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Physical Chemistry

Yu. I. Ermakov, Corresponding Member of the Academy of
Sciences of the USSR, G. K. Boreskov,

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Abstract

Full Text

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Yu. I. Ermakov, Corresponding Member of the Academy of Sciences of the USSR, G. K. Boreskov,
V. A. Dzisko, and L. I. Ivanova

Low-Temperature Polymerization of Ethylene on an Oxinochromium Catalyst

A number of authors have investigated the polymerization of ethylene on oxinochromium catalysts at temperatures of 125–150°, i.e., above the melting point of the polymer ([1]–[3]). This was explained by the need to dissolve the polymer so that the catalyst surface would not be blocked by the polyethylene formed. However, there are data indicating that the formation of polyethylene on oxinochromium catalysts also occurs at temperatures below the melting point of the polymer ([4]). In this case the polymer formed does not go into solution, but is present as a suspension in the solvent. As a result, the viscosity is sharply reduced and the thermal conductivity of the reaction medium is increased, which considerably facilitates stirring and heat removal.

The present work is devoted to the study of the low-temperature polymerization of ethylene.

The oxinochromium catalyst was prepared according to the procedure described previously ([1]). For polymerization we used ethylene containing about 1–2 parts per million of oxygen and about 3 parts per million of water (dew point below −65°) ([1]). As the solvent we used *n*-heptane, which was treated at least twice with freshly ignited aluminum oxide. In all experiments the heptane had a constant moisture content (about 25 parts of water per million); for this purpose, before use the required amount of water was added to the heptane, and it was then purged, to remove oxygen, with nitrogen purified from water and moisture. The moisture content of the heptane was checked after purging with nitrogen.

Fig. 1. Kinetic curve obtained at a pressure of 9 atm, 75°, and a catalyst concentration of 0.336%.

Polymerization was carried out in a stainless-steel autoclave of 1 liter capacity, equipped with a stirrer with a shielded electric motor, according to the procedure described previously (^{1}).

The temperature and pressure in the autoclave during the reaction were kept constant. During polymerization, ethylene was fed from a graduated thermostated vessel; by periodically measuring the pressure in this vessel, the amount of ethylene absorbed was calculated, and then the reaction rate. Comparison of the calculated data with the weight of the polymer formed showed that the accuracy of measuring the polymerization rate was $±$5%.

All experiments were carried out at 75°. A characteristic kinetic curve is shown in Fig. 1. In most experiments a clearly pronounced induction period was observed, during which the reaction either did not proceed at all or proceeded at a rate 5-10 times lower than the steady-state rate. The duration of the induction period ranged from 30 to 150 min.; as a rule, with increasing pressure and catalyst concentration in the solvent, the induction period became shorter. After the end of the induction period

period, the reaction rate remains constant for a long time. The magnitude of this constant rate was taken as a measure of the activity of the catalyst. The duration of the period of constant activity depends on the concentration of the catalyst in the solvent; at a low catalyst concentration its activity remained constant for 20 hours (see Table 1). Apparently, the decrease in activity occurred as a result of the accumulation in the autoclave of a considerable amount of polymer: usually, soon after the drop in activity, the autoclave stirrer stopped. This indicates that the activity decreases as a result of deterioration of the mixing conditions, which leads to a decrease in the concentration of ethylene in the solution compared with the equilibrium concentration.

The product obtained at 75° consists of polyethylene granules 0.2 to 3 mm in size, grayish or white in color (at low catalyst content). Fig. 2 shows a photograph of a polymer grain, taken under a microscope at a magnification of 87.5 times, from which it is evident that there is no catalyst inside the polymer granule: catalyst grains are present only on that part of the granule which lies outside the cut surface. This indicates that in the course of polymerization the catalyst is comminuted, while at all times remaining on the surface of the polymer granules. The size of the catalyst particles located on the surface of the granules is 1-10 μ, whereas the initial catalyst had grains 0.5-1 mm in size. In Fig. 2, for clarity, a photograph is shown of a sample with an ash content of 1.7% (the polymer was obtained at 9 atm). In samples with lower ash content (down to 0.1%), under the microscope up to a magnification of 800 times, the same picture was observed in the distribution of the catalyst.

Fig. 2. Photograph of a polymer granule. 87.5×. Part of the granule surface has been cut away.

The dependence of the catalyst activity on its concentration in the solvent was studied. As follows from the data shown in Fig. 3, the polymerization reaction begins only after a certain threshold concentration of catalyst in the solvent

Fig. 2. Photograph of a polymer granule. 87.5×. Part of the granule surface has been cut away.

Figure 2: Fig. 2. Photograph of a polymer granule. 87.5×. Part of the granule surface has been cut away.

Fig. 3. Dependence of catalyst activity on its concentration in the solvent at 75° and solvent moisture content (n-heptane) ~25 parts of water per million (1 –for 15 atm; 2 –for 9 atm).

Figure 3: Fig. 3. Dependence of catalyst activity on its concentration in the solvent at 75° and solvent moisture content (n-heptane) ~25 parts of water per million (1 –for 15 atm; 2 –for 9 atm).

has been reached; with further increase in concentration, the reaction rate rises sharply and then remains constant. The appearance of a threshold concentration and the decrease in activity at low catalyst concentrations are probably explained by the fact that part of the catalyst surface is poisoned by impurities initially present in the reaction system (1).

Fig. 3. Dependence of catalyst activity on its concentration in the solvent at 75° and solvent moisture content (*n*-heptane) ~25 parts of water per million (1 –for 15 atm; 2 –for 9 atm).

Preliminary data were obtained on the dependence of the rate of ethylene polymerization on pressure. As can be seen from Fig. 4, the reaction rate

depends very strongly on the pressure; the relationship between the activity of the catalyst and the pressure cannot be described by a simple power dependence of the form $A = aP^n$ (where A is the activity of a unit weight of catalyst, P is the pressure, and n and a are constants). It may be assumed that, with increasing pressure, the exponent n changes from a value close to 2 (in the pressure region up to 9 ata) to a value close to 3 (in the pressure region 11-15 ata).

The molecular weight of the polymer does not depend on the catalyst concentration; for the polymer obtained at 9 ata it is 110-125 thousand; for the polymer obtained at 15 ata, 400-600 thousand.

At 15 ata very high yields of polyethylene per unit weight of catalyst were obtained (see Table 1).

Thus, in the low-temperature polymerization of ethylene, the catalyst during the reaction is found on the surface of the growing polymer grains and does not lose its activity for a prolonged period, which makes it possible to obtain high yields of polyethylene per unit weight of catalyst.

Fig. 4. Dependence of the polymerization rate on pressure (75°, water content in the solvent $\sim$ 25 parts per million)

Table 1

Results obtained in the polymerization of ethylene at 15 ata, 75°, and solvent moisture content (*n*-heptane) of 25 parts of water per million

Experiment No.	Charge, g	Catalyst conc. in solvent, wt. %	Catalyst activity, g C_2H_4 per 1 g catalyst per hour	Duration of stationary period, min	Weight of polymer obtained, g	Yield, g C_2H_4 per 1 g catalyst
1	0.155	0.0274	0	–	–	–
2	0.14	0.0325	55	1200	127	910
3	0.17	0.0465	170	660	255	1510
4	0.19	0.0520	110	1000	347	1800
5	0.23	0.0625	160	700	325	1430

Note. In all experiments the reaction stopped because the stirrer stopped.

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Note: Figure translations are in progress. See original paper for figures.

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