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Fig. 1. Kinetics of isoprene polymerization by the washed catalyst precipitate with addition of an R_2AlCl solution, at ratios $R_2AlCl/\beta-TiCl_3$: 1 –0.3; 2 –0.5; 3 –1.0; 4 –2.0; 5 –4.0; 6 –control experiment on a catalyst not subjected to washing

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Abstract

Full Text

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THE ROLE OF SOLUBLE ORGANOALUMINUM COMPOUNDS IN THE POLYMERIZATION OF ISOPRENE BY A COMPLEX CATALYST

The role of the soluble part of the cocatalyst in the reaction of stereospecific polymerization of isoprene remains unclear, although many authors have dealt with this question (1-6).

The catalyst is usually prepared by mixing equimolecular amounts of solutions of titanium tetrachloride $[TiCl_4]$ and triisobutylaluminum $[R_3Al]$. In this process a brown precipitate of $\beta-TiCl_3$ is formed, containing from 10 to 40% organoaluminum compounds. Part of the latter is bound to titanium chloride so firmly that it cannot be washed out with ordinary hydrocarbon solvents (7-9). The remaining amount of diisobutylaluminum chloride $[R_2AlCl]$ is present in the solution above the precipitate.

The prevailing opinion is that the solid part of the catalyst, separated from the solution and washed with solvent, does not cause polymerization of unsaturated hydrocarbons. The catalytic activity can be restored by adding a fresh portion of trialkylaluminum or dialkylaluminum chloride (4, 6). Experiments carried out by us showed that the $\beta-TiCl_3$ precipitate indeed does not cause polymerization of isoprene if its separation from the solution and the washing out of organoaluminum compounds are carried out in an atmosphere of argon, i.e., under the conditions in which experiments of this kind are usually performed.

Fig. 1. Kinetics of isoprene polymerization by the washed catalyst precipitate

Figure 2 graph

Figure 2: Figure 2 graph

with addition of an R_2AlCl solution, at ratios $R_2AlCl/\beta-TiCl_3$:

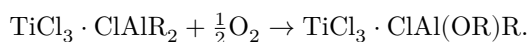
1 –0.3; 2 –0.5; 3 –1.0; 4 –2.0; 5 –4.0; 6 –control experiment on a catalyst not subjected to washing.

The catalytic activity of the $\beta-TiCl_3$ precipitate is restored after “grinding” the precipitate in an R_2AlCl solution. We carried out this operation in thick-walled ampoules half-filled with glass rods. The ampoules were shaken with an electrovibrator for 50 hours at a temperature of 20° .

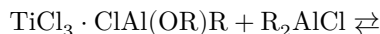
The limit to which the activity of the catalyst can be restored depends on the ratio $[R_2AlCl]/[\beta-TiCl_3]$, but in none of the experiments was it possible to attain the activity characteristic of the original catalyst before removal of the soluble part (Fig. 1).

If one proceeds from the assumption that the active centers of polymerization are complex compounds of the $\beta-TiCl_3 \cdot R_2AlCl$ type, formed at sites of disruption of the crystal lattice of $\beta-TiCl_3$, then “grinding” the precipitate in an R_2AlCl solution should lead to complete restoration of the catalyst activity. The absence of such restoration compels one to assume the presence of irreversible oxidation of the active centers of polymerization by traces of oxygen contained in the argon atmosphere in which the ...

all operations with the catalyst were carried out. For example, according to the scheme:



Then the restoration of the catalyst activity upon addition of R_2AlCl will not be the result of adsorption of the latter on the active sites of the $\beta-TiCl_3$ surface, but the result of an exchange reaction:



analogous to the case of vanadium catalysts for the polymerization of isoprene ⁽¹²⁾.

Fig. 2. Dependence of $W_0/(W_0 - W_x)$ on n_0/r_0 .

1—results of experiments presented in Fig. 1; 2—6—data from experiments on polymerization on unwashed catalyst in the presence of impurities: 2—oxygen, 3—ethyl alcohol, 4—acetone, 5—formic acid, 6—dimethylamine.

Figure 3 apparatus

Figure 3: Figure 3 apparatus

Proceeding from such concepts of the mechanism of “poisoning” and restoration of catalyst activity, it proved possible to explain the experimental data obtained by us, as well as the effect of certain impurities on the rate of the polymerization reaction ⁽¹³⁾.

Let us introduce the notation: $n^* = [\text{TiCl}_3 \cdot \text{R}_2\text{AlCl}]$, $n = [\text{R}_2\text{AlCl}]$, $r^* = [\text{TiCl}_3 \cdot \text{RAl(OR)Cl}]$, $r = \text{RAl(OR)Cl}$. Then the total amount of the one and the other type of organoaluminum compound will be: $n_0 = n + n^*$ and $r_0 = r + r^*$. Before deactivation of the catalyst, the number of active centers is equal to: $n_0^* = n^* + r^*$, and the polymerization rate is described by the equation: $W_0 = kn_0^*m$, where m is the monomer concentration. To determine the expected reaction rate after complete deactivation and partial restoration of activity ($W_x = kn^*m$), we shall use the following assumptions. The equilibrium constant for the above reaction of restoration of catalyst activity is determined by the expression:

$$K = \frac{r \cdot n^*}{n \cdot r^*} = \frac{[r_0 - (n_0^* - n^*)] n^*}{(n_0^* - n^*)(n_0 - n^*)}$$

Since the fraction of organoaluminum compounds adsorbed on the active sites of the catalyst surface is comparatively small, it may be assumed without appreciable error that $n_0 \gg n^*$ and $r_0 \gg (n_0^* - n^*)$. Consequently,

$$K = \frac{r_0 n^*}{(n_0^* - n^*) n_0}$$

or

$$\frac{W_0}{(W_0 - W_x)} = 1 + K(n_0/r_0).$$

The experimental values of the quantities $[W_0/(W_0 - W_x)]$ and $[n_0/r_0]$ lay around the calculated straight line at $K \cdot (1/r_0) = 0.135$ (Fig. 2, points 1). The polymerization rate was determined from the slope of the tangent to the kinetic curve in the initial period of the process.

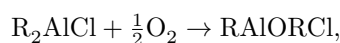
Fig. 3. Apparatus for washing the catalyst and carrying out polymerization in vacuum.

a—vessel for the catalyst suspension, *b*—vessel for isoprene solution in hexane, *v*—receiver for the washed organoaluminum compounds, *g*—porous glass filter, *d*—glass partition.

This series of experiments was carried out on one sample of catalyst separated from solution and washed. If it is assumed that, during the washing of the catalyst, the complex-bound organoaluminum compounds are completely oxidized, then $r_0 = 0.17$ g-mole/mole TiCl_3 and $K = 0.023$

On the basis of the results obtained, the following two conclusions may be drawn:

1. If polymerization is carried out on a catalyst that has not been washed, in the presence of certain impurities capable of reacting with organoaluminum compounds, for example according to the scheme



then the inactive organoaluminum compounds formed must enter into an equilibrium-exchange reaction with the active centers of polymerization and thereby cause "poisoning" of the catalyst. The decrease in the polymerization rate as a function of the amount of impurity should obey the equation derived above. It was found that the values of $W_0/(W_0 - W_x)$ versus n_0/r_0 , calculated on the basis of the experimental data from work ⁽¹³⁾, lay, with some scatter, around the straight line obtained in the present study (Fig. 2, points 2-6).

Table 1

Results of experiments on polymerization of isoprene with a catalyst precipitate washed with hexane in the absence of contact with argon

Experiment No.	Number of catalyst washings	Amount of R_2AlCl in the catalyst after washing, % of initial	Polymerization		Polymer properties: mol. wt.	Polymer properties: content of 1,4-cis units
			duration, h	Polymer yield, %		
1	no	100	2	77.2	460 000	88
2	no	100	2	86.0	350 000	93
3	no	100	10	98.0	390 000	90
4	5	100*	10	88.5	430 000	88
5	1	51.4	2	79.0	376 000	96
6	2	23.3	2	83.0	326 000	94
7	4	20.5	2	87.0	350 000	94
8	5	21.3	10	93.8	440 000	86
9	6	18.5	2	81.2	370 000	93

* Fresh diisobutylaluminum chloride was introduced into the washed catalyst before polymerization in an amount equal to that removed.

2. If the catalyst precipitate is separated from the soluble fraction and washed while observing special precautions ensuring the absence of traces of molecular oxygen or moisture, then removal of the soluble organoaluminum compounds should not cause a decrease in catalyst activity. Indeed, carrying out the indicated operations in vacuum in the apparatus shown in Fig. 3 demonstrated that, at least in the case of catalysts prepared with an equimolecular ratio of the components, the catalytic properties of the catalyst precipitate are practically independent of the amount of soluble organoaluminum compounds removed (Table 1).

These experiments prove that the catalyst for isoprene polymerization consists of stable complex compounds of β -TiCl₃ with dialkylaluminum chloride. Soluble organoaluminum compounds, or organoaluminum compounds only weakly adsorbed by the precipitate, do not influence the activity of the catalyst, but constitute a "protective" medium that prevents it from being "poisoned" by traces of certain impurities.

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