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Abstract

Full Text

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PHYSICAL CHEMISTRY

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THE EFFECT OF WATER AND OXYGEN ON THE POLYMERIZATION OF ETHYLENE ON A CHROMIUM OXIDE CATALYST

In carrying out deep polymerization of ethylene in the presence of a chromium oxide catalyst, the yield of polymer per unit weight of catalyst varies over wide limits ([1–3]). It is natural to suppose that these fluctuations are associated with the influence of impurities present in varying amounts in the ethylene or in the solvent. The present work is devoted to investigating the effect of the water and oxygen content in ethylene on the polymer yield.

The catalyst was prepared by impregnating an aluminosilicate support with a solution of chromic acid. As the support, a spherical aluminosilicate catalyst was used, with a bulk density of 0.43, a predominant pore radius of 40-60 Å, and a surface area of 300 m^2/g*. After impregnation the support was dried at 110° and calcined in a muffle furnace at 250°. Activation was carried out by heating for 4 hr at 400° and a pressure of 10^{-3} mm Hg. For this purpose, a weighed portion of the catalyst was placed in thin-walled ampoules, which were sealed to the manifold of a vacuum apparatus. Upon completion of activation, the ampoules were sealed off and weighed. The finished catalyst contained about 5% CrO_3.

Initially, experiments were carried out with the most complete possible purification of the ethylene. The initial ethylene at a pressure of 50 atm passed through a charcoal filter, a column with a nickel-chromium catalyst for purification from oxygen, and two columns with active alumina for removal of moisture. The ethylene entering polymerization contained less than three parts of oxygen per million; the dew point was below −65°, which corresponds to a water content of less than three parts per million. BR-1 gasoline, cyclohexane, heptane, and others were used as solvents. The solvents were preliminarily purified by threefold treatment with freshly calcined alumina and by purging with nitrogen purified from oxygen and water. The water content in the solvent purified in this way was about 5 parts per million.

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Figure 1. Autoclave for the study of catalytic polymerization: 1—autoclave body, 2—stirrer, 3—cup for the ampoule, 4—thermocouple, 5—flange, 6—cover, 7—bolt with nut, 8—cooler, 9—stator, 10—rotor, 11—hollow shaft, 12—rod, 13—handle

Figure 1: Figure 1. Autoclave for the study of catalytic polymerization: 1—autoclave body, 2—stirrer, 3—cup for the ampoule, 4—thermocouple, 5—flange, 6—cover, 7—bolt with nut, 8—cooler, 9—stator, 10—rotor, 11—hollow shaft, 12—rod, 13—handle

Fig. 2 and Fig. 3 graphs

Figure 2: Fig. 2 and Fig. 3 graphs

Catalytic polymerization was carried out in an autoclave of about one liter capacity, made of stainless steel. Special measures were taken to prevent impurities from entering the reaction system during the pro-

Fig. 1. Autoclave for the study of catalytic polymerization:
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of the experiment. The autoclave (Fig. 1) was equipped with an electromagnetic stirrer, a pocket for a thermocouple, and a device for breaking ampoules.

The procedure for carrying out the experiments was as follows. An ampoule with the catalyst was attached to the rod passing through the stirrer shaft. The autoclave was closed with a lid, placed in a split electric furnace, and connected to the ethylene-purification unit. The autoclave was then heated to 200° and evacuated with a fore-vacuum pump for 2 h, after which it was cooled to 100° and washed several times with purified ethylene. Into the evacuated autoclave, using dry nitrogen, 300 g of purified solvent was forced in, and dry ethylene was fed until a pressure of 35 atm was reached. After

Fig. 2. Dependence of the amount of polymer formed on the catalyst concentration in the solvent. *I* —water content in the solvent 5 h/ml, *II* —water content in the solvent 20 h/ml.

Fig. 3. Dependence of the catalyst productivity on its concentration in the solvent. *I* —water content in the solvent 5 h/ml, *II* —water content in the solvent 20 h/ml.

the regime had been established, the ampoule with the catalyst was crushed by pressing on the rod. As ethylene polymerization proceeded, the pressure in the autoclave fell, and it was again brought to 35 atm by admitting new

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Fig. 4

Figure 3: Fig. 4

portions of ethylene from the purification system, where a pressure of 50 atm was maintained. The polyethylene discharged from the autoclave was dried to constant weight and weighed. In determining the polymer weight, a correction was introduced for the weight of the ampoule with the catalyst.

The results of the study of ethylene polymerization under conditions of maximum purification are presented in Fig. 2, *I*. The curve of the dependence of the amount of polymer formed on the catalyst concentration in the solvent has an S-shaped form. The left-hand part of the curve (section *a*) shows that, if the catalyst concentration is below a certain "threshold" value, the reaction does not take place. Increasing the catalyst concentration above the "threshold" causes a sharp increase in the polymer yield (section *b*). After a certain limiting value has been reached (section *v*), which depends on the duration of the experiment, the amount of polymer formed does not depend on the catalyst concentration in the solvent.

This regularity leads to the appearance of a sharp maximum on the curve expressing the dependence of catalyst productivity (in grams of polymer per gram of catalyst) on its concentration in the solvent. As is seen from curve 1 in Fig. 3, for experiments with evacuation of the autoclave at 200°, with maximum purification of the ethylene and solvent, the threshold catalyst concentration in the solvent is 0.15%. When the catalyst concentration is increased above the threshold, the catalyst productivity rises sharply, reaching a maximum of about 600 g per 1 g of catalyst at a catalyst concentration in the solvent equal to 0.2%. With a further increase in the catalyst concentration, its productivity gradually decreases. With an increase in the content of impurities in the reaction

in the polymerizing system the shape of the curves for the dependence of polymer yield on catalyst concentration does not change; however, the threshold concentration increases. As a result, the maximum productivity of the catalyst decreases. Curves 2 in Figs. 2 and 3 characterize the dependence of polymer yield on catalyst concentration in the case of a solvent containing water in an amount of 20 parts per million. As is seen from the figures, increasing the water concentration in the solvent from 5 to 20 parts per million raises the threshold concentration from 0.14 to 0.24%. Correspondingly, the maximum productivity of the catalyst decreases from 610 to 360 g/g of catalyst.

Fig. 4. 1 –0.0003%; 2 –0.001%;
3 –0.01%; 4 –0.1% O_2

The oxygen content in ethylene also has a substantial effect on the yield of polyethylene. Figure 4 presents the dependence of catalyst productivity on its concentration in the solvent for different oxygen contents in ethylene. The duration of the experiments was 4 hours. As is seen from Fig. 4, with an increase in the oxygen content in ethylene, the threshold concentration of the catalyst increases considerably, as a result of which the maximum productivity of the catalyst decreases. In the case of ethylene containing 0.1% oxygen, polymerization does not occur. Various explanations are possible for the effect of impurities on the threshold catalyst concentration. The simplest supposition is that the impurities block the surface of the catalyst, and only when the amount of catalyst is so large that the impurities introduced with the ethylene and the solvent cannot cover all of its active surface can polymerization proceed at a high rate.

Preliminary measurements of the dependence of the polymerization rate on time showed that the polymerization rate initially increases, reaches a maximum, and then decreases. The period of increase in the reaction rate, associated with an increase in the number of growing polymer chains, depends on the purity of the ethylene and the solvent. This gives grounds to suppose that the action of impurities is manifested in two ways: both as a result of irreversible, slowly proceeding blocking of the active centers of the catalyst, and as a result of reversible sorption of impurities on the same centers, slowing the primary process of increasing the number of chains.

At high purity of the ethylene and solvent and with large catalyst charges, the total amount of polymer formed is approximately the same and corresponds to its concentration in solution of about 50%. This is associated with a sharp decrease in the rate of dissolution of ethylene as a result of a considerable increase in the viscosity of the polymer solution.

The maximum polymer yield makes it possible to estimate the number of chains produced by each atom of the active component of the catalyst. The average molecular weight of the polymer in our experiments was 100,000, which at a yield of 600 g corresponds to $6.0 \cdot 10^{-3}$ moles formed by one gram of catalyst. The total number of gram-atoms of chromium in 1 g of catalyst is $5 \cdot 10^{-4}$. Thus, if all chromium atoms performed the role of catalyst, there would be 12 chains per chromium atom.

In reality, however, only a small fraction of the chromium oxide is accessible to the reacting ethylene, and the number of chains produced by each atom is considerably larger. This provides grounds for concluding that, in the present process, chromium oxides are not the initiator of the reaction, but an actual catalyst, interacting repeatedly with the reacting substance.

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

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