Supported Chromium Oxide Catalysts for Olefin Polymerization. VI. Activation Process and Catalytic Activity Versus Ethylene Polymerization

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SUMMARY

The influence of the temperature, time, and heating rate of the activation process of a chromium oxide catalyst, supported on silica-alumina, on the activity vs. ethylene polymerization has been studied. The function of the activation process is to develop the potential active sites through a rapid interaction between the chromium oxide and the support which depends only on the temperature, and also to cause a minimum time- and temperature-dependent dehydration of the solid. Pretreatments by limited amounts of hydrogen, ethylene, or other hydrocarbons lead to an increase of the activity through optimal conditions; the optimal activity results from a compromise between a proper reduction of the chromium and the desorption of the oxidized products. The better pretreatment agent is the monomer itself in limited amount at high temperature.

INTRODUCTION

Although a large amount of work, recently reviewed by Clark [1], has been devoted to the study of olefin polymerization on supported chromium oxide catalysts, many uncertainties remain about the nature of the catalytic sites and about the relative influence of the various parameters of the activation process. A proper definition of the catalytic activity was essentially coarse until our previous study in this series [2]. It has been shown that catalytic activity is reached only after an induction period, which means that the last step of the activation process is accomplished by the monomer itself; such a result is not new, and there are many data in the literature [3-10] about the influence of a pretreatment with monomer or other reducing agent (H_2, CO, hydrocarbons, etc.). However, these data are generally in a limited range of conditions, so that some of them seem to be contradictory. Moreover, most of the authors have used the activation conditions recommended by the earlier patents of the Phillips Petroleum Co. [11], but the influence of the various parameters of the heat treatment were not thoroughly studied.

The purpose of the present work is to describe some new results which allow most of the literature data to be rationalized. In the first part we deal with the activation process and in the second part with the pretreatments by the reducing agents and the monomer. Most of the data are concerned with 3.6% chromium catalysts prepared by impregnating a silica-alumina (13% Al_2O_3) cracking catalyst with a solution of chromic acid. The activity has been generally measured at 145°C under an ethylene pressure of 0.09 bar, in an integral dynamic reactor without solvent, following the method previously described [2] and is expressed by the first-order rate constant k:

$$k = \frac{1}{m} \left[rD - d_0 \ln (1 - r) \right]$$

where r is the conversion ratio, and D and d_0 monomer and carrier gas flow-rates, respectively.

ACTIVATION PROCESS

It has been recognized that the function of the activation process is twofold: removal of adsorbed and chemisorbed water which acts

as a poison [4], and interactions between chromium oxide and the support [1, 12]. Thermogravimetric data [10] show that the loss of water is a continuous process with increasing temperature from 120 to 700°C. The interaction between chromium oxide and the support, described by Hogan [10] as being the formation of a chromate, is an exothermic process [12] which takes place between 200 and 400°C. This interaction leads to the stabilization of hexavalent chromate ions and does fix the dispersion state of the chromium oxide onto the surface of the support [13].

The activation process is generally a thermal treatment of the catalyst suspended by the stream of gas in a fluid bed. In some laboratory experiments this is done under vacuum. The various experimental parameters, in addition to the initial composition of the system (Cr content, nature of the support) are the temperature, the heating rate, the duration of the thermal treatment, and the composition and velocity of the gas stream. The standard conditions are 5 hr at 550°C in a 300 v/v/hr stream of dry air. In a previous paper [14] we have shown that the catalytic activity was not dependant on the duration of the treatment under air at 550°C or after a 15 hr drying stage at 300°C under nitrogen, although the texture of the catalyst and the dispersion state of the chromium oxide were slightly modified. That confirms that the active sites represent only a minor portion of chromium atoms and that the relation between the dispersion state of the chromium and the activity is not straightforward.

In this work we have studied the influence of the activation temperature and the heating rate. It is well known that the activity of these catalysts decreases at very high temperatures, so we have limited our study to the 300-600°C range.

The results are shown on Fig. 1. The impregnated solid may have been previously dried at 120°C. The rate constant is low at 300°C and levels off around 500°C. The development of the full activity does imply a minimum duration of the heat treatment, which is shorter when the temperature is higher. This minimum duration does correspond to the dehydration of the catalyst, while the level of the maximum potential activity is dependant on the interaction of the chromium oxide and the support which is governed by the temperature. Contrary to the results of Matsuda et al. [15], we have observed that the heating rate is not an important factor. For a final temperature of 550°C, a slow heating rate, after drying at 300°C, gives the results illustrated by Curve III. By using a heating rate of 15°/min, a slightly higher activity was observed; this is due to the fact that a limited amount of chromium has been extracted from the catalyst by the stream of wet gas so that the
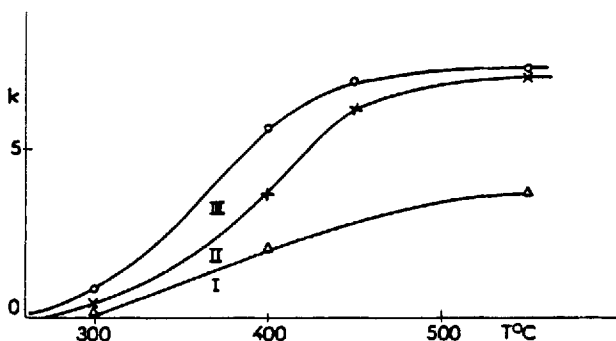
FIG. 1. Activity in ethylene polymerization at 145°C vs. activation treatment at a heating rate of 10°/min.   (I) Heating up to the temperature T. (II) Similar heating followed by a 1-hr treatment at T. (III) Similar heating and 15 hr at T.

Cr content is lowered and closer to the optimum value of 2%.
    The above results have been obtained using N_2 as the gas. Results were the same with either helium or air. Of course, the average oxidation number, which is 4.5 with an inert gas, is higher than 5 and depends on the space velocity with air. The result of this observation is that the activity vs. C_2H_4 polymerization is not governed by the average oxidation number of Cr for values higher than 4.5. It may be noted that the induction period (time needed to get maximum activity in a run) is shorter the lower the average oxidation number. The situation is quite different for the propylene polymerization for, as shown by Daniel [16] in our laboratory, the activity increases strongly with this number.
    After an activated catalyst is exposed to the atmosphere, it loses its activity, being poisoned by air and moisture. Heating for 4 hr up to 350°C in an inert atmosphere is sufficient for the recovery of the activity in all cases. Heating at 250°C generally results in a partial recovery of the activity, which increases with the duration of the first activation treatment; total recovery is observed after 4 hr at 250°C if the first activation treatment was at least 2 hr in duration.
    It may be concluded from the above results that the maximum number of active sites depends essentially on the temperature of the activation process. Interaction between chromium oxide and

support is a rapid reaction; slower interactions are observed also but do not change the active sites. On the contrary, dehydration is a rather slow process which is very dependant on the actual texture of the catalyst.

PRETREATMENTS WITH REACTANTS

Clark, Finch, and Ashe [8] were the first to show that a pretreatment with CO at 250°C under 100 torrs increases the activity and allows it to be observed at low temperatures (-55°C). The authors explained these facts by the formation of a complex carboxylate ion, as evidenced by IR spectroscopy. Russian workers [17] have reproduced these experiments and shown that the enhanced activity was not due to an increase of the number of the active sites but was the result of an enhanced activity of all the sites. Hill [7] has carried out the treatment at 400°C and 35 torrs; he observed a sharp maximum of the activity for a duration of 55 min, followed by a vacuum treatment. Finally, Hogan [10] has shown that the complex CO-site was displaced by the monomer which gives a monomer-site complex, but that another CO molecule adsorbed at a secondary position was not displaced, and thus blocked the polymerization.

Clark et al. [8] have also observed that a pretreatment at various temperatures with C_2H_4 does permit the polymerization at -55°C. Ayscough et al. [3] reported that the maximum activity at -22°C was observed if a pretreatment by the monomer has been made at 130°C. Later, Kazanski and Turkevich [4] reported a tenfold increase of the activity at 0°C after a 30-sec pretreatment at 150°C under 30 torrs of monomer. However, the activity was suppressed after the same treatment at 250°C. Eden et al. [5] used 0.5 mmole of monomer per gram of catalyst; maximum activity was obtained when the treatment had been at 300°C and followed by vacuum treatment, but at this temperature 0.075 mmole of monomer were sufficient to obtain the entire activity increase. The activity was again zero after a treatment at 400°C. Habeshaw and Hill [6] reported that there was no polymerization at 250°C. Later Hill [7] observed a two-step chemisorption process of C_2H_4 at 250°C. When these treatments were followed by evacuation, a high activity was observed only if the pretreatments had been limited to the first step.

Clark [8] has reported that many hydrocarbons, including the solvents, may improve activity. More recently [9] he has shown

that a 1-hr treatment at 300°C by 100 torrs H_2 causes a maximum
activity for various Cr contents.

From all these literature results it may be concluded that optimal
conditions are obtained for pretreatments with various reactants.
The following factors appear to be important: temperature, time,
nature and pressure of the reactant, and evacuation of the oxidized
products. We have made a rather extensive study using the simplest
reactant, H_2, which gives only one oxidized product, water, which
can be easily desorbed. Comparative experiments were also made
with other reactants: propane, ethylene, and propylene. In all
cases the catalysts were previously activated under an air stream
at 550°C for at least 1 hr.

Pretreatment with Hydrogen

After pretreatment with H_2 it is necessary to desorb the water
by rapid heating (20 min) under a helium stream up to 550°C. In
the absence of desorption the activity is low and the induction period
is very long.

Several pretreatments have been made in the reactor [2] under a
stream of a mixture of H_2 (40 ml/min) and He (20 ml/min) with
varying temperature and time. The results, given in Tables 1-3 and
Fig. 2, indicate a sharp maximum for the activity at 145°C, the posi-
tion of which depends on the temperature (within ±1°C) at a fixed
time, and on the time (within ±15 sec) at a fixed temperature. The
dependance of the optimal activation time on the temperature fol-
lows the Arrhenius law with an activation energy of 33 kcal/mole.
The pretreatment induces a decrease of the induction period which
becomes lower when the temperature has been higher. However,
this induction period never disappears totally. A maximum in the
activity is also observed for polymerization at 90°C; as shown in
Fig. 2, it is sharper but the level of activity remains lower than
in the absence of pretreatment. For polymerization at room tem-
perature the activity is always lower than that of direct measure-
ment, and no maximum has been observed. No induction period is
observed at 90°C, but if the temperature is raised to 145°C an
induction period is observed, while the activity reached is about
the same value as that obtained directly after the same pretreatment.
These data suggest that water is not totally desorbed by the drying
process under helium but has to be desorbed by the monomer during
the induction period. However, a prolongated drying stage at 550°C
leads to a decrease of the activity, so that the compromise chosen
has been adopted in order to reach maximum activity.

TABLE 1. Activity vs. Ethylene Polymerization at 145°C after 2 hr Pretreatment by H₂ (0.66 bar, 40 ml/min)

Temperature of the treatment (°C)	No treatment	200	240	249	251	253	256	275	300	450	550	550 [a]
Activity k (mmole/min/g/bar)	7.05	7	6	7.5	7.6	11.1	7	5.5	3.3	2.4	1.5	0.1
Induction period (min)	5					2					~0	

[a] Activation under H₂ (40 ml/min, 1 bar).

TABLE 2. Activity vs. Ethylene Polymerization at 145°C after Pretreatment by H₂ at 295°C (0.66 bar, 40 ml/min)

Time (min)	0	7	12.5	12.9	14	15 [a]	15.5	30	120
Activity k (mmole/min/g/bar)	7.05	6.3	7.2	9.3	7.05	3.2	5.55	5.25	4.45
Induction period (min)	5	3	1.7	1.7	1.7	10	1.7	1.7	1.7

[a] Without intermediate drying.

TABLE 3.   Time and Temperature of Pretreatment by H_2 for
Maximum Activity in C_2H_4 Polymerization at 145°C

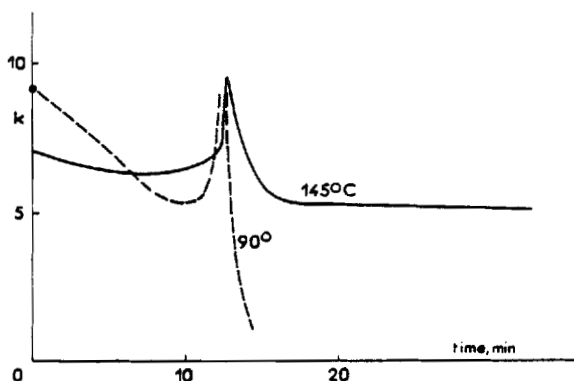| Temperature (°C)	253	275	295	307
Time (min)	120	30	12.85	6.5

FIG. 2.   Activity in ethylene polymerization at 145°C (——) or
90°C (- -) as a function of the time of pretreatment with H_2 at
295°C.

Pretreatments at 295°C have also been carried out on catalysts
with various Cr content or supported on silica instead of silica-
alumina. The results are presented in Table 4. The optimal time
increases slowly with the percentage of Cr up to 2% (maximum
value) and more rapidly beyond. The time is very long with silica
as carrier. These results may be compared with the reduction
profiles reported by Holm and Clark [9], and they show that the
development of the maximum activity is closely related to the
reducibility of the chromium. The temperature range in which the
reduction occurs is displaced toward higher temperatures when
the support is silica, but the variation of the reducibility of the Cr
content indicates that only a smaller part of the total Cr is involved.
A method of investigation where the total Cr is studied does not
allow separation of the active atoms.

TABLE 4. Optimal Time for Pretreatment by H_2 at 295°C and
Activity vs. Ethylene Polymerization at
145°C for Various Catalysts

Support	Silica-alumina					Silica
% Cr	0.5	1	2	3.6	9	2.5
Optimal time (min)	8.65	9	9.5	12.9	16.25	>40
Activity k (mmole/min/ g/bar)	6.6	11.1	12.9	9.3	6.6	>4.8
Activity k without pre- treatment	4.2	8.1	11.0	7.05	5.7	3.6
Induction period (min) (acti- vation under air)	1	1	2	5	10	15

Pretreatments with Ethylene

Ethylene (6.5 ml/min) was mixed in a stream of helium (65 ml/
min), so its partial pressure was 0.09 bar and its flow-rate was
0.07 mmole/min. The ethylene flow was stopped after a definite
time and the temperature was maintained for a few minutes in order
to allow the desorption of the oxidized products. Then the polym-
erization was done at the desired lower value.

A study was made at 250°C, and Fig. 3 shows the experimental
kinetic curve. Its shape is quite similar to that of a normal polym-
erization curve [2], indicating that some polymerization occurs.
The activity rapidly developed, and after an induction period of
36 sec it reached a maximum of k = 3. It decreased rapidly and
became negligible after about 2 min of contact. The amount of
polymer formed was too low to block the surface, so that this is
a reduction process which deactivates the catalyst.

Some pretreatments have been carried out at 250°C or lower
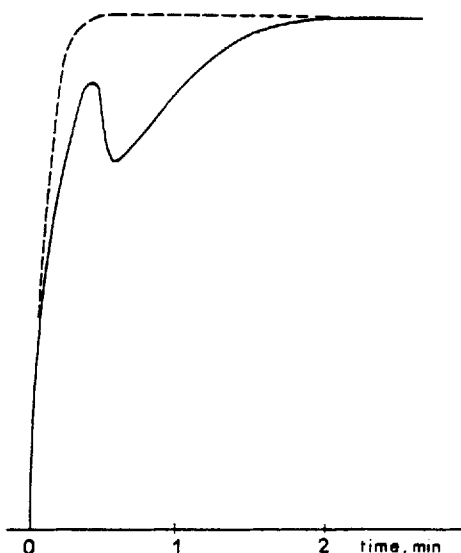temperatures and have been followed by polymerization at lower

FIG. 3. Experimental curve for ethylene polymerization at 250°C:
deflection without catalyst (- -) and in presence of catalyst (——).

temperatures. The results are illustrated in Figs. 4 and 5 and in
Table 5 for a series of successive treatments before polymerization.
It may be seen that the optimal duration of pretreatment at 250°C for
polymerization at 145°C corresponds roughly to the induction period
at 250°C. A large decrease of activity is observed together with a
large increase of the induction period if the pretreatment has been
prolongated. Also, after successive pretreatments the activity
depends only on the conditions of the higher temperature pretreatment.
For pretreatment at 145°C and polymerization at 90°C the activity
decreases at first and then increases slowly with the time of treatment.
The corresponding curve of Fig. 5 seems to closely follow the kinetic
curve of a direct polymerization at 145°C. It may also be noted that
the induction period has decreased and is very short.

    These facts may be satisfactorily explained if one admits that two
major factors govern the activity: the reduction state of the chromium
and the desorption of the oxidized products. The first factor may be
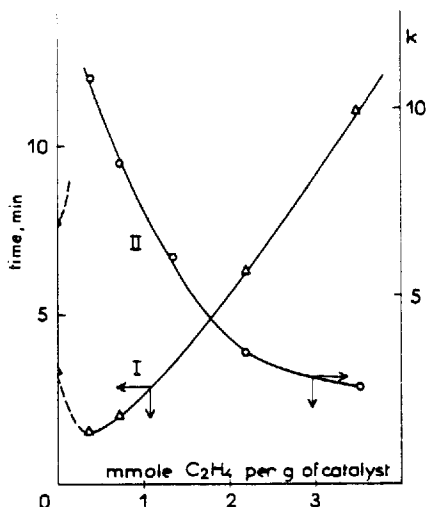controlled by treating at a sufficiently high temperature and adjusting

FIG. 4. Variations of the induction period (I) and activity (II) at 145°C in C_2H_4 polymerization vs. C_2H_4 pretreatment at 250°C.

the duration. All the sites are not formed at 145°C, but at higher temperatures of 250°C, or even 330°C, they are built up rapidly and slowly destroyed by a longer treatment. Secondary phenomena appear above these temperatures, as a result of the degradation of hydrocarbon compounds. The second factor is a result of the nature and quantity of these oxidized products which remain adsorbed and depend on the temperature. Their desorption by the monomer also depends on the temperature. With increasing duration of treatment at 250°C, the large induction period at 145°C indicates a slow desorption. After a pretreatment at 145°C followed by polymeriza- tion at 90°C, the very short induction indicates that nothing is desorbed. These results are to be compared with those of Hill [7] who studied the action of C_2H_4 at 250°C on silica-based catalysts: he notes two stages in the reaction, the second one being a strong chemisorption blocking the sites and the need for high-temperature desorption (400°C) for the recovery of activity.

Pretreatments by H_2 and C_2H_4 have determined the character- istics of the sites formation and the resulting activity, but it was
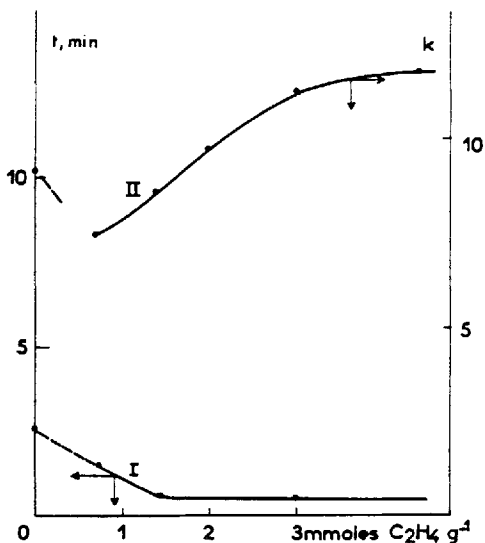
FIG 5. Variations of the induction period (I) and activity (II) at 90°C in C_2H_4 polymerization vs. C_2H_4 pretreatment at 145°C.

important to check their general validity by 1) another monomer (propylene) whose polymerization has been studied, and 2) with a similar but nonpolymerizable hydrocarbon (propane). These two reactants can be used in the polymerization temperature range.

Pretreatments with Other Hydrocarbons

Pretreatments with these other hydrocarbons have been carried out under the same conditions of pressure used for ethylene. The results are reported in Table 6. Once again a maximum in the activity after a pretreatment is observed, but the reducing power of these hydrocarbons, and chiefly propylene, is greater than that of ethylene as indicated by the shorter optimal time. After treatment with either propylene or ethylene the activity is about the same, and it is interesting to point out that oligomerization does not reduce the activity. The use of propane leads to a smaller

TABLE 5. Ethylene Polymerization after Successive
Pretreatments by C_2H_4

Pretreatment (mmole C_2H_4/g catalyst) at			Rate constant k at	
250°C	145°C	90°C	90°C	23°C
0	0	0	9.1	
0.36	1.44		15.2	
0.72	1.79		18.2	
1.47	4.42		10.4	
2.14	5.70		6.6	
3.44	7.90		5.6	
0.8	0		18.5	
0	0	0		0.7
0.36	1.44			5.4
0.72	1.79	2.15		6.1
1.47	4.42	2.21		4.3
2.14	5.70	2.85		3.1
3.44	7.90	2.06		2.1
0.8				7.1
	0.72	2.16		2.7
	1.40	2.10		3.2
	3.02	2.26		6
	4.32	2.16		4.4

activity, probably because some partially oxidized products are not
desorbed. If desorption is made up to 250°C under helium, the
activity is destroyed. However, there is no induction period in
either case.

TABLE 6. Activity vs. Ethylene Polymerization at 145°C after Various Pretreatment Conditions

Hydrocarbon	None	C_3H_8	C_3H_8	C_3H_8	C_3H_8	C_3H_6	C_3H_6	C_3H_6	C_3H_6
T (°C)		145	145	145	145	145	145	250	250
Time (min)		2.8	3	6.5	16	0.2	0.35	0.7	4.5
Activity k (mmole/min/ g/bar)	7.05	6.6	7.75	3.9	0	8	8	11	1.5

CONCLUSIONS

The activation of a supported chromium oxide catalyst involves five essential steps before the polymerization process may begin.

1) Interaction between chromium oxide and support. This is essentially a rapid process which depends on the temperature and which fixes the dispersion state of the chromium and the number of potentially active sites.

2) Dehydration and desorption of water. This is a time- and temperature-dependant process.

3) Reduction of the chromium oxide to a definite state. This depends on the temperature and the amount of reducing agent; it requires well-defined conditions to obtain a catalyst surface with high activity.

4) Desorption of the oxidized products. This depends on the temperature and on the nature of the reactants.

5) Complexation of the monomer onto the sites. This can also be done during pretreatment with a hydrocarbon.

An important difference appears between the results of treatments with H_2 and C_2H_4. With the hydrocarbon the site is actually active and stabilized against impurities. On the other hand, H_2 leads to a potential site. This is shown by the results of low temperature (0°C) polymerization of C_2H_4 [4, 8] where an activity is found only after pretreatment with C_2H_4 or CO.

After a conventional activation process, the easiest way to reach the maximum activity is by pretreatment with a properly limited amount of ethylene at a rather high temperature. Such a treatment has been adopted for the further studies to be published in this series.

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