

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Supported Chromium Oxide Catalyst for Olefin Polymerization. V. Measurement of Catalytic Activity in an Integral Dynamic Reactor

G. Willaume^a; A. Revillon^a; R. Spitz^a; A. Guyot^a

^a Institut de Recherches sur la Catalyse C.N.R.S., Lyon, Villeurbanne, France

To cite this Article Willaume, G. , Revillon, A. , Spitz, R. and Guyot, A.(1971) 'Supported Chromium Oxide Catalyst for Olefin Polymerization. V. Measurement of Catalytic Activity in an Integral Dynamic Reactor', Journal of Macromolecular Science, Part A, 5: 3, 559 — 573

To link to this Article: DOI: 10.1080/00222337108061044

URL: <http://dx.doi.org/10.1080/00222337108061044>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Supported Chromium Oxide Catalyst for Olefin Polymerization. V. Measurement of Catalytic Activity in an Integral Dynamic Reactor

G. VUILLAUME, A. REVILLON, R. SPITZ, and A. GUYOT

Institut de Recherches sur la Catalyse

C.N.R.S.

Lyon-Villeurbanne, France

SUMMARY

An integral dynamic reactor has been used for the continuous measurement of the instantaneous polymerization rate. With ethylene as monomer, the rate goes through a maximum after a few minutes, then levels off, and finally decreases owing to the blocking of the surface by the polymer. The catalytic activity may be calculated safely from the maximum instantaneous rate, after correction for the monomer consumption along the column of catalyst. As examples of application, it is shown that the catalytic activity goes through a maximum with either the chromium content at a fixed temperature of polymerization or with the temperature at a fixed chromium content.

INTRODUCTION

Although a great deal of work has been carried out on olefin polymerization with supported chromium oxide as catalyst [1], little attention has been paid to the correct definition and measurement of the catalytic

activity. It is estimated by most authors as an average value, for instance, the amount of polymer produced after a fixed time, and obviously such a measurement has poor reliability. Better results have been obtained by measuring the decrease of monomer pressure, and a number of studies have been made using a static reactor charged with dry catalyst and monomer [2-5]. In this case the results may be strongly dependent on the blocking of the catalyst surface with a film of polymer and also on an uncontrolled temperature increase due to the heat of polymerization. These difficulties are partially avoided in solution or suspension [6-10], but it has been shown that the curve has a complex shape, with the rate going through a maximum and then decreasing to a plateau value with half the maximum value. Therefore catalytic activity is not easy to define; for example, Ermakov [7] expressed it as the average amount of polymer produced per unit of time for the whole process.

Other methods have been used: weight of polymer formed as measured by a recording microbalance [11, 12] or gas chromatographic analysis of samples picked up from the reactor which contains propane as an internal concentration reference [13, 14]. In both cases the system was a static one with the inconveniences mentioned above. Clark et al. [15] polymerized in a dynamic reactor where the gaseous monomer passed through a column of catalyst and was detected and measured with a filament catharometer. With such a system the polymerization rate may be measured continuously, but unfortunately Clark gives no details about the shape of the rate curve and thus on the values chosen for measurement of the catalytic activity. Moreover, due to the rather large amount of catalyst used (several grams), it is possible that the difficulties of the static system were not avoided.

We improved the method of Clark by using conditions under which the catalyst is fluidized by the stream of diluted monomer in an inert gas. In this way the temperature is well controlled and the sticking of catalyst grains is avoided until polymerization is well advanced. The other advantages of the reactor are the possibilities of carrying out the activation process *in situ*, to regenerate the catalyst after poisoning, and finally to measure the surface area. Based on the shape of the polymerization curve, a reliable method of measuring the catalytic activity is described, discussed, and applied to a few problems.

EXPERIMENTAL

Apparatus

An inert carrier gas (high purity helium: 5 ppm O_2 , H_2O), purified through molecular sieves (Union Carbide 5 Å), flows through the reference cell C_R of a catharometer (GOW MAC W2X), and then is mixed with a stream of purified ethylene in a special mixing chamber (Fig. 1a) designed similarly to the injection chamber of a gas chromatograph. After a final purification step, the gas passes through a U-shaped reactor (U_3 in Fig. 2)

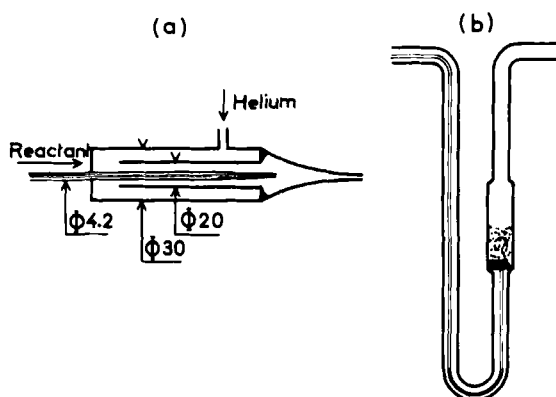


Fig. 1. (a) Design of the glass mixing chamber. (b) Design of the polymerization cell.

and finally into the measuring cell C_M of the catharometer. The detailed scheme of the apparatus is given in Fig. 2. The monomer may be replaced by nitrogen or air for the measurement of the surface area and for the activation or the regeneration of the catalyst. Each flow is controlled by means of a Brooks Flow-meter B and may be measured accurately by means of soap-bubble flow-meter D. The purification U tubes are filled with a hydrogen-reduced supported catalyst, inactive in ethylene polymerization, at liquid nitrogen temperature (U_1) or glass wool at Dry Ice temperature (U_2). The reactor (U_3) is placed in a temperature-controlled oven; its detailed shape is shown in Fig. 1b. It has a U tube with a capillary entrance. A larger reaction chamber at the bottom of the U tube contains a few glass beads which prevent the powdered catalyst from going down; actually, the stream of gas keeps the catalyst in a fluidized bed. Different taps (V_1 to V_4) allow all the necessary circuits to be established.

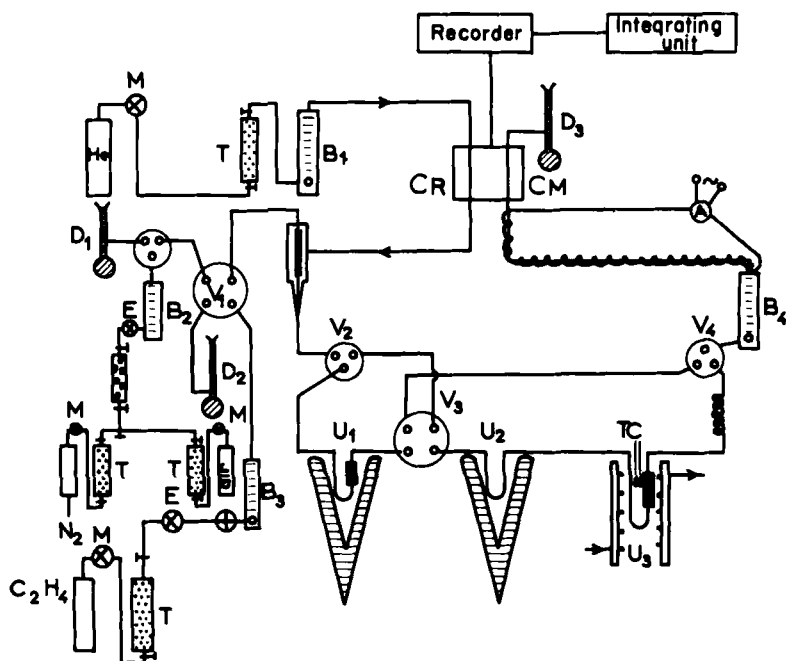


Fig. 2. General scheme of the apparatus. (B_1 to B_4) Brooks float-flow meters. (D_1 to D_3) Soap-bubble flow meters. (M) Manometer. (E) Precision tap. (V_1 to V_4) Taps. (TC) Thermocouple. (C_R, C_M) Catharometer (reference and measure). (T) Molecular sieves. (U_1 to U_3) U-shape cells, purification and polymerization.

Catalyst

The catalyst is prepared as described before [16] by impregnating a silica-alumina carrier with a solution of chromic acid. It is activated independently or in situ by treating with air at high temperature (generally 550°C). Initially it has to be reactivated by being treated with dry helium at 350°C for at least 4 hr before contact with the monomer. If the amount of polymer is not too large, the catalyst may be regenerated by treating with air at 550°C for 2 hr.

The average oxidation number of the catalyst after treatment is measured by water-soluble chromium oxide titration as described before [16].

Polymerization

The catalyst (less than 1 g) is activated in the U_3 cell, and the temperature

fixed to the desired value under a stream of helium, then the gas mixture containing the monomer (generally helium, 65 ml/min, and ethylene, 6.5 ml/min) first goes directly to the measuring cell. The deviation H (Fig. 3, Curve a) increases rapidly and levels off after 1 min to a straight line which is the zero conversion line. Then by proper handling of the taps V_3 and V_4 ,

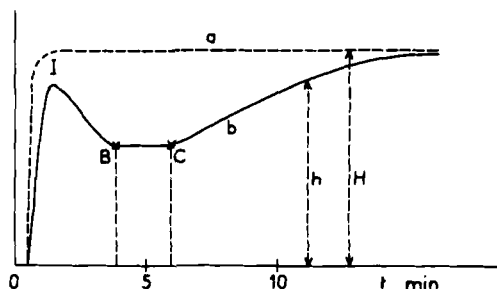


Fig. 3. Deviation of the catharometer. Curve a: Without active catalyst. Curve b: Conversion curve during polymerization. See text for identification of I, B, C, H, and h.

the mixture is flushed through U_2 and U_3 and the measuring cell which gives a deviation h . The shape of the complex curve is shown in Fig. 3, curve b. The equation $Y_t = (H - h)/H$ gives the instantaneous conversion at time t . It goes through a first minimum at Point I (about 1 min) to a maximum plateau value between B and C, after 5 to 15 min, and finally decreases slowly to zero conversion in 1 hr.

Surface Area Measurements

The adsorbate is either nitrogen or ethylene. With nitrogen, the gas mixture first flows through cell U_1 at -196°C and then through cells U_2 and U_3 at room temperature. When a fixed deviation has been obtained, cell U_3 is dipped in liquid nitrogen. The adsorption of nitrogen causes a deviation of the catharometer, which is nul after saturation of the surface. The amount of adsorbed nitrogen is obtained from the integrating unit. The surface area is obtained by comparison with the adsorption of a product of known surface area (silica-alumina Ketjen with 13,5% alumina, $620\text{ m}^2/\text{g}$). With ethylene as adsorbate, the temperature of adsorption is fixed at -100°C and the same method is used. The results of the two sets of experiments were similar, and it may be concluded that measurement with liquid nitrogen correctly described the accessibility of the catalyst to the monomer molecule.

RESULTS AND DISCUSSION

Shape of the Conversion Curve. The consumption of the ethylene comes from either adsorption or oxidation or polymerization. At the polymerization temperature (around 100°C), adsorption is rapid and negligible as shown by experiments with reduced, inactive catalysts. Complete reduction of the catalyst corresponds to a weak consumption of ethylene (4 mg/g of a typical catalyst with 3.6% chromium of an initial average oxidation number, AON, of 5.6). Figure 4 shows the results of the study of the AON

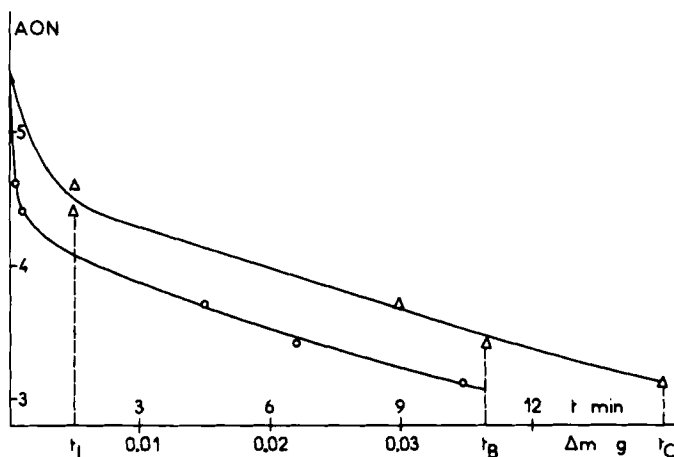


Fig. 4. Average oxidation number (AON) vs. time (Δ) or total amount of ethylene consumed (\circ).

during polymerization at 145°C , together with the amount of ethylene consumed vs. time. It may be seen that the reduction is at first very rapid and then progresses more slowly to be practically complete when the rate begins to decrease (Point C). Between Points B and C the consumption of ethylene by reduction may be practically neglected and then is due only to polymerization. The reduction rate depends on the temperature and, for instance, at 90°C the AON at Point C is 4.3 instead of 3.1 at 145°C .

From Figure 4 it may be supposed that the rise in activity is directly related to the reduction of the chromium oxide. However, another possibility is the desorption of the oxidation products which may act as poisons for the catalyst site. Actually the time t_B necessary to reach the maximum decreases with increasing temperature but increases with the weight of catalyst

engaged. The two first points indicate either a reduction or a desorption, but the last point favors desorption.

The desorption products have been studied by a set of thermodesorption experiments. In each trial polymerization was stopped after time t and, after flushing 5 min with pure helium at the polymerization temperature, the thermodesorption was carried out up to 350°C. A chromatographic peak was observed at 320°C. Analysis of the gas by mass spectroscopy (Atlas, Chapter 4) indicates, in agreement with the results of Hill [17], that the major product was CO₂, then H₂, and finally CO in a minor amount. Less oxidized products such as aldehydes were absent. The relative amount of CO₂ was largest if the polymerization was stopped before Point B, so that it may be supposed that CO₂ was slowly desorbed by the gas stream. Finally, it may be concluded that the final activation process is accomplished by the monomer by proper reduction of the chromium oxide sites and that the total development of the activity involves the desorption of the oxidation products.

After the maximum rate has been reached, the decrease may be due to either a deactivation process or a blocking of the sites by the polymer. Surface area measurements indicate the second process is the responsible one. Typical results, illustrated in Fig. 5, clearly show a parallelism between the residual rate and the residual area. Such results do not depend on the polymerization temperature from 80 to 160°C, i.e., on each side of the melting range of the polyethylene crystallites. It may also be seen that the blocking of the total surface is very limited at Points B and C.

From all these results we suggest that, in a first approximation, the maximum specific conversion $(Y_t)_{\max}/m$, where m is the mass of the catalyst engaged, would be a correct measurement of the catalytic activity. A more precise value will be deduced in the next section.

Effect of the Experimental Conditions. The parameters studied here are the mass of the catalyst m , the flow rate, the monomer pressure p , and the temperature. All the results are relative to the same catalyst defined as follows: a support, silica-alumina Ketjen 13.5% Al₂O₃, 3.6% chromium, activated either independently at an AON of 5.6 and reactivated before use in situ under a helium stream at 350°C, or directly in situ.

Mass of the Catalyst

The catalyst was diluted with nonporous glass beads in order to determine if the reaction was diffusion-controlled. The results are shown in Fig. 6.

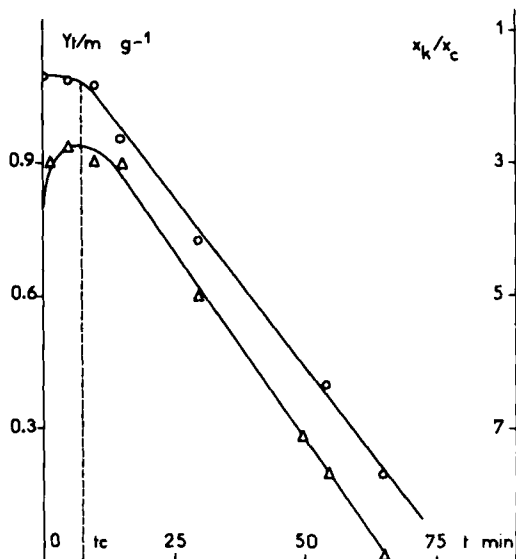


Fig. 5. Comparative evolution of the instantaneous specific conversion Y_t/m (Δ) and the relative surface area (\circ) [ratio of the surface areas of the reference solid Ketjen (x_k) to the actual catalyst (x_c)] (0.5 g catalyst, temperature 90°C)

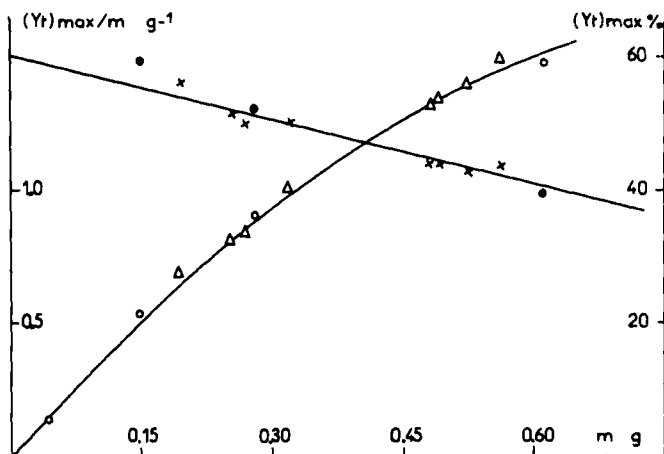


Fig. 6. Plots of $(Y_t)_{\text{max}}$ (Δ , undiluted; \circ , diluted) and $(Y_t)_{\text{max}}/m$ (\times , undiluted; \bullet , diluted) vs. m ($T = 145^\circ\text{C}$, ethylene pressure 0.09 bar). Catalyst with 3.6% chromium.

The maximum specific conversion increases when the catalyst mass decreases. The points corresponding to the diluted catalysts follow the same pattern, and thus it may be concluded that the reaction was not diffusion-controlled. The results correspond to the typical behavior of an integral dynamic reactor when the instantaneous conversion is high (in our experiments it rises up to 60%). This may be easily explained by the existence of a monomer concentration gradient along the catalyst column. As will be shown below, it may be assumed that, when the maximum rate has been reached, the specific conversion ratio τ is constant through the whole column of height l , area S , volume V , and average density ρ . If C_0 is the initial monomer concentration and C_x is the monomer concentration at a distance x from the bottom of the column, we can write:

$$-dC_x = Sdx\rho\tau C_x \quad (1)$$

Upon integration

$$C_x = C_0 e^{-S\rho\tau x} \quad (2)$$

The final concentration C_1 is related to Y_t by

$$Y_t = (C_0 - C_1)/C_0$$

Then

$$Y_t = 1 - e^{-Sl\rho\tau} = 1 - e^{-m\tau} \quad (3)$$

Expanding the exponential and rearranging gives

$$Y_t/m = \tau - m\tau^2/2 + \dots \quad (4)$$

Equation (4) defines a straight line which is a good approximation of the relationship between Y_t/m and m . This holds for low values of m , i.e., for the poorly active catalysts. For the best catalysts, Equation (3) must be used after rearrangement

$$m\tau = \ln(1/(1 - Y_t)) = \ln H/h \quad (3')$$

So the exact conversion is expressed as $\tau = (1/m) \ln H/h$. The differences between τ and $(Y_t)_{\max}/m$ are largest for the more active catalysts.

Flow Rate

If at constant temperature and monomer partial pressure the flow rate of the gas stream is increased, the concentration gradient along the catalyst column is expected to decrease and so is the monomer conversion. The maximum specific polymerization rate R , which is the product of $(Y_t)_{\max}/m$ and the monomer flow rate D , increases and becomes closer to the corrected value τD . The results, illustrated in Fig. 7, agree with that view, and it may be shown that τD has a constant value independent of the catalyst mass and the monomer flow rate.

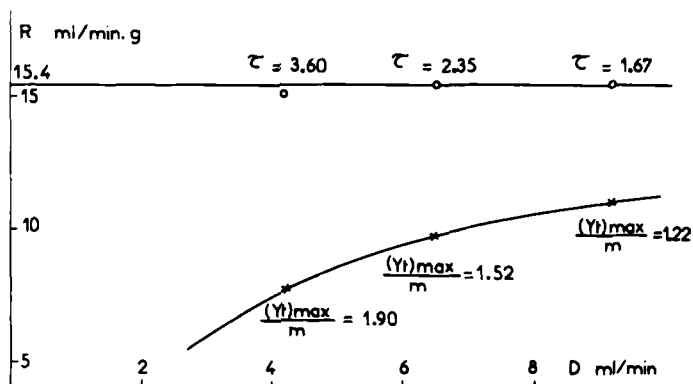


Fig. 7. Maximum specific polymerization rate (X) and product D (O) vs. the monomer flow rate τD . Temperature 145°C , catalyst weight 0.4 g, ethylene pressure 0.09 bar.

These results confirm that the maximum specific polymerization rate R is a correct measurement of the catalytic activity of a given catalyst.

Monomer Pressure

The value of τ depends on the monomer pressure p_E according to a complex law. It is proportional to p_E for low values of p_E and becomes independent of p_E for values larger than 0.09 bar. This means that the reaction is second-order vs. monomer concentration for low values and becomes first-order beyond a certain limit. The rate τD may be described by $\tau D = R = Ap_E^2/(1 + Bp_E)$. A plot of p_E/R vs. $1/p_E$ is linear (Fig. 8). Apparently these results make the assumption that τ is constant along the catalyst column incorrect if the monomer pressure is close to the critical value of 0.09 bar. However, in order to check our assumption the following

experiment has been made: with an initial monomer pressure of 0.1 bar, polymerization was carried out up to the maximum rate (Point B). The monomer pressure was then decreased in two steps to 0.045 and 0.035 bar successively. The conversion Y_t was unchanged. Thus, because the catalyst is in a fluidized bed, each catalyst particle may be activated at the maximum ethylene pressure at the bottom of the column, and the hypothesis of a constant value of τ is justified.

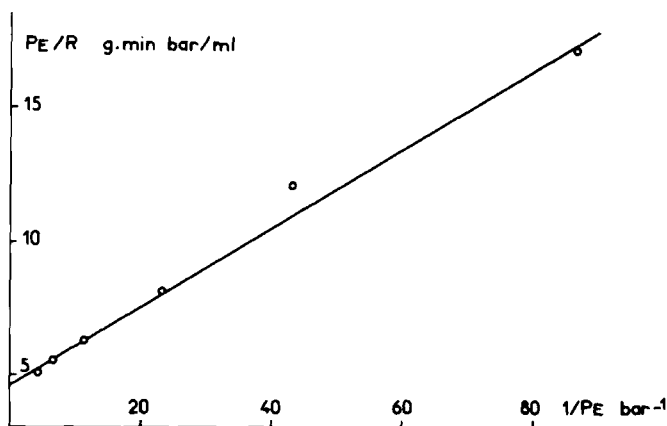


Fig. 8. Plot of p_E/R vs. $1/P_E$. Temperature 145°C.

Finally, it may be concluded that the propagation reaction is actually first-order vs. the monomer concentration, but the extent of the initiation reaction is proportional to the monomer concentration at low monomer pressure.

Our kinetic results are similar to those reported by Schindler [18] for ethylene polymerization with Ziegler catalysts. In this case the results have been explained on the basis of a spontaneous transfer reaction yielding inactive Cat . . . H sites which may be reactivated upon reaction with monomer to active Cat . . . CH_2-CH_3 sites. This mechanism leads to one vinyl and one methyl group chain ends. Although it is known [1] that these are the chief chain ends in Phillips polyethylene, the mechanism suggested by Schindler cannot be applied to the Phillips catalyst because it disagrees with the last experiment described above. Here, the value of the monomer pressure affects only the first reaction but not a possible reactivation reaction taking place after a possible transfer step. The reasons for the monomer dependence of the activation reaction are not clear now and will be discussed in a later paper.

The results given in the literature for the reaction-order vs. monomer concentration are varied [2, 5, 19]. Depending on the experimental conditions, values between 0 and 2 have been reported.

Temperature

A number of studies have mentioned a maximum of catalytic activity with temperature, but the position of the maximum is located either at 20°C [2], or 70-80°C [20, 21], or even at around 100°C [4]. The discrepancies in the published results may come from differences in the methods of measurement and evaluation of the catalytic activity, and from other causes, i.e., the activation process and the purification of the reactants.

For a catalyst activated in situ at 550°C under a stream of nitrogen (AON 4.5), the results illustrated in Fig. 9 show a sharp maximum between 90 and 120°C. But if the catalyst was activated independently at 550°C under an air stream and reactivated in situ by treatment at 350°C under an helium stream, the activity was greater at 145°C than at 90°C. The purification is also very important. In the absence of the U₂ cell the value of τ drops only from 1.6 to 1.3 at 145°C but becomes null at temperature below 40°C.

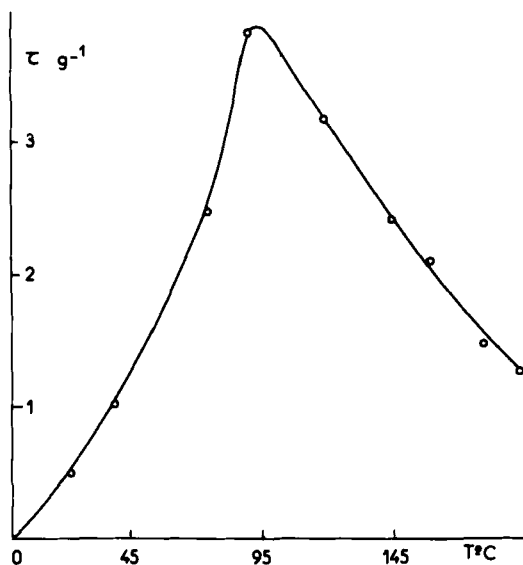


Fig. 9. Corrected specific maximum conversion τ vs. temperature (catalyst with 3.6% chromium activated in situ at 550°C under a stream of nitrogen, pressure 0.09 bar).

The existence of the maximum is probably due to an optimum reduction state which allows either a maximum amount of chromium atoms to be at intermediate oxidation number as suggested by several authors (for instance, Ref. 4) or a better dispersion state of the chromium oxide on the surface of the carrier. Further work, in progress in our laboratory, supports this explanation.

Application

This definition of the catalyst activity, expressed by the corrected value τ of the maximum instantaneous (at constant flow rate) conversion, has been applied to a few studies. The influence of the chromium content of the catalyst on τ has been determined. The results are shown in Fig. 10 for a

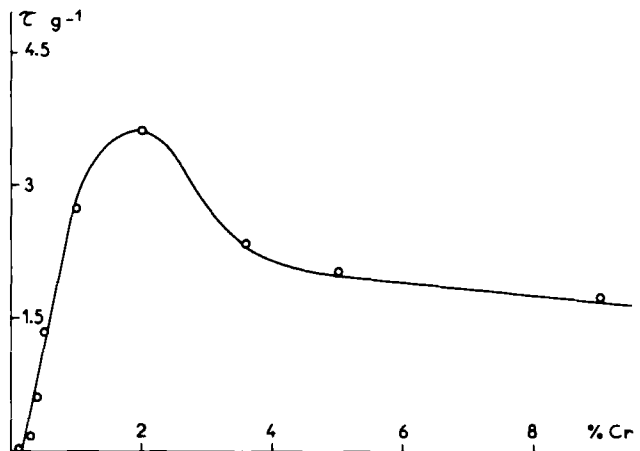


Fig. 10. Specific activity τ as a function of the chromium content. Temperature 145°C, pressure 0.09 bar.

temperature of 145°C. In agreement with various authors [1], the activity rises proportionally to the chromium content and goes through a maximum for 2% chromium. It has also been shown that, for the same chromium content and the same activation conditions, activity does not depend on the impregnation compound [CrO_3 , $(\text{NO}_3)_3\text{Cr}$, or $\text{Na}_2\text{Cr}_2\text{O}_7$] contrary to the results reported by Zul'fugarov et al. [22, 23].

CONCLUSION

The maximum instantaneous ethylene conversion, after correction for the concentration gradient along the catalyst column in a dynamic integral reactor, gives a reliable measure of the catalytic activity. The monomer pressure must be greater than a critical value necessary for the complete activation of the sites. This maximum rate is obtained after proper reduction of the chromium oxide by the monomer and probably also after desorption of the oxidized products which may act as poisons. It can be maintained for only a limited time because of the blocking of the surface by the polymer. The value of the maximum is very sensitive to the experimental conditions and also, as will be shown in the next paper in this series, to the activation conditions.

REFERENCES

- [1] A. Clark, *Catal. Rev.*, **3**, 145 (1969).
- [2] P. B. Ayscough, C. Eden, and H. Steiner, *J. Catal.*, **4**, 278 (1965).
- [3] C. Eden, H. Feilchenfeld, and Y. Haas, *J. Catal.*, **9**, 367 (1967).
- [4] V. B. Kazansky and J. Turkevitch, *J. Catal.*, **8**, 231 (1967).
- [5] K. Tarama, J. Yoshida, and Y. Doi, Fourth International Congress on Catalysis, Moscow, 1968, Paper 13.
- [6] K. G. Miessero, *J. Polym. Sci., Part A-1*, **4**, 3047 (1966).
- [7] Yu. I. Ermakov, L. P. Ivanov, L. Ya. Al'T, A. I. Gel'bshtein, and V. G. Anufrienko, *Kinet. Katal.*, **9**, 352 (1968).
- [8] Yu. I. Ermakov and V. A. Zakharov, Fourth International Congress on Catalysis, Moscow, 1968, Paper 16.
- [9] H. L. Whitaker and G. B. Wills, *J. Appl. Polym. Sci.*, **13**, 1921 (1969).
- [10] L. H. Krauss, E. Weber, and N. Mövik, *Z. Anorg. Allg. Chem.*, **338**(3-4), 121 (1965).
- [11] J. Habeshaw and T. Hill, in *Proceedings of the Third International Congress on Catalysis* (Sachtler, Schuit, and Zwietering, eds.), North-Holland, Amsterdam, 1965, p. 975.
- [12] V. C. F. Holm and A. Clark, *J. Catal.*, **11**, 305 (1968).
- [13] A. Guyot and J. C. Daniel, *J. Polym. Sci., Part A*, **1**, 2989 (1963).
- [14] A. Revillon and A. Guyot, *J. Chim. Phys.*, **65**, 845 (1968).
- [15] A. Clark, J. N. Finch, and B. Ashe, in *Proceedings of the Third International Congress on Catalysis* (Sachtler, Schuit, and Zwietering, eds.), North-Holland, Amsterdam, 1965, p. 1010.

- [16] H. Charcosset, A. Revillon, and A. Guyot, *J. Catal.*, **8**, 326, 334 (1967).
- [17] T. Hill, Communication at the "Congress of Industrial Chemistry," Paris, 1968.
- [18] A. Schindler, *J. Polym. Sci., Part C*, **4**, 81 (1964).
- [19] Yu. I. Ermakov and L. P. Ivanov, *Kinet. Katal.*, **6**, 889 (1965).
- [20] M. A. Landau and V. V. Shchekin, *Neftekhimiya*, **3**, 713 (1963).
- [21] V. A. Zakharov, Yu. I. Ermakov, L. P. Ivanov, and V. B. Skomorokhov, *Kinet. Katal.*, **9**, 605 (1968).
- [22] Z. G. Zul'fugarov, L. Sh. Zul'fugarova, E. M. Dzhafarova, E. B. Sharifova, and S. A. Muradova, *Kinet. Katal.*, **9**, 185 (1968).
- [23] G. Vuillaume, Thesis, Lyon, 1970.

Accepted by editor September 15, 1970

Received for publication October 12, 1970