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Supported Chromium Oxide Catalyst for Olefin Polymerization. X. Propylene Polymerization-Activity Measurements at Low Pressure

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ABSTRACT

The experimental determination of the activity of silica-alumina-based chromium oxide catalyst vs propypene polymerization at low monomer pressure is discussed. A reduction pretreatment of the catalyst under optimal conditions is necessary to obtain an activity stable enough to be accurately measured. Surface area measurements show that it remains a noticeable activity at subzero temperature.

INTRODUCTION

In the first paper of this series [1, 2] and in previous papers [3, 4] propylene polymerization under rather high pressure (about 50 bars) has been studied. Besides the polymerization process leading to high polymers, one observes an oligomerization process, mostly important at the beginning of the reaction and at high temperature, which is caused by the support of silica-alumina [5] and which may be kinetically differentiated from the polymerization process [4]. A comparison of the polymerization activity with the distribution of the chromium oxide over the surface of the support has led us to describe the active site as chromium oxide clusters deposited on the silica part of the silica-alumina and comprising between two and three layers of chromium oxide. There was no activity or a low activity was found for catalysts with an average of one layer of chromium oxide. Such a result was surprising because it is totally different from the situation described for ethylene polymerization. However, for technical reason it was not easy to study ethylene polymerization through the kinetic method used for propylene polymerization.

New techniques have now been developed for low pressure and applied successfully to the study of ethylene polymerization [6]. A number of kinetic studies [7, 8] have led us to propose a new model for the active sites in ethylene polymerization. The site is viewed as a set of three chromium atoms, in different oxidation degrees (Cr^{3+}, Cr^{6+}, Cr^{3+}) before contacting with monomer, and located at the boundary between the flat chromium oxide domains and the uncovered support of silica or silica-alumina [9].

The present paper deals with the determination of activity vs propylene polymerization at low pressure under various conditions. Also described is the measurement of the drop of surface area after propylene polymerization in the same way as this phenomenon was observed during ethylene polymerization. A full discussion of the comparison between ethylene and propylene polymerization will be presented in the next paper of this series [10].

The results are chiefly concerned with catalysts based on silica-alumina (13% Al_2O_3) with a chromium content of 3.6%.

PRELIMINARY EXPERIMENTS

We first tried to apply the technique used to measure catalytic activity vs ethylene polymerization at low pressure (0.1 bar): a continuous stream of inert gas goes through a U-shaped reactor, followed by a catharometer cell. Prior to the reactor, a mixing chamber allows the introduction of a partial pressure of monomer. The reactor may be by-passed, in which case the catharometer leads to a zero-conversion trace. By allowing the diluted monomer to pass through the reactor, the instantaneous conversion may be deduced from the difference between the zero-conversion trace and the actual trace of the recorder. The reactor operates as an integral dynamic reactor.

An example of the results obtained with propylene polymerization is given in Fig. 1. The instantaneous polymerization rate decreases

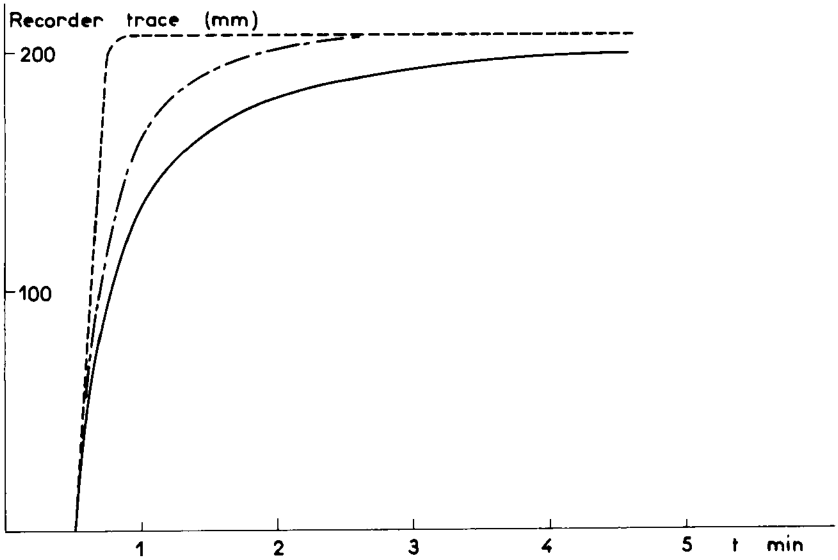

FIG. 1. Recorder trace for propylene polymerization at 90°C under 0.1 (— -) and 0.2 (——) bar.

very rapidly and the initial rate, which is difficult to measure, remains low.

A pulse technique was then used, and the trace of the recorder is a series of peaks of decreasing height. However, owing to the amount of monomer consumed at the beginning of the process through reduction of the chromium oxide and oligomerization, the error on the first peaks is rather large and an extrapolation procedure is questionable.

RESULTS WITH CATALYST WITHOUT PRETREATMENTS

The technique finally adopted was to work under a moderate pressure of 1 bar with a modified system wherein the gas stream of pure monomer goes through the two branches of the catharometer. A calibration procedure was then necessary to determine the exact consumption of the monomer. A certain time is necessary to establish the equilibrium conditions of flow, so the measurement of the rate is only possible after about 1 min. The value obtained after that time was adopted as a measure of the initial rate. The influence of the oligomerization process, which is important chiefly at the very beginning of

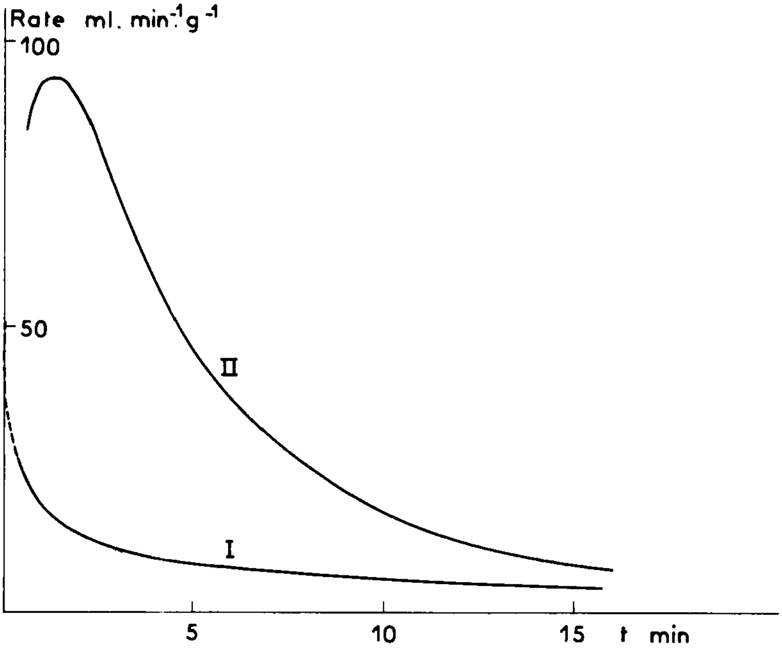

FIG. 2. Rate of polymerization at 90°C under 1 bar pressure for propylene (I) and ethylene (II).

contact with the monomer, is then minimized. Further, under a pressure of 1 bar, the amount of polymer formed is most important, so that the consumption by the oligomerization is not important and is even, at low temperature, negligible. Thus the amount of polymer formed may be compared with the measured polymerization rate. A typical polymerization curve is illustrated in Fig. 2 (Curve I).

Several results are reported in Table 1. It may be seen that there is a rather good correspondence between the results obtained under 1 bar and under 50 bars pressure. The activity is rather bad and may be null if the support is pure silica or contains only a small percent of residual alumina (after a dealumination treatment by HCl [2]). For catalysts based on silica-alumina with 13.5% alumina, the maximum activity is obtained for a chromium content of about 4% instead of the 6% for experiments carried out under 50 bars. Here, as well as for 50 bars experiments, the activity depends very much on the magnitude of the rate of flow of the gas stream of activation. It is advantageous to use oxygenated gas at a high flow-rate. After such an activation treatment the average oxidation degree of the chromium

TABLE 1. Activity of Various Catalysts

Solid support		Activation conditions, air, 4 hr, 550°C, hourly spatial velocity (HSV)	Differential reactor, 1 bar pressure			Static reactor, 50 bars pressure, 84°C,
% Al_2O_3	% Cr		Temp (°C)	Rate (1 min) [ml/(min)(g)]	Overall yield (15 min) (mg polymer/g catalyst)	rate constant × 10^5
0 (silica)	2.5	500	90	6.8	122	0
0.015	0	500	90	0		0
0.015	2.35	500	90		68	3
0.015	6	500	90	6.7	84	
0.25	2.3	500	90	6.4	65	2.6
1.9	3	500	90	10.8	125	3.5
13.5	0	500	90	1.4	0.2	Oligomerization
13.5	0	500	145	3.9	68	Oligomerization
13.5	1	500	90	10.2	58	10 and oligomerization
13.5	2	500	90	13.1	80	4
13.5	5	500	90	12.5	121	17,2
24.8	3	500	90	7.2	63	3.5
13.5	3.6	0[a]	90	7.2	70	1.6
13.5	3.6	200	90	7.6	61	4.2
13.5	3.6	250	90	7.6	63	6
13.5	3.6	400	90	12.5	120	10.5
13.5	3.6	450	90	16.0	221	13
13.5	3.6	450	145	3.6	20	
13.5	3.6	500	90	18.3	214	16
13.5	3.6	500	145	4.1	23	

[a] In N_2.

is close to six. Finally there is a dramatic drop of activity when the temperature increases from 90 to 145°C. The drop is, however, less important under 1 bar than under 50 bars. Other experiments have shown that the activity decreases by lowering the temperature and becomes negligible at room temperature. However, measurements at low temperature become inaccurate because much of the monomer is physically adsorbed. An estimate of the activity may be obtained through surface area measurement, as shown in a further section of this paper.

A few experiments have been carried out with this apparatus for ethylene polymerization. A kinetic curve is illustrated in Fig. 2 (Curve II). As in the case of experiments carried out previously [6] under 0.1 bar pressure, a maximum rate, which has been related to be catalytic activity, is observed, but it is reached after a shorter time because the reduction process by the monomer, which is the last step of the activation, is a function of the monomer pressure. The results obtained are reported in Table 2. Compared to the results obtained before [6], it may be seen that the optimum temperature is in the range of 90 to 120°C. The drop of activity at 145°C is very low compared with that observed in propylene polymerization.

TABLE 2. Ethylene Polymerization (Differential Reactor, Pressure 1 bar)

			Activity	
% Al_2O_3	% Cr	Temp (°C)	R (1) [ml/(min)(g)]	Overall yield after 15 min (mg polymer/g catalyst)
13.5	3.6	90	43.5	355
13.5	3.6	120	105	383
13.5	3.6	145	100	377
0.25[a]	2.3	90	55.8	566
0.25	2.3	145	60.8	400
Silica	2.5	90	53.1	220
(Davidson)	2.5	145	58	263

[a] Through dealumination of silica-alumina 13.5% Al_2O_3.

TABLE 3. Effect of Pretreatment with H_2 at 295°C (or C_2H_4 at 250°C) on Activity

Duration (min) of pretreatment	0	11.75	12.5	12.66	12.8	13	0.5[a]
Activity [mmole/(min)(g)(bar)]	1-1.5	3.65	4.5	5.2	5.5	3.9	8

[a] With ethylene.

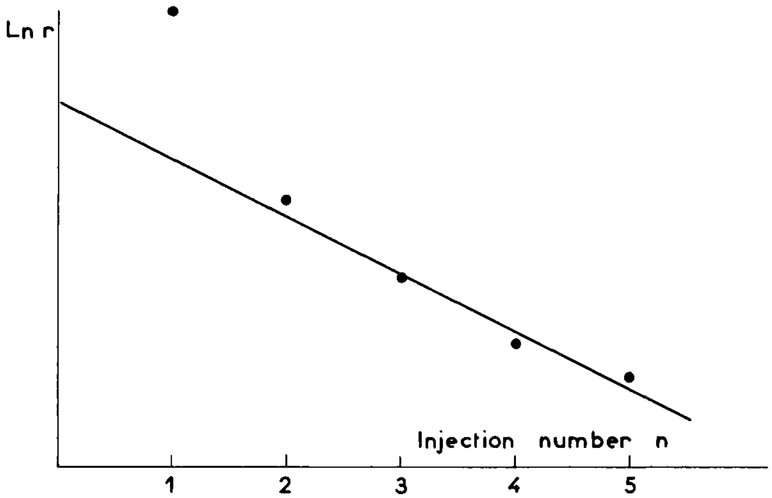

FIG. 3. Measurements of the rate of polymerization at 90°C with the pulse technique.

RESULTS WITH CATALYST PREHEATED IN THE PRESENCE OF ETHYLENE

It has shown in the case of ethylene polymerization that a reduction treatment, carried out under proper conditions, leads to a maximum activity. This is also true for propylene (Table 3). The best conditions used throughout this section involve a short time (30 sec) at a high temperature (250°C) of exposure to ethylene. Such a treatment eliminates the monomer consumption caused by the reduction of the catalyst. It is then possible to use the pulse method described in the preliminary results. The pulse time is 10 sec with a mixture of helium (20 ml/min) and propylene (40 ml/min). A plot of the logarithm of the conversion ratio r [7] vs the number of injection gives, as shown in Fig. 3, a reasonable straight line if one neglects the first point where oligomerization is important. This line first shows that the law of the decrease of activity vs time is exponential, as in the case of ethylene polymerization, and second that it is possible to obtain the value of the initial rate by extrapolation to zero pulse.

The influence of monomer pressure, i.e., the order of the reaction vs the monomer, has been studied at 90°C, using successive pulses of two very different partial monomer pressures. It is then observed that the conversion remains unchanged; this means that the reaction obeys a first-order law. At lower temperatures, it is possible to measure directly the conversion, as in the case of ethylene polymerization. A first-order law is again observed at 65, 50, and 23°C. It is not possible to carry out measurements at lower temperature owing to the physical adsorption of propylene. Thus the saturation phenomena (zero order) observed for ethylene polymerization at low temperatures is not present in the case of propylene. In this case a first-order law remains valid in a large range of pressures (0.1 to 50 bars) and temperatures (20 to 90°C).

The influence of temperature on the polymerization rate constant is reported in Table 4. It corresponds to an apparent activation energy of 10 kcal/mole instead of about 0 to 6 kcal/mole as found for ethylene polymerization. As shown in Fig. 4, at high temperature the rate is initially high but drops very rapidly. The oligomerization process is increasingly important so that the measurement of the polymerization rate becomes indefinite. However, the situation is very different from that observed in the previous section, without pretreatment, where the polymerization activity at 145°C was negligible.

In spite of the rapid drop of the activity with increasing time, the catalyst remains active for ethylene polymerization at 0°C without an induction period (Table 5). Thus the sites are neither destroyed nor poisoned, but have been stabilized by the ethylene pretreatment.

A long exposure to propylene at high temperature is necessary to cause deactivation of the catalyst.

TABLE 4. Effect of Temperature on Rate

Temp, °C	21	50	65	90
k [mmole/(min)(g)(bar)]	0.24	1.26	1.80	5.5

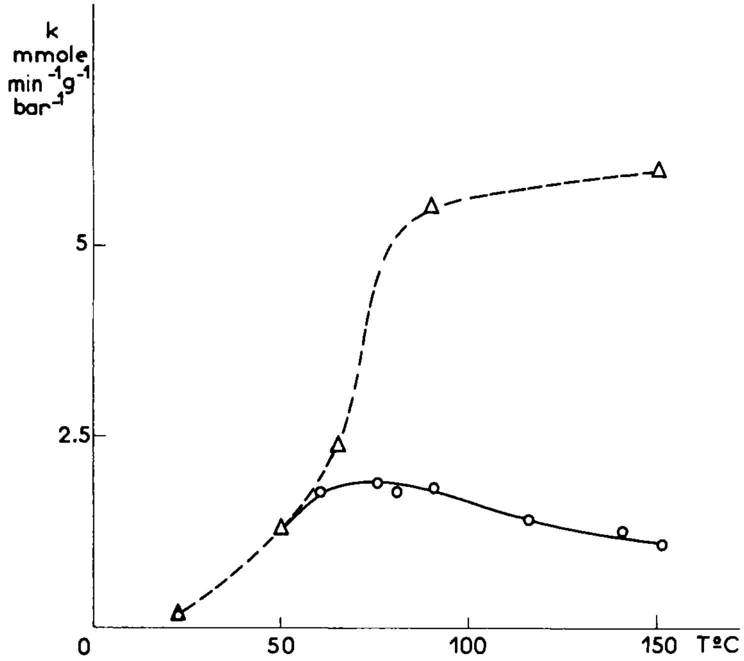

FIG. 4. Activity: initial (△) and after 2 min of propylene polymerization at 0.1 bar pressure (○).

TABLE 5. Rate Constant at Various Temperatures after 2 min Polymerization of Propylene and Rate Constant at 0°C for Ethylene

Temp, °C	75	95	115	140	150
k propylene	1.92	1.85	1.45	1.31	1.12
k ethylene	7.85	9.07	9.74	5.65	3.46

SURFACE AREA MEASUREMENTS

In a previous paper [6] related to ethylene polymerization, it was shown that the decrease of activity, after the maximum plateau value had been reached, was related to a blocking of the active site by the polymer produced, which spreads over the surface of the carrier so that the surface area is decreased. In the case of propylene polymerization, dynamic measurements of nitrogen adsorption at different

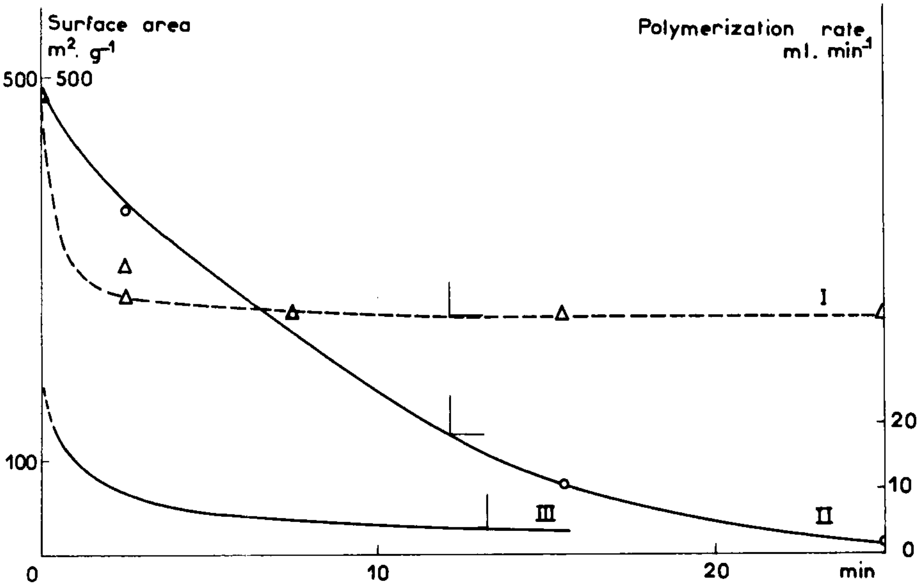

FIG. 5. Evolution of the surface area of the catalyst vs time at a 1-bar pressure propylene polymerization at 145°C (I) and 90°C (II) and the rate at 90°C (III).

steps of the reaction again show a drop of the surface area down to a very low value after half an hour reaction time. Typical curves of surface area, together with polymerization rate, vs time are illustrated in Fig. 5. At 90°C the drop of surface area is rather slow but complete (after about 30 min). At 145°C the drop is very rapid but a large area remains uncovered. At the same temperature there is no change in surface area with a silica-alumina support (without chromium) which is a very active oligomerization catalyst. Thus the surface area drop is caused by the polymer. Some results are reported in Table 6. There is some correlation between the catalytic activity and the surface area drop. This observation shows that the catalyst is active at low temperatures where direct measurements are not possible owing to physical adsorption of the monomer. It is interesting to note a maximum in surface area drop at 0°C; possibly the amount of monomer available at the site may be increased by physical adsorption, and then the catalyst may work in conditions closer to the saturation of the surface with monomer.

TABLE 6. Decrease of the BET Surface Area of the Catalyst after Various Polymerization Reactions

Solid	Reaction	Surface area (m^2/g)
Silica-alumina (Ketjen)	Initially	620
	After oligomerization (30 min)	620
This support with 3.6% Cr	None	450
"	After 7 min at 90°C	224
"	After 30 min at 90°C	10
"	Pretreatment and 7 min at 90°C	186
"	After 30 min at 20°C	353
"	After 30 min at 0°C	260
"	After 30 min at -15°C	292
"	After 7 min at 145°C	240
"	After 30 min at 145°C	240

CONCLUSIONS

The measurement of catalytic activity vs polymerization at low pressure is much more difficult in the case of propylene than in the case of ethylene. The main reasons are the rapid drop of catalytic activity vs time and the presence of secondary processes (oligomerization and reduction). In the absence of pretreatment the results are comparable with those obtained previously under high pressure, and they support the previous conclusion that the active sites are different for the two monomers considered. However, reduction pretreatment with ethylene leads to an optimal polymerization rate in exactly the same conditions as for ethylene, and the covering process with the polymer also obeys the same law. These results, in spite of the differences noted for the reaction order and for the influence of temperature, might indicate that the active site are the same. A full discussion of the comparison of the behavior of the two monomer is given in the next paper of this series.

REFERENCES

[1] H. Charcosset, A. Revillon, and A. Guyot, J. Catal., 8, 326 (1967).
[2] H. Charcosset, A. Revillon, and A. Guyot, Ibid., 8, 334 (1967).
[3] A. Guyot and J. C. Daniel, J. Polym. Sci., A1, 2989 (1963).
[4] A. Revillon and A. Guyot, J. Chim. Phys., 65, 845 (1968).
[5] A. Revillon, A. Guyot, and Y. Trambouze, Ibid., 65, 849 (1968).
[6] G. Vuillaume, A. Revillon, R. Spitz, and A. Guyot, J. Macromol. Sci.—Chem., A5, 559 (1971). Part V of this series.
[7] R. Spitz, G. Vuillaume, A. Revillon, and A. Guyot, Ibid., A6, 153 (1972). Part VI of this series.
[8] R. Spitz, Ibid., A6, 169 (1972). Part VII of this series.
[9] R. Spitz, A. Revillon, and A. Guyot, J. Catal., In Press. Part VIII of this series.
[10] R. Spitz, A. Revillon, and A. Guyot, J. Macromol. Sci.—Chem., A8, 1129 (1974). Part XI of this series.

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