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### Supported Chromium Oxide Catalysts for Olefin Polymerization. VII. Kinetics of Ethylene Polymerization

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## Supported Chromium Oxide Catalysts for Olefin Polymerization. VII. Kinetics of Ethylene Polymerization

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### SUMMARY

The mechanism of ethylene polymerization on a Phillips-type catalyst has been studied by kinetic measurements in an integral dynamic reactor. The proposed Langmuir-Hinshelwood mechanism agrees well with the various published results concerning reaction order and rate-maximum temperature.

The kinetic laws of ethylene polymerization on a Phillips-type catalyst have been widely studied. There have been some contradictory results concerning the reaction order with respect to monomer, for which values of zero [1, 2], one [2-4], and even two [4, 5] have been reported, and the location of the rate temperature maximum which has been found to be either at 20°C [1], 70-80°C [1, 6, 7], 90-100°C [3, 5], or even 130°C [9]. As long as there is no proven reaction mechanism, it is difficult to compare experiments carried out with or without solvent at pressures varying from 0.01 to 50 bar. Moreover, the final state of the catalyst depends on the first contact with ethylene [10].

We have tried to study the variations of the reaction order when the temperature is varied from  $-50$  to  $145^{\circ}\text{C}$  at low pressure. The catalyst is fixed in a definite state by pretreatment with monomer at the highest temperature ( $145^{\circ}\text{C}$ ) under conditions which have been shown to lead to a maximum of activity at all lower temperatures [10]. The ethylene consumption rate is measured in an integral dynamic reactor. We will first present a mathematical study of the reactor for the case of a simple reaction (first-order), and then we will present a complete study of the reaction.

### STUDY OF THE REACTOR

The integral dynamic reactor used has been described previously [4]. The conversion ratio is high (up to 90%) and there is a gradient of ethylene pressure in the ethylene-helium mixture which passes through the catalyst column. The determination of the real instantaneous rate requires a correcting calculation. A simplified attempt has been previously reported [4]. We will apply a correction calculation to the case of a first-order reaction.

The cylindrical catalyst column is held in a fluid bed by the gas stream which is flowing through it. It is therefore continuously stirred and homogeneous.

It is first necessary to establish the relationship between the measured conversion ratio  $r$  and the true activity. The first-order law can be written  $v = kp$ , where  $v$  is the polymerization rate,  $p$  the monomer pressure, and  $k$  the first-order rate constant. Other notations are  $S$  for the section area of the reactor,  $\rho$  for the density of the catalyst,  $m$  for its mass,  $d_0$  for the flow-rate of the inert gas,  $D$  for the flow rate of the monomer which enters the reactor,  $D_r$  for the outgoing monomer flow-rate, and  $D_x$  for the flow rate at a distance  $x$  from the bottom of the column. The partial pressure of the monomer is

$$P_x = \frac{D_x}{D_x + d_0}$$

The reaction balance in a differential section  $dx$  of the catalyst may be written

$$d(D_x) = -\rho S dx k p_x = \rho S dx k \frac{D_x}{D_x + d_0}$$

After integration upon the whole catalyst,

$$D - Dr + d_0 \ln \frac{D}{Dr} = km$$

and replacing by the conversion ratio  $r = (D - Dr)/D$ :

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

This general expression relates the measured conversion ratio  $r$  to the flow rates and to the mass of catalyst.

## EXPERIMENTAL

It has earlier been shown that ethylene polymerization is a first-order reaction at 145°C and low pressure [4]. In Table 1 the calculated values for  $k$  at 0.09 bar are reported. It may be seen that these values remain constant when the mass varies over a large range. The same verification for varying flow-rates is reported in Table 2.

We are therefore justified in applying the above mathematical model to the polymerization activity calculations under the experimental conditions quoted. We will now extend the calculation to reactions other than first-order.

### Study of the Reaction

When the reaction order is  $\alpha$  ( $0 < \alpha < 1$ ), the same calculation may be made as in the preceding section. The balance of the reaction is

$$d(Dx) = -\rho S dx k \left[ \frac{Dx}{Dx + d_0} \right]^\alpha$$

so we have

$$k = -\frac{1}{m} \int_D^{Dr} \left[ \frac{Dx}{Dx + d_0} \right]^\alpha d(Dx)$$

TABLE 1. Activity as a Function of the Mass of Catalyst<sup>a</sup>

Catalyst No.	Mass (mg)	Conversion ratio		k (mmole/min/g/bar)
		Measured (%)	Specific (g <sup>-1</sup> )	
I	516	85.1	1.65	10.96
I	315	66.8	2.12	10.35
I	257	61.7	2.40	11.00
II	600	79.8	1.33	7.97
II	435	70.0	1.61	8.24
II	288	54.4	1.89	8.08
III	594	75.4	1.27	7.08
III	482	68.4	1.42	7.14
III	423	63.4	1.50	7.08
III	364	57.8	1.59	7.06
III	212	39.4	1.86	6.98

<sup>a</sup>Ethylene polymerization. T = 145°C. Helium flow-rate, 65 ml/min; ethylene flow-rate 6.5 ml/min.

TABLE 2. Activity Calculation for Varying Flow-Rates<sup>a</sup>

Ethylene flow-rate (mmole/min)	Helium flow-rate	Specific conversion ratio (g <sup>-1</sup> )	k (mmole/min/g/bar)
0.187	1.87	1.9	6.83
0.29	2.9	1.52	6.78
0.4	4.0	1.22	6.92

<sup>a</sup>Ethylene polymerization. T = 145°C. Mass of catalyst, 0.4 g.

The integration cannot be expressly performed for all values of  $\alpha$ . However, a valuable approximation consists in a development limited to the two first terms. The relative error remains smaller than 0.005 for  $D/d_0 < 0.2$

$$\left[ \frac{Dx}{Dx + d_0} \right]^{-\alpha} \approx \left[ \frac{Dx}{d_0} \right]^{-\alpha} \left[ 1 + \alpha \frac{Dx}{d_0} \right]$$

Replacing and integrating leads to

$$k = \frac{D}{m} \left[ \frac{d_0}{D} \right]^\alpha \left[ \frac{1 - (1 - r)^{1-\alpha}}{1 - \alpha} + \frac{\alpha}{2 - \alpha} \frac{D}{d_0} [1 - (1 - r)^{2-\alpha}] \right]$$

### EXPERIMENTAL

The catalyst (3.6% chromium) is pretreated with ethylene at 145°C and 0.09 bar up to the maximal activity at 145°C. Then it is desorbed by the helium stream at this temperature for a few minutes and cooled to the polymerization temperature. The measurement of an apparent reaction order is made by alternate contact between catalyst and monomer at two widely different pressures, as are the conversion ratios  $r_1$  and  $r_2$ . The pressure is controlled by varying  $D$ ,  $d_0$  remaining fixed. The order in that pressure range is obtained by resolving the equation in  $\alpha$ :

$$D_1 \left[ \frac{d_0}{D_1} \right]^\alpha \left[ \frac{1 - (1 - r_1)^{1-\alpha}}{1 - \alpha} \frac{\alpha}{2 - \alpha} \frac{D_1}{d_0} [1 - (1 - r_1)^{2-\alpha}] \right] =$$

$$D_2 \left[ \frac{d_0}{D_2} \right]^\alpha \left[ \frac{1 - (1 - r_2)^{1-\alpha}}{1 - \alpha} \frac{\alpha}{2 - \alpha} \frac{D_2}{d_0} [1 - (1 - r_2)^{2-\alpha}] \right]$$

Because the activity drifts slightly downward during the experiment, this is corrected by repeating the measurement several times and by interpolating the results. Thus values for  $\alpha$  and  $k$  are obtained.

The experimental results at different temperatures are reported in Table 3. The pressure varied from 0.07 to 0.18 bar.

It may be seen that the reaction is first-order at 145°C, confirming the previous results, and the order decreases continuously down

TABLE 3. Variation of Reaction Order and Activity vs. Temperature<sup>a</sup>

Temperature (°C)	145	90	23	0	-22	-50
Reaction order	1	0.93	0.73	0.63	0.46	0.25
k (mmole/min/ g/bar)	6.8	13.4	5.58	2	0.71	0.13

<sup>a</sup>Catalyst: 3.6% chromium supported on silica-alumina.

to values near zero at -50°C. No reliable results can be obtained below -50°C because of physical adsorption and the slow polymerization rate. As has already been shown, there is a maximum for the polymerization rate as a function of the temperature near 90°C. The values of k correspond to an activation energy of about 6 kcal at low temperatures.

### INTERPRETATION

Both the existence of a rate maximum temperature and the variation of the reaction-order from zero to one as the temperature increases suggest that polymerization occurs in an adsorbed layer according to a Langmuir-Hinshelwood mechanism. Such a mechanism has already been proposed by Clark and Bailey [8, 9] on the basis of rate and molecular weight measurements. But, as was shown by Guyot [11], neither the experimental results nor the proposed theory are unambiguously convincing. In the case of a polymerization it must be noted that the growing center (the end of the polymer chain) remains attached and that the polymerization occurs after adsorption of a molecule of monomer on an adjacent position.

Simplified equations for the monomer consumption can be written with the notation of  $V$  = the polymerization rate,  $V_1$  = the adsorption rate, and  $V_2$  = the desorption rate. Under steady-state conditions, if adsorption occurs close to  $N$  out of  $N_0$  sites of polymerization, the balance of the reaction can be written as

$$V_1 (N_0 - N) - V_2 N - VN = 0$$

and the measured rate  $v$  is

$$v = NV = \frac{N_0 V_1 V}{V_1 + V_2 + V}$$

At sufficient pressure and low temperature the denominator becomes equivalent to  $V_1$  and the reaction is zero-order. On the other hand, at high temperature  $V_1$  is negligible versus  $V_2 + V$  and the reaction is first-order.

When the energy of activation for  $V$  is not too high with respect to that for desorption, there is a rate maximum when the temperature increases. This maximum will be displaced at higher temperatures when the pressure is increased. We have experimentally noticed that it rises from 90 to 120°C when pressure varies from 0.09 to 1 bar.

The conclusion from our simplified calculations is that the polymerization of ethylene obeys a Langmuir-Hinshelwood mechanism. The measured values for the energy of activation are not of great significance for such a complex reaction. Most authors report small values of 6-8 kcal at low temperature [2, 3, 12] but Ayscough et al. [1] have found 14 kcal and a zero-order reaction below 0°C. It seems unlikely that such a value would permit the existence of a rate maximum temperature. The reported maximum is the only one at such a low temperature (20°C), so no direct comparison with our results is possible. As demonstrated in a previous paper [4], reaction orders greater than one result from inadequate reduction of the catalyst. All other reported values are satisfactorily explained by the proposed mechanism.

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