

Hydrogenation of Olefins and Polymerization of Ethene over Chromium Oxide/Silica Catalysts

IV. Kinetics of the Polymerization Reaction

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The kinetics of the polymerization of ethene over chromium oxide/silica catalysts were investigated from 225 to 475 K by two methods, one in which ethene was flowing over the catalyst (dynamic method) and another in which polymerization was carried out in a static atmosphere. Initially the reaction was readily observable, but after a while the polymerization came to a rather sudden stop. The kinetics of the reaction in the initial period were first order in ethene partial pressure. The first-order rate constant increased with temperature up to about 300 K (activation energy 53 kJ/mole) after which it declined until at 475 K hardly any polymerization could be observed. The ultimate amount of polymer formed was maximal at two temperatures, at about 275 K and around 415 K. Starting from the minimum at about 335-365 K, increasing (405 K) and subsequently decreasing the temperature to 273 K led to additional polymer formation. CO was found to be an inhibitor but the inhibition was reversible. Feeding ethene over a CO-poisoned catalyst led to removal of CO, thereby restoring its catalytic activity. The activity of the catalyst depended to a considerable extent on the pretreatment procedure. An extensively reduced catalyst, which showed hardly any activity, could be activated by passing dry helium over it at 775 K. On the other hand, a less extensively reduced and more active catalyst was deactivated by a similar treatment. Models are given for the kinetics and the catalyst (de)activation. The kinetic model combines elements of the mechanism of the polymerization with pore diffusion limitations; the other model explains the (de)activation phenomena in terms of interactions between Cr cations and silanol groups.

INTRODUCTION

In the first paper of this series (1) dealing with the $\text{CrO}_x/\text{SiO}_2$ catalyst, the structure of the catalyst was investigated and a model of its structure was developed. In the present paper studies on the kinetics of the polymerization of ethene on this catalyst are reported.

The kinetics have already been studied

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many times, although not always with similar results. For instance, on varying the temperature some investigators find a maximum activity at -20 to 20°C (2, 3); others locate this maximum at 70 - 100°C (4-7). The pressure dependence of the rate differs between zero (3, 4, 8), one (2-5, 8), and higher (9). Research in this field was directed predominantly toward the influence of the activation conditions and again results and conclusions obtained by the various investigators differ considerably. Therefore polymerization activity was measured in our laboratory according to the two methods that are frequently applied, namely, the dynamic method and the static method.

In the first method ethene flows through the catalyst bed and the amount of residual

ethene after passage over the catalyst is determined. A measure for activity in this case is the amount of polymer formed during a certain time period. The static method consists of measuring the ethene pressure as a function of time; in this case activity can be defined as the rate of the pressure drop.

As in the earlier reported studies (1, 10, 11) the $\text{CrO}_x/\text{SiO}_2$ catalyst used was an ion-exchange catalyst on a silica support; the silica applied had a large surface area ($\sim 500\text{--}600\text{ m}^2/\text{g}$) and a relatively low pore volume ($0.4\text{ cm}^3/\text{g}$). Although probably somewhat similar to the commercial Phillips polymerization catalyst our catalyst may be expected to deviate from it in some important characteristics.

EXPERIMENTAL

Materials

The catalyst preparation was described earlier (1). The catalyst used contained 2.1 or 1.7 wt% Cr (110°C dry) and the particle size was $0.175\text{ mm} < d < 0.60\text{ mm}$ (or 28 mesh $< d < 80$ mesh). The catalyst was calcined in air for 4 hr at 500°C and after that the specific surface area was about 500

m^2/g . The support was Davison silica gel grade 12 (pore volume $0.4\text{ cm}^3/\text{g}$).

Ethene, helium, and carbon monoxide were purified over a copper catalyst to remove oxygen traces and over a molecular sieve bed to remove moisture. Hydrogen was purified by diffusion through a palladium membrane.

Dynamic Method

Helium (space velocity about $90\text{ cm}^3/\text{min}$) was passed through the catalyst bed (1 g of catalyst), which was placed in a U-shaped quartz reactor with a central thermowell and thermocouple. The reactor could be heated up to 500°C , and temperatures below 200°C down to -45°C could be achieved with a liquid bath using various liquids. In this way the temperature could be controlled within 1°C . Prior to the polymerization measurements the catalyst could be reduced by treating it with a controlled number of carbon monoxide pulses (1.39 cm^3 ; 470°C) or ethene pulses (0.60 cm^3 ; 400°C). After the reduction, polymerization was carried out at the desired temperature by feeding an ethene gas stream ($5.60\text{ scm}^3/\text{min}$) together with the carrier gas through the catalyst bed. A heat con-

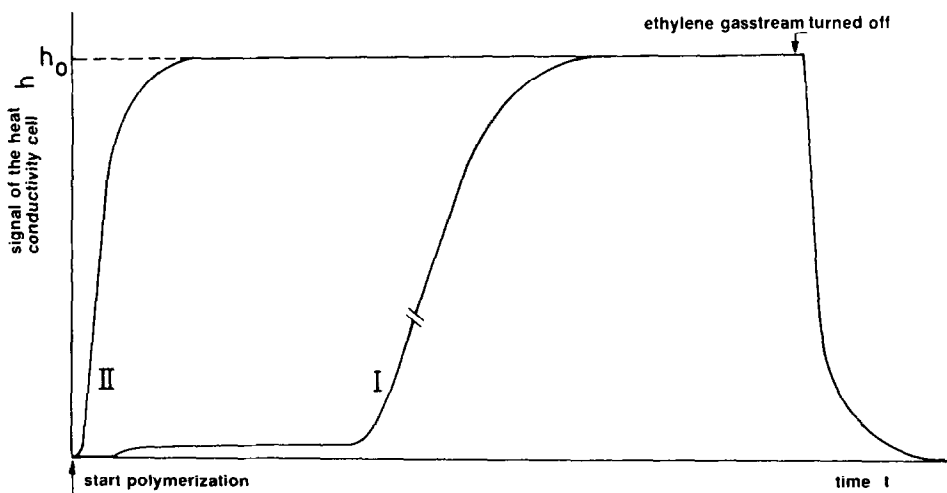


FIG. 1. Example of the signal of the heat conductivity cell during polymerization at 0°C by the dynamic method. Curve I, after activation by CO pulses (1.39 cm^3) at 470°C ; curve II, without activation.

ductivity cell placed in the gas stream behind the reactor measured ethene concentration in the effluent as a function of time (see Fig. 1). It can be seen that at first all ethene was consumed but after a while polymerization activity slowed down and eventually became nil. This effect is generally ascribed to blocking of the active sites by the polymer. The amount of polymer produced between t_1 and t_2 (or the amount of ethene that did not leave the reactor) was calculated as

$$W = \frac{M_e \cdot f}{V_{\text{mol}} \cdot h_0 \cdot g} \left[h_0(t_2 - t_1) - \int_{t_1}^{t_2} h dt \right]$$

(mg/g catalyst),

M_e = molecular weight of ethene (= 28),
 V_{mol} = molar volume at 0°C and 101.3 kPa
 (= 22.4 dm³),

f = gas space velocity of ethene (normally 5.60 scm³/min),

g = weight of catalyst (normally 1 g),

h = detector signal,

h_0 = detector signal when polymerization no longer occurs,

t = time in minutes.

Static Method

The apparatus was a conventional glass system for measuring gas adsorption on solids (12). The volume of the actual reactor was 19.4 cm³ and that of the reacting gas, 731.4 cm³. Pressures were measured using a U-tube mercury manometer. Different reactor temperatures could be achieved by using heating or cooling methods similar to the dynamic method. Reduction of the catalyst was carried out in the system for dynamic measurements, after which the reactor was transported to the apparatus for static measurements under exclusion of air.

Since for practical reasons only 0.1 g of catalyst was used in each experiment, reduction was carried out under more moderate conditions than in the dynamic method. The reduction temperature was 350°C and the carbon monoxide was led with the he-

lium carrier gas through the catalyst bed as a constant gas stream (29 scm³/min) for a certain time period. Afterward the reactor was heated to 500°C and at that temperature the catalyst was flushed with pure helium for some time (to remove chemisorbed CO). The two variables with this reduction method were reduction time and flushing time. The activity was measured at 0°C and 6.4 kPa. When other parameters were varied (polymerization temperature or pressure) reduction time and flushing time were normally 1 and 10 min, respectively. To enable a comparison reduction was sometimes carried out using CO pulses (0.60 cm³) at 470°C. For some experiments the amount of carbon dioxide produced during reduction was measured gravimetrically (natron asbestos).

When the reactor was coupled to the static system it was evacuated to 1 mPa, ethene with the desired pressure (1–20 kPa) was admitted at the desired temperature (–60 to 200°C), and the pressure was measured as a function of time. The amount of ethene consumed (W) was calculated from the pressure drop and plotted against time. A typical example of such a plot is shown in Fig. 2, in which the result is given at –38.7°C and 7.15 kPa. Three parts can be differentiated in Fig. 2: an initial rapid pressure decrease, followed by a slower but constant decrease, and finally a period during which the pressure decrease diminishes until the reaction rate becomes negligible. The fast initial pressure decrease is probably caused by physical adsorption since it is absent at higher temperatures; moreover it is also observed on the support in the absence of Cr. Activity was defined as the slope of the curve $W-t$ during the period of constant polymerization; it is denoted W' and expressed in milligrams of polymer formed per minute per gram of catalyst. The amount of ethene consumed during a complete measurement after correction for physical adsorption is denoted W_{max} and expressed in milligrams of polymer per gram of catalyst.

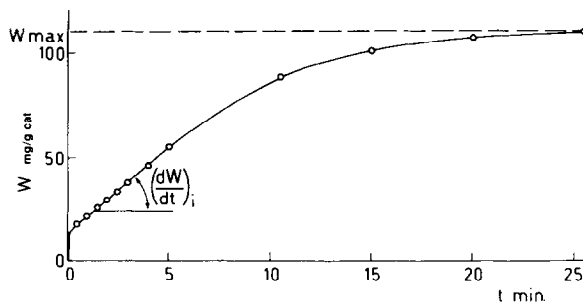


FIG. 2. Example of a static polymerization experiment at -38.7°C and 7.15 kPa.

RESULTS

The results of the static measurements are shown in Figs. 3–8. Figure 3 shows that on varying the CO reduction time, activity

passes through a maximum. Also shown in this graph is the valency state of the chromium calculated from the amount of carbon dioxide produced. When reduction was carried out with CO pulses similar results were

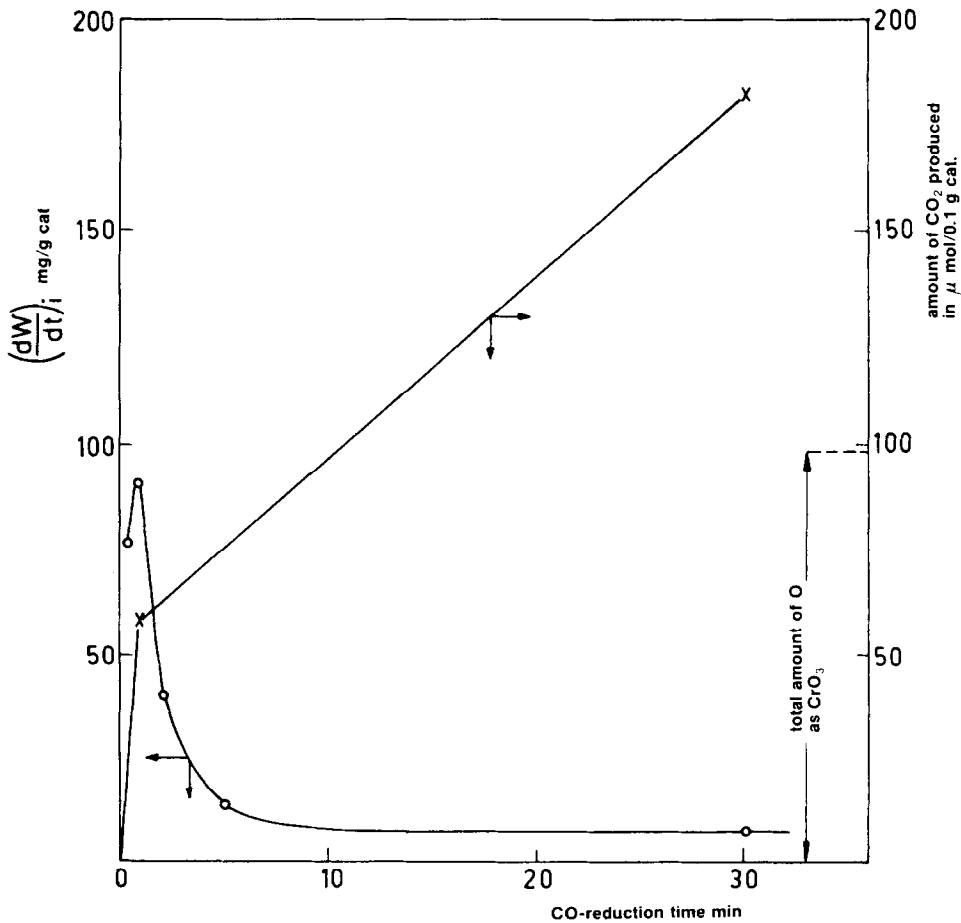


FIG. 3. Activity at 0°C after reduction by a CO stream at 350°C followed by flushing in helium at 500°C for 10 min.

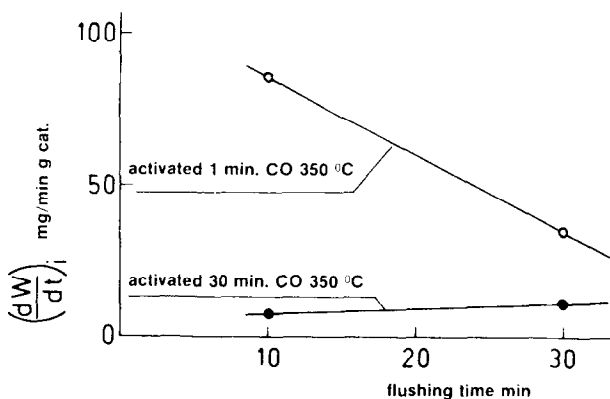


FIG. 4. Activity at 0°C as a function of the flushing time at 500°C with helium.

obtained, thereby showing that there is no essential difference between the two reduction methods. It is noteworthy that maximal activity almost coincides with the point of complete reduction of the chromium to Cr^{2+} . Carbon dioxide production after this point is caused by an intermediate reoxidation of Cr^{2+} ions by surface hydroxyl groups (1) and actually indicates a process of dehydration of the surface, whereby $2\text{OH}^- + \text{Cr}_2^{2+} \rightarrow \text{Cr}_2^{3+}\text{O}^{2-} + \text{O}^{2-} + \text{H}_2$ (see also (11)).

When the flushing time was varied pecu-

liar results were obtained (Fig. 4). An active catalyst obtained after a 1-min reduction was largely deactivated when the flushing time was increased from 10 to 30 min. On the other hand, an "overreduced" catalyst was clearly reactivated by increasing the flushing time. Since during flushing only diffusion of hydroxyl groups will take place, this again indicates the importance of these groups.

When reduction was carried out with hydrogen, somewhat similar results were obtained (Fig. 5). Reduction carried out at a

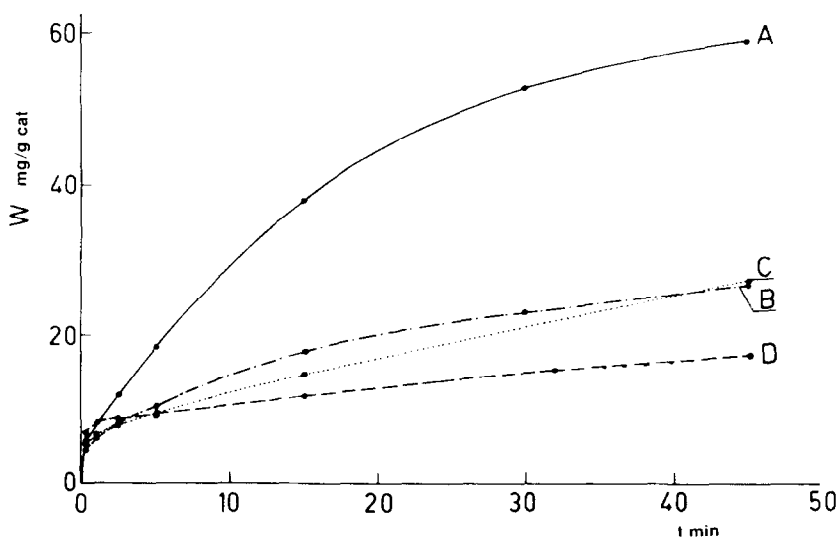


FIG. 5. Polymerization activity after activation by H_2 : (A) reduction carried out at a low heating rate and a high space velocity, cooled in helium; (B) reduction carried out at a high heating rate and a low space velocity, cooled in helium; (C) as in A, but treated with wetted helium after reduction; (D) as in A, but cooled in hydrogen.

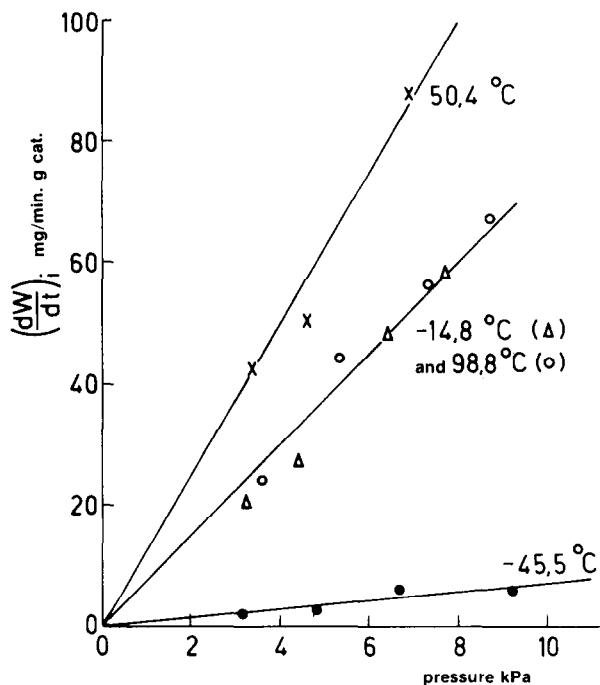


FIG. 6. Polymerization activity as a function of ethene pressure.

low heating rate and/or a high space velocity resulted in a blue catalyst (10), which, after reduction, was active when cooled in helium (A), but became almost inactive when cooled in hydrogen (D). Reduction carried out at a high heating rate and/or a low gas space velocity resulted in a green catalyst (11) which was only slightly active (B). Finally when an active blue catalyst was treated with wetted helium at 470°C, activity again was significantly decreased (C); it was shown elsewhere (13) that such a treatment involves the oxidation of Cr^{2+} to Cr^{3+} .

On varying the ethene pressure a linear relationship was found between activity and pressure at all temperatures between -50 and 200°C (Fig. 6). From the first-order plots experimental first-order reaction constants could be deduced and an Arrhenius plot of $\log k$ vs $1/T$ (Fig. 7) showed a maximum at about 30°C . To check whether the maximum was real two experiments were performed (Fig. 8): temperature was lowered from 200 to 120°C or raised from -60

to 10°C during polymerization, and in both cases an increase in activity resulted.

As to the ultimate amounts of polymer formed, both methods agree in that poly-

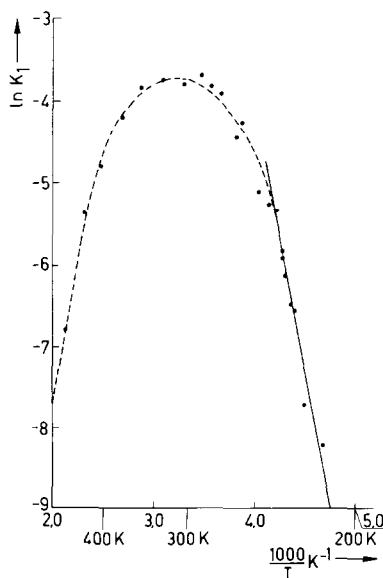


FIG. 7. Arrhenius plot of the experimental first-order reaction constant.

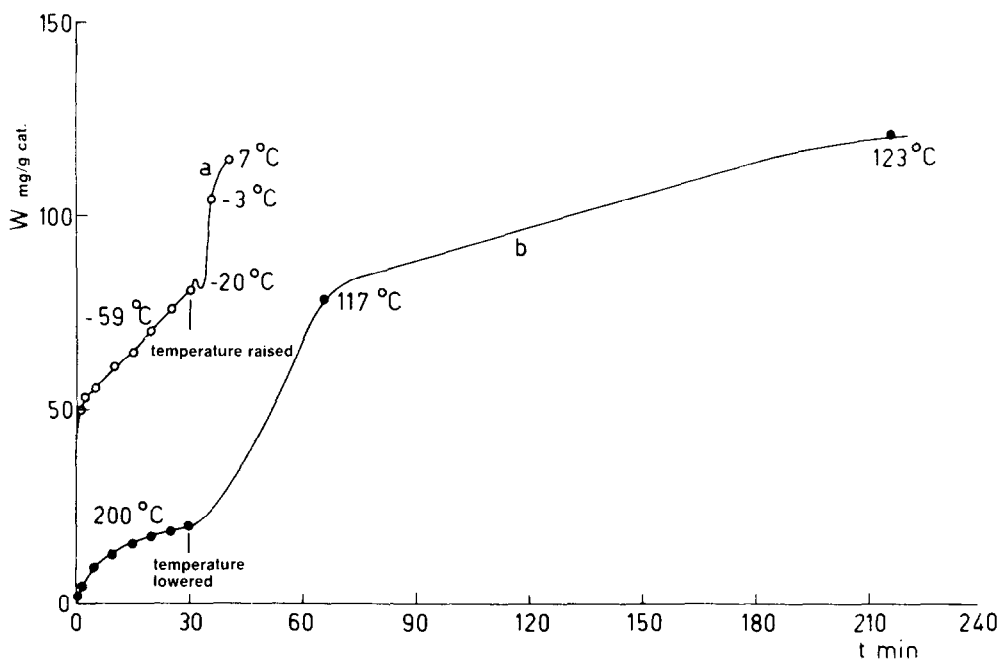


FIG. 8. Effect of raising or lowering the temperature during polymerization; polymer remains solid or molten.

merization stops after some time. Details as to the rate decline as a function of run time are more easily obtained from the dynamic experiments. Judging from the results at a 20-min run time maximal production is observed at 0 and 140°C. The amounts of polymer formed at longer run times show a similar picture with two maxima: they are observed to have shifted to lower and higher temperatures (Fig. 9). Ultimately, most polymer is formed at the higher temperature applied. The smallest polymer production takes place at 70–90°C. At these temperatures polymerization stopped suddenly at a certain time. At lower temperatures this happened after a longer reaction time, and at temperatures above 140°C there was no sudden stop but only a gradually decreasing rate. To clarify this phenomenon further experiments were performed. When after complete polymerization at 60°C the reaction temperature was lowered to 0°C, no further polymerization occurred. On the other hand, increasing the temperature *in vacuo* to 130°C fol-

lowed by rapid cooling to 0°C led to an appreciable activity at this temperature. Polymerization at 0°C up to the limit followed by an increase in temperature to 130°C again led to further polymerization (Fig. 10).

Inspection of the catalyst samples after reaction between 20 and 90°C showed that some of the catalyst particles were white, while others were still colored. It was established that the difference in color was due to a difference in polymer content, the white particles containing more polymer. Below 20 and above 90°C no white catalyst particles were observed. After reaction above 100°C the catalyst particles tended to stick together.

Another factor investigated was the dependency of the maximal amount of polymer on the Cr content of the catalyst; Fig. 11 shows this in the form of a log-log plot. A line through the experimental points is almost horizontal, indicating that the maximal amount is already obtained at very low Cr content. The figure also contains two

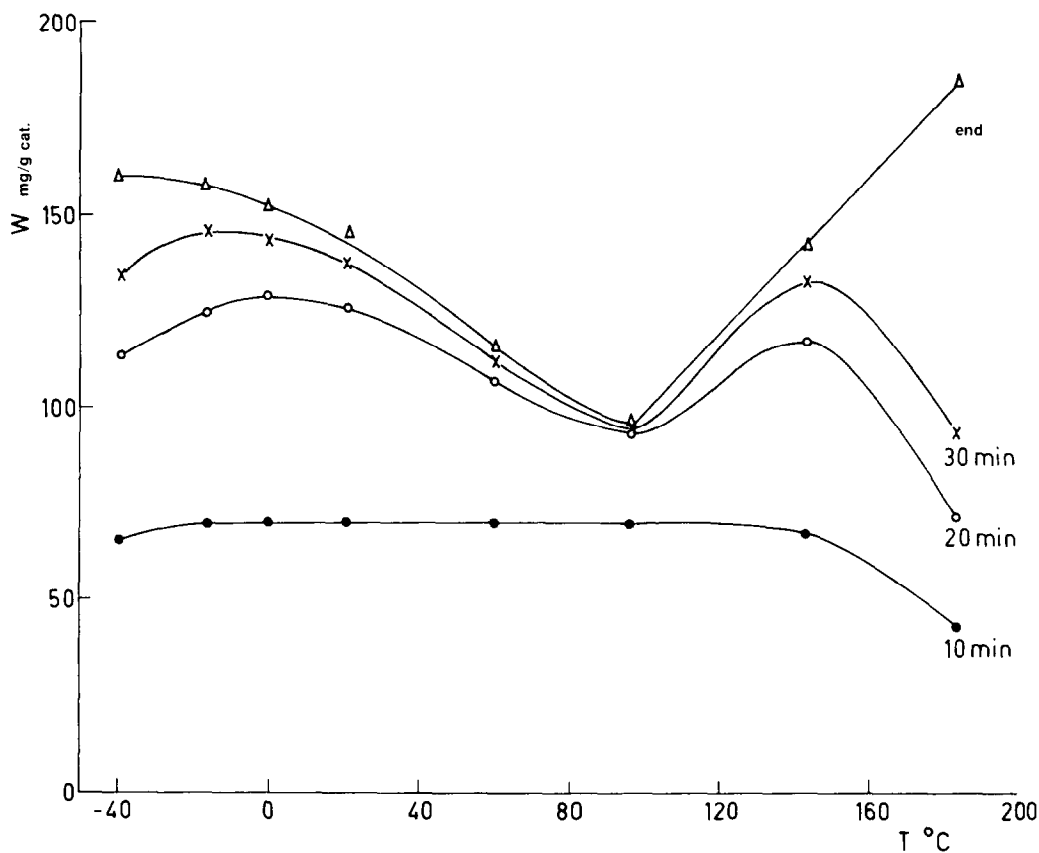


FIG. 9. Polymerization in the dynamic system at different temperatures after activation by 60 CO pulses (1.39 cm^3) at 470°C .

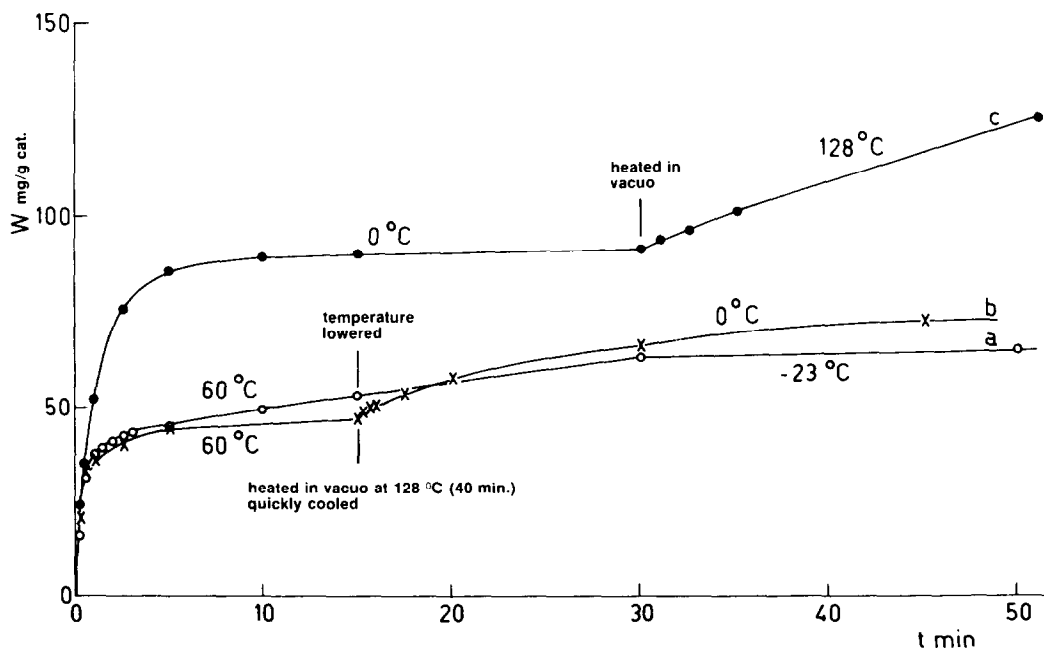


FIG. 10. Effect of raising or lowering the temperature during polymerization with phase transition occurring in the polymer.

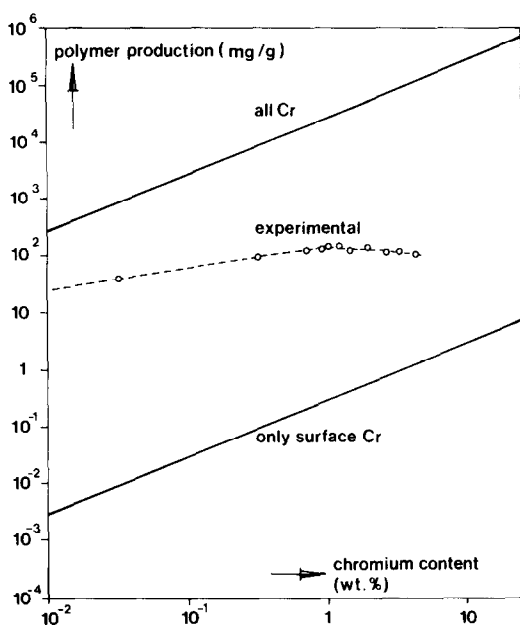


FIG. 11. Polymer production as a function of the chromium content of the catalyst. Straight lines are calculated productions assuming *all* chromium atoms active or only chromium atoms at the particle surface (polymer molecular weight assumed 140,000).

straight lines; these give the calculated maximum amounts assuming that the average molecular weight per polymer molecule is not dependent on the Cr content. The top line represents a case for which all Cr cations are equally active while the bottom line counts only the Cr cations on the surface of the catalyst particles as active. The molecular weight of the polymer was fixed at 140,000, in anticipation of results to be published in a forthcoming paper (14). The data appear to support a hypothesis in which polymerization becomes more concentrated on Cr cations in the outer particle layers as more Cr is present.

When investigating polymerization according to the dynamic method the influence of CO as a poison also was studied. The method consisted of injecting variable amounts of CO before ethene was fed to the catalyst. After the CO injection but before the start of the polymerization experiment no CO could be detected in the helium carrier gas after the reactor, unless more than

9 cm³ CO was used. Figure 12 shows the results of the polymerization experiments. When small amounts of CO were used, a small peak was noted after which the polymerization set in at full strength. For larger amounts the peak became higher and polymerization did not attain the rate observed for nonpoisoned catalysts (no complete elimination of the ethene from the gas phase). The peak after analysis was found to represent ethene with small amounts of CO. The time of the occurrence of the peak approximately coincides with the time at which ethene was detected in the absence of a catalyst (curve II, Fig. 1). The explanation seems clear: CO is adsorbed on the catalyst and blocks the polymerization sites, but in the presence of ethene it desorbs, thus "freeing" the sites for the polymerization reaction.

Pulsing oxygen at 0°C leads to an irreversible deactivation of the catalyst, the amount of polymer maximally found decreasing linearly with the amount of O₂ introduced (Fig. 13). The catalyst changes color from blue to brown black. At higher polymerization temperatures such as 100°C the poisoning proved reversible (Fig. 14). Peaks similar to those for CO poisoning were found, suggesting reactivation of the catalyst from reduction by ethene. In fact, the peak again represented ethene with CO and not O₂.

DISCUSSION

The phenomena observed as a consequence of variations in the activation procedure suggest that silanol groups play an important role in determining catalyst activity. Silanol groups can reoxidize Cr²⁺ to Cr³⁺ under formation of H₂ as was shown before (1, 11). Catalysts that are reduced exhaustively and thus can be presumed to contain only Cr²⁺ were shown above to be only slightly active. On the other hand, catalysts that are reoxidized extensively by adding water and thus may be assumed to contain mainly Cr³⁺ are also not active. It might be surmised that an active catalyst

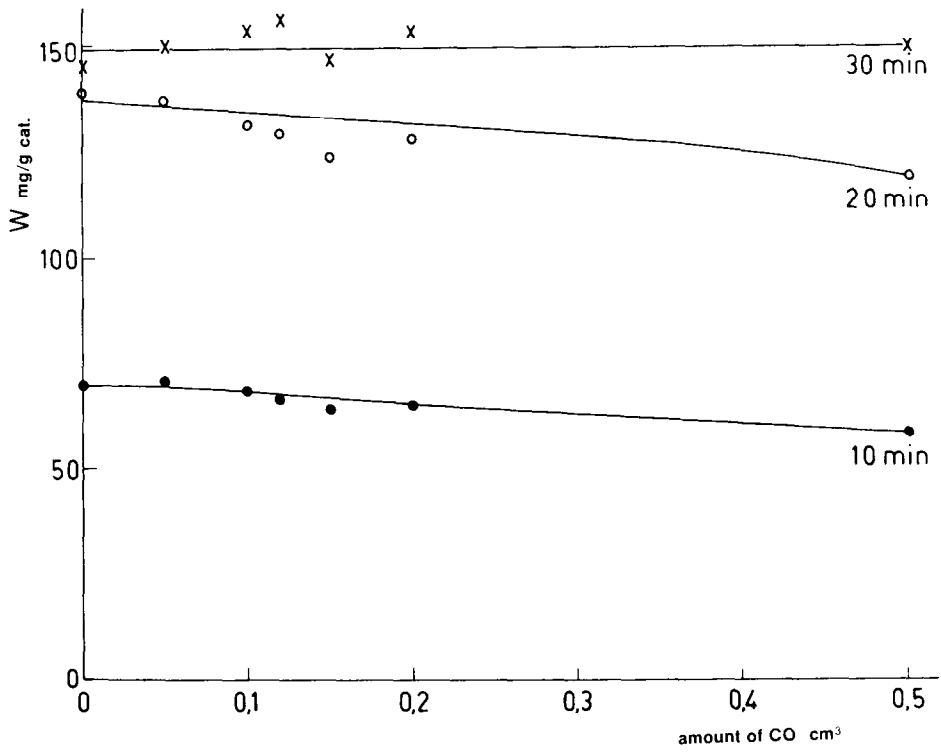


FIG. 12. Polymerization in the dynamic system at 0°C after CO poisoning.

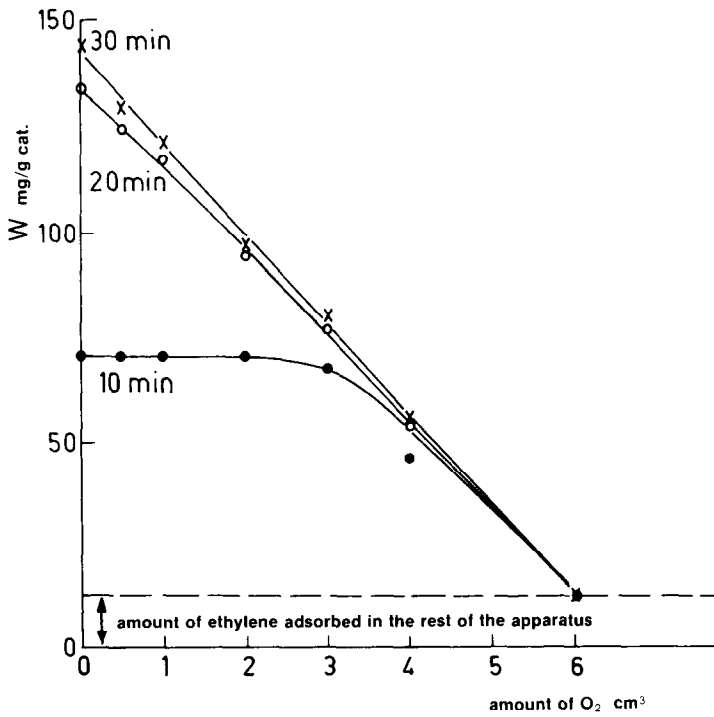


FIG. 13. Polymerization in the dynamic system after O₂ poisoning (0°C).

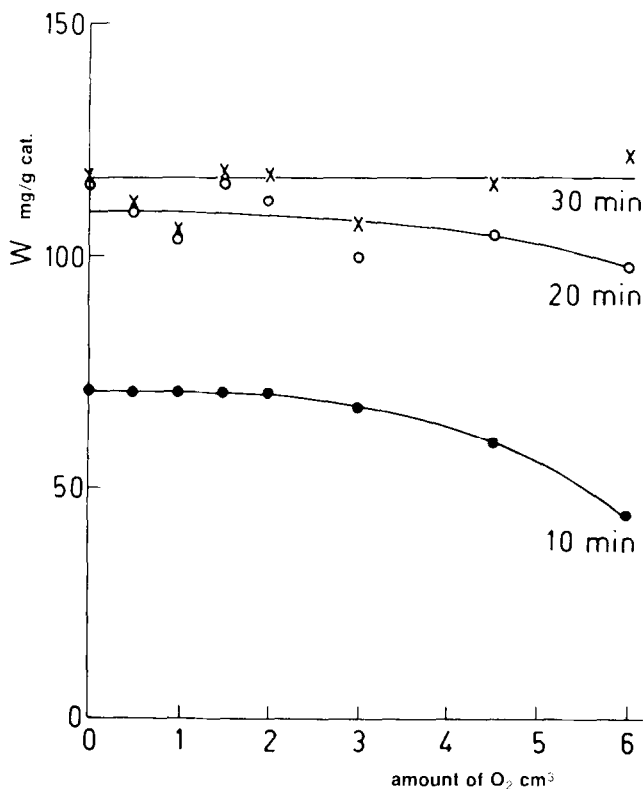


FIG. 14. Polymerization in the dynamic system after O₂ poisoning (100°C).

should possess Cr³⁺ and Cr²⁺, as pairs, but it is difficult to rationalize such a hypothesis. We therefore postulate at this time that the active site for the polymerization reaction consists of a silanol group next to a Cr²⁺ cation. We shall return to this point in more detail in a future paper, where infrared data are discussed (14).

As to the kinetics of the polymerization the data obtained from the static method appear particularly suitable for discussion since they give information concerning the initial situation where material transfer does not play a predominant role. On the other hand, the dynamic method is expected to shed more light on the mechanism of the decline in catalytic activity. We shall therefore discuss the results separately.

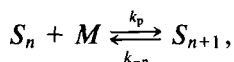
From the static method it follows that polymerization is first order in ethene pressure at all temperatures. This can be explained by a Rideal mechanism (polymer-

ization directly from the gas phase) or by a Langmuir-Hinshelwood mechanism assuming low coverage of the surface by adsorbed ethene. The results of the CO-poisoning experiments can be explained by assuming that ethene molecules have to adsorb on chromium ions to which CO molecules are attached. In that case two adsorption sites are normally available on these chromium ions and judging from the inhibiting effect of CO, both of these sites are needed for the polymerization reaction. In a future paper (14) further evidence will be presented that polymerization actually takes place according to a Langmuir-Hinshelwood model and also in that paper a model of the propagation reaction will be evaluated, incorporating an adsorption step and an insertion step.

An optimal polymerization temperature is reported by many investigators; they do not agree, however, about the value of the

temperature and the explanation of the existence of an optimal temperature. One explanation can be found by assuming an almost complete surface coverage at low temperatures and a very small coverage at high temperatures. Then at low temperatures activity depends on the rate of the insertion reaction, while at higher temperatures adsorption is rate determining. However, in that case the reaction order would change from zero to one on raising the temperature which does not agree with our experiments. Ermakov and co-workers (7) explain an optimal activity at 70°C by assuming a poisoning effect at higher temperatures. However, in that case it is hard to see why a catalyst poisoned at 200°C would become active again at 120°C (Fig. 8).

Let us first consider the reversible propagation reaction



in which S is the growing polymer chain, M is the monomer molecule, and k_p and k_{-p} are the reaction rate constants of the propagation and its reverse reaction, respectively. k_p and k_{-p} can be written

$$k_p = k_p^0 \exp(-E_p/RT), \quad (1)$$

$$k_{-p} = k_{-p}^0 \exp(-E_{-p}/RT), \quad (2)$$

$$\frac{k_p}{k_{-p}} = K_{\text{pol}} = \exp\left[\frac{(-\Delta h_{\text{pol}}^0 + T\Delta s_{\text{pol}}^0)/RT}{RT}\right], \quad (3)$$

in which E_p and E_{-p} are the activation energies of the propagation and its reverse reaction, respectively, K_{pol} is the polymerization equilibrium constant, and Δh_{pol}^0 and Δs_{pol}^0 are the molar polymerization enthalpy and entropy, respectively.

Since E_p is about 107 kJ/mole ($=\Delta h_{\text{pol}}^0$) smaller than E_{-p} , the reverse reaction will be relatively very slow at lower temperatures. In that case propagation is predominant and since its rate will increase with temperature, overall activity will increase as well. It is also known that above a certain temperature polymer cannot be

formed, because then the rate of the reverse reaction is larger than the propagation rate. On calculating this temperature (called the ceiling temperature when the monomer concentration $[M]$ is 1 mole/liter) for our conditions with

$$T_c = \frac{\Delta h_{\text{pol}}^0}{\Delta s_{\text{pol}}^0 + R \ln[M]} \quad (4)$$

and substituting $\Delta h_{\text{pol}}^0 = -106.5$ kJ/mole (for crystalline polymer (15)), $\Delta s_{\text{pol}}^0 = -173.5$ J/mole K (for crystalline polymer (15)), and $[M] = 0.0035$ mole/liter, we find $T_c = 485$ K. This is in very good agreement with the temperature of 210°C at which the polymerization rate becomes negligible (Fig. 7); so the existence of an optimal temperature seems to be a logical consequence of a typical polymer property, the depolymerization.

According to the model developed above it is possible to express the experimentally determined rate constant k_{exp} as

$$k_{\text{exp}} = k_p N_s - K_{-p} \frac{N_s}{[M]}, \quad (5)$$

in which N_s is the number of active sites. After substituting Eqs. (1)–(3) and after differentiating Eq. (5) with respect to T , it is found that the temperature at which k_{exp} is maximal can be expressed by

$$T_m = \frac{\Delta h_{\text{pol}}^0}{\Delta s_{\text{pol}}^0 + R \ln[M] - R \ln(E_{-p}/E_p)}. \quad (6)$$

E_p can be found from Fig. 7 by assuming that at low temperatures we have measured the real propagation rate. We therefore substitute

$$\Delta h_{\text{pol}}^0 = -106.5 \text{ kJ/mole (for crystalline polymer)}$$

$$\Delta s_{\text{pol}}^0 = -173.5 \text{ J/mole K (for crystalline polymer)}$$

$$R = 8.3 \text{ J/mole K}$$

$$[M] = 0.0035 \text{ mole/liter}$$

$$E_p = 53 \text{ kJ/mole}$$

$$E_{-p} = 160 \text{ kJ/mole}$$

to find $T_m = 464$ K and this is not in agreement with the experimentally found temperature of 310 K.

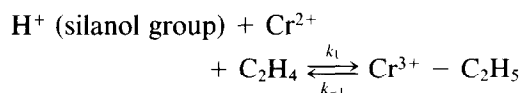
The observed discrepancy between calculated and experimentally found T_m can be explained in two ways. First, it should be noted that the numbers cited above for the various thermodynamic parameters are typical for the solid crystalline polymer. It is very well possible that these values are quite different for a growing polymer in a porous catalyst system, because the polymer may not always be completely crystalline and because the polymer will be hindered sterically by the pore walls. If the polymer is not crystallized the molecules will have less interaction with each other or with other parts of their own chains than in the crystallized state and the molecules will also have more degrees of freedom.

Therefore both the true Δh_{pol}^0 and Δs_{pol}^0 will be lower than the adopted values and it is hard to predict what the net effect will be on T_m . The steric hindrance will also have a lowering effect on Δh_{pol}^0 , as one would expect the polymer molecules to be repelled rather than to be attracted by the hydrophilic silica surface. On the other hand the steric hindrance will reduce the degrees of freedom for the molecules, thereby raising the entropy drop. Since a lower Δh_{pol}^0 and a higher Δs_{pol}^0 will both lower T_m , steric hindrance will have the largest effect on T_m , the effect of the crystallization being small. Therefore it is understandable, although not quantitatively, that the experimental T_m will be lower than 464 K. In fact when Δh_{pol}^0 is -71.1 kJ/mole or when Δs_{pol}^0 is -287.5 J/mole K the calculated T_m will equal the experimental one exactly.

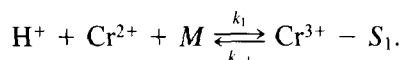
This explanation is not in conflict with the already mentioned coincidence of the calculated and the observed upper polymerization temperature since this temperature will be determined by the sites on which Δh_{pol}^0 is highest and Δs_{pol}^0 is lowest, which will be the ones on which there is no steric hindrance, i.e., lying on the pore ends. Although at this temperature the

polymer will not be crystalline, the effect of this on T_c will be small, as was the case with T_m ; so by substituting in Eq. (4) for Δh_{pol}^0 and Δs_{pol}^0 the values of the crystalline polymer, a fairly good approximation is obtained for the real T_c . The main difference therefore between T_c and T_m is that T_c is determined by the few sites on which Δh_{pol}^0 is highest and Δs_{pol}^0 is lowest, while T_m is determined by the distribution of Δh_{pol}^0 and Δs_{pol}^0 among the various sites.

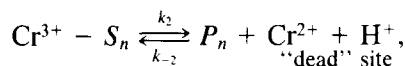
Another explanation for the observed discrepancy between calculated and experimental T_m involves the introduction of initiation and termination reactions. A site active for polymerization is assumed to be formed by the interaction of a silanol group, a Cr^{2+} cation, and a monomer:



or



Termination is introduced as a somewhat similar reaction



where P_n is an olefinic, dead polymer molecule covering a potential site and S_n is a polymeric alkyl group. We further assume that during the initial period the fraction of active sites is θ_A , the fraction of "dead" sites is θ_D , and the fraction of empty sites is therefore $1 - \theta_A - \theta_D$. Furthermore $d\theta_A/dt$ and $d\theta_D/dt$ are taken as zero (steady-state conditions). So for the initial period we obtain

$$-\frac{d[M]}{dt} = k_p \theta_A N_s [M] = k_{\text{exp}} [M], \quad (7)$$

$$\frac{d\theta_A}{dt} = 0 = k_1 (1 - \theta_A - \theta_D) - \theta_A (k_2 + k_{-1}) + k_{-2} \theta_D, \quad (8)$$

$$\frac{d\theta_D}{dt} = 0 = k_2 \theta_A - k_{-2} \theta_D. \quad (9)$$

Since both initiation and termination can actually be written as $H + C_nH_{2n} \rightleftharpoons C_nH_{2n+1}$ we simplify these equations by putting $k_2 = k_{-1}$ and $k_{-2} = k_1$. This gives

$$k_{\text{exp}} = \frac{k_p}{1 + (2k_{-1}/k_1)} \quad (10)$$

We found that a reasonable agreement with experiment can be obtained by letting

$$\ln k_p = -\frac{6390}{T} + 21.44 \quad (11)$$

and

$$\ln \frac{k_{-1}}{k_1} = -\frac{8220}{T} + 30.91. \quad (12)$$

Finally we shall discuss the results of the dynamic method. A decreasing polymerization rate in a fixed catalyst bed is generally ascribed to a blocking of the active site by polymer and therefore we tried to calculate a diffusion coefficient of ethene through polyethene by using a mathematical model of gradually filling pores. On doing so it was found that this diffusion coefficient decreased with increasing polymerization time. At temperatures above 120°C, however, this effect is not as pronounced as at lower temperatures. This and also the other previously mentioned results can be explained by assuming a crystallization of the produced polymer, since diffusion through crystallized polymer is much slower than diffusion through amorphous polymer (15). The crystallization rate appears to be most effective at 70–90°C which means that at this temperature the produced polymer will have the highest degree of crystallinity. At lower temperatures (e.g., 0°C), solidification is so fast that only a part of the polymer will be crystalline, the rest being amorphous.

With the concept of crystallization the results pictured in Fig. 10 are readily understood. At 60°C the polymer is almost completely crystalline and therefore no more polymerization will occur on lowering the temperature. However, when the polymer

is heated and then cooled down to 0°C, the physical state of the polymer will be more amorphous and so now polymerization can take place again. After a prolonged polymerization at 0°C, increasing the temperature up to 130°C results in an appreciable rise in polymerization activity, which merely reflects the melting of the polymer.

The conclusion that sites are blocked by polymer formation is also supported by the experiments shown in Fig. 11. The maximal amount of polymer formed remains almost constant while the amount of Cr increases and the system proceeds from a situation with most Cr atoms active at low Cr concentrations to a situation in which only Cr atoms at the periphery of the particle are active. Adding Cr causes new Cr atoms at the periphery to block admission of ethene to Cr in the bulk of the particles. This process is particularly well demonstrated in our catalyst because of the high surface area and low pore volume of the support; pores were very narrow and their number was relatively small. It seems that in actual practice yields are obtained in the order of 10⁴ g/g catalyst instead of 10⁻¹ g/g as in our catalyst, a ratio of about 10⁵. This is roughly comparable to the ratio "bulk Cr atoms to peripheral Cr atoms." Apparently, commercial catalysts succeed in having all their Cr atoms as accessible as our peripheral Cr atoms presumably because the commercial catalyst has such a large pore volume that it fragments during polymerization. Differences in rates of polymerization are similarly great and can be explained analogously. In summary, the results of our activity measurements, as well as those obtained by other investigators, can be explained by typical polymer properties, viz., depolymerization and crystallization.

We have more difficulty in explaining the results of Beck and Lunsford (16) and more so since their article does not report pore volumes of the support used. In experiments on reduction similar to those described here they find the maximum activity at Cr³⁺ while we find it at Cr²⁺ but with

the reservation that something else should be present, presumably silanol groups. Surprisingly enough, their rates of polymerization are a factor of 100–1000 lower than ours (compare 24°C, 81 mg ethene/g cat/min at 7 kPa for our experiments versus 0.72 mg ethene/g cat/min at 40 kPa in their experiment). We tend to believe that their catalyst was overoxidized to Cr³⁺ and lacked silanol groups.

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