treatment. When used as an impregnated material, it does not restore the activity of a catalyst obtained from a partially dealuminated support, and it does not increase the activity of a typical catalyst.

The uneffectiveness of this product in the polymerization activity is consistent with the fact that the chromia–alumina catalysts are not active. It inclines one to think that the trivalent chromium oxides involved in the active sites are most probably linked to parts of the support rich in silica.

If one supposes that the model proposed by Topchieva is representative, one can think that the aluminosiloxan bonds present in the mixed oxide zone between pure silica and pure alumina domains are broken during the impregnation, giving chromosiloxan and chromoaluminoxan bonds. Because all the chromium can be extracted with water, these two new bonds can be hydrolyzed when the impregnated solid has not undergone thermal treatment. This situation is valid until the thermal treatment does not cause the exothermic reduction of any chromium. After this reduction, or after a normal activation treatment, the hexavalent chromium and a part of the alumina may be extracted and the dealumination may be pursued further; the part of chromium which is reduced is thus probably issued from the chromosiloxan initial bonds. If this view is right, the base of the active site, silica and trivalent oxide, must resist the extraction treatments and the dealumination treatments. It may be supposed that it would be sufficient to deposit upon this base some hexavalent chromium oxide to develop the activity but that the manner of deposition would not be critical. In other words, after water extraction of an activated catalyst, a reimpregnation with chromium oxide would be sufficient to restore its activity if a thermal treatment is carried out in order to eliminate the poisons, such as the adsorbed and chemisorbed water and oxygen. Further, unlike the predealumination treatment, postdealumination carried out after activation would not cause the destruction of the activity. Experiments were carried out in this way. Table 7 gives the results. The treatments indicated in the first column were carried out successively. The fact that the final activity of the catalyst is still half the initial confirms the validity of the above statement. It is to be noted that the dealumination treatment causes a partial extraction of the trivalent chromium.

TABLE 7. Activity, Composition, and Texture of a Catalyst After a Postdealumination Treatment

Treatment	Cr, %	AOD	Al_2O_3, %	SCr, m^2/g	S, BET	Activity
Initial impregnation and activation	3.0	5.4	12.5	21	440	12
Water extraction	0.65	3.0	10.5	—	—	0
Chromic acid impregnation	18%	—	—			
Water extraction	0.44	3	5.91	3.25	484	0
Impregnation and activation	3	5.5		24.6	441	6

It has been noted, in fact, that the whole trivalent chromium could be extracted by hot concentrated hydrochloric acid. We think that this partial extraction is responsible for the loss of a part of the activity. It can be observed also that during the final activation treatment, the amount of hexavalent chromium which is reduced is very small.

Finally, it is important to recall that the above results and discussions are valid considering only the propene polymerization. We think that probably the same catalyst contains a higher number of active sites for ethylene polymerization and that some catalysts, such as those supported on pure silica, are active only for the ethylene polymerization, unless more severe conditions of activation (700°C) are used [2].

In the last case, these activation conditions allow a deeper interaction between the chromium oxide and the silica, which promotes the activity vs. propene polymerization.

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Zusammenfassung

Die Differentiale Thermische Analyse (DTA) und die Komposition-, Textur-, und Überdeckung Messungen zeigen deutlich die Existenz von chemischen Wechseleinwirkungen Zwischen Chromoxyd und dem Silika-Alumina Träger eines Olefinpolymerisierung Katalysators. Diese Wechseleinwirkungen sind mit der Aktivität gegenüber der Propen Polymerisierung verbunden; die erhaltenen Wechselbeziehungen erlauben anzunehmen, dass die aktiven Zentren aus einer dreiwertigen Schicht von Chromoxyd bestanden sind; diese Schicht ist mit Chromsiloxan Verbindungen an dem Träger gebunden und mit einer oder mehreren sechswertigen Chromoxyd Schichten bedeckt.

Résumé

L'analyse thermique differentielle et les mesures de composition, texture, et recouvrement, mettent en évidence l'existence d'interactions chimiques entre l'oxyde de chrome et le support de silice-alumine d'un catalyseur de polymérisation des oléfines. Ces interactions sont reliées à l'activité vis-à-vis de la polymérisation du propylène; les corrélations obtenues permettent de suggérer que les centres actifs sont constitués par une couche d'oxyde de chrome trivalent liée au support par des liaisons chromosiloxaniques et recouverte par une ou plusieurs couches d'oxyde de chrome hexavalent.