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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON CATALYTICALLY ACTIVE PARTICLES IN THE SYSTEM $TiCl_4$–Et_2AlCl IN THE PROCESS OF ETHYLENE POLYMERIZATION

(Presented by Academician N. N. Semenov, June 12, 1963)

Deep polymerization of alpha-olefins is readily carried out on systems that include titanium trichloride or tetrachloride in combination with R_3Al or R_2AlCl. In the case of systems containing $TiCl_3$, the system is catalytically active from the moment the monomer is introduced; in the case of $TiCl_4$, however, the appearance of catalytically active particles is associated with the development of oxidation-reduction processes occurring over time. It has been established that in the reduction of $TiCl_4$ not only $TiCl_3$ is formed, but also solid products of more complex composition containing aluminum ([1], [2]). The sharp difference in the molecular weights of the polymers obtained ([3]) also characterizes the different nature of the catalytically active particles in these systems. The aim of the present investigation was to establish the nature of the catalytically active particles in the $TiCl_4$–Et_2AlCl system, present both in the solid phase and in solution. The most detailed study of the composition was carried out for two special cases: when the activity of the system reached its maximum value and when the activity practically did not change with time.

Fig. 1. Dependence of the initial rate of polymerization of C_2H_4 on the aging time of the $TiCl_4$–Et_2AlCl system without monomer

The experiments were carried out at a $TiCl_4$ concentration of 10 g/l ($5.28 \cdot 10^{-2}$ mol/l), a molar ratio $TiCl_4 : Et_2AlCl = 1 : 1$, and 30°. The solvent was dry, spectroscopically pure *n*-heptane. The precipitates formed in the interaction of $TiCl_4$ and Et_2AlCl were isolated by filtration or centrifugation, washed repeatedly with *n*-heptane, and dried under vacuum.

The composition of the precipitate was determined by volumetric methods: chlorine by Folgard, titanium colorimetrically with H_2O_2 ([4]), aluminum qualitatively with alizarin and quantitatively by complexometric titration ([5]), and alkyl groups by the volume of gas evolved upon decomposition with alcohol. The composition of the gas was determined chromatographically. Colorimetric determination of titanium in the filtrates and of trivalent titanium in the hydrolysis products of the precipitates and filtrates was also carried out with the aid of $FeCl_3$ ([6]). Polymerization experiments were performed in a metal apparatus. The reaction vessel, of volume 0.25 l, was equipped with a stuffing-box stirrer ([7]). During the experiment, constant temperature and C_2H_4 pressure were maintained.

In order to establish how the activity of the system under study changes with time, experiments were carried out in which the monomer was introduced at different time intervals (from 0 to 6 hr) after mixing $TiCl_4$ and Et_2AlCl. The dependence of the initial rate of polymerization on the aging time of the system without monomer is presented in Fig. 1. The curve shown characterizes the change in activity of the system with time in the absence of monomer. Under the conditions studied, the maximum rate of polymerization (500 g C_2H_4/hr $\cdot$ l $\cdot$ atm) is reached 30-40 min after mixing the catalyst components. By 4 hr the activity decreases to 300 g C_2H_4/hr $\cdot$ l $\cdot$ atm and then remains practically constant. The intrinsic viscosity $[\eta]$ of the polyethylene formed, when the aging time is increased from 0.5 to 4 hr, increases from 1.1 to 1.5 $\cdot$ 100 ml/g.

The amount and composition of the precipitate also change with time. In 30 min, about 1.5 g of precipitate (1) with a specific surface area of 28 m^2/g is formed in 1 liter (determined by the BET method (^8)). By 4 h, the concentration of the precipitate reaches 6.4 g/l. The surface area of this precipitate (2) is 90 m^2/g.

Table 1

Composition of precipitates formed after 0.5 h (precip. 1) and after 4 h (precip. 2) after mixing $TiCl_4$ and Et_2AlCl (molar ratio 1:1; $TiCl_4$ concentration 10 g/l; 30°C)

Precipitate no.	Method of analysis	Ti	Cl	Et	C	H	Σ
1	Volumetric	26.5*	58	16			100.5
1	Elemental microanalysis**	29.12	57.71		8.93	1.90	97.66
1	Theor. for $EtTiCl_3$	26.00	58.2	15.8	13.10	2.73	100.00
2	Volumetric	35	52.8	6.4	6.77	24	11

Fig. 2. Kinetic curves of C_2H_4 polymerization in the presence of various catalysts and precipitate (1). $P_{C_2H_4}$ = 3.5 atm.; 30°C. Solvent: *n*-heptane. 1 –filtrate after separation of (1), diluted 11.7-fold with *n*-heptane (Ti content 1.77 g/l); 1a –the same + (1) (1.2 g/l), 2 –precipitate (1) (1.2 g/l) without cocatalyst, 3 –Et_2AlCl (0.5 g/l) and (1) (1.2 g/l), 4 –Et_2AlCl (0.45 g/l), $TiCl_4$ (0.7 g/l) + (1) (1.2 g/l)

Figure 2: Fig. 2. Kinetic curves of C_2H_4 polymerization in the presence of various catalysts and precipitate (1). $P_{C_2H_4}$ = 3.5 atm.; 30°C. Solvent: *n*-heptane. 1 –filtrate after separation of (1), diluted 11.7-fold with *n*-heptane (Ti content 1.77 g/l); 1a –the same + (1) (1.2 g/l), 2 –precipitate (1) (1.2 g/l) without cocatalyst, 3 –Et_2AlCl (0.5 g/l) and (1) (1.2 g/l), 4 –Et_2AlCl (0.45 g/l), $TiCl_4$ (0.7 g/l) + (1) (1.2 g/l)

* After decomposition of the precipitate, all Ti is titrated as trivalent.

** The analysis was carried out by staff member of the Institute of Chemical Physics V. N. Likhashertova.

The data on the composition of the isolated precipitates are given in Table 1. Aluminum is absent from precipitate (1). The chlorine and titanium contents in this precipitate and the amount of gas evolved upon its decomposition (in the case of alcohol this is mainly ethane) correspond to $EtTiCl_3$. This is also confirmed by the results obtained in elemental analysis for C, H, and Cl. A qualitative reaction with Michler' s ketone (ˆ9) indicates the presence of a Ti–C bond. Precipitate (1) and the filtrate after its separation give no EPR signal at room temperature. It is interesting that after decomposition of precipitate (1) with alcohol or with an aqueous solution of H_2SO_4, the titanium contained in this precipitate (which can be titrated with $FeCl_3$) as trivalent (ˆ2) has a more complex composition, described by the general formula $Ti_3Cl_6 \cdot AlEt$ (see Table 1), and gives an EPR signal at room temperature. Both precipitates are poorly soluble in hydrocarbons, but in the presence of $TiCl_4$ their solubility increases sharply (the solutions are colorless). For example, at 20°C the solubility of precipitate (1) increases from $8.5 \cdot 10^{-5}$ to $4.5 \cdot 10^{-2}$ mol/l upon introduction into *n*-heptane of $TiCl_4$ in an amount of $8.4 \cdot 10^{-2}$ mol/l. This explains the presence in the filtrates of compounds, evidently $EtTiCl_3$, which hydrolyze with formation of Ti^{3+}. Under the conditions studied, the content of these compounds in solution reaches $1.56 \cdot 10^{-2}$ mol/l by 0.5 h (with a total amount of Ti in solution of $4.56 \cdot 10^{-2}$ mol/l); by 2 h it decreases to $0.52 \cdot 10^{-2}$, and by 4 h to $0.15 \cdot 10^{-2}$ mol/l (the total amount of Ti in the filtrate then decreases correspondingly to $2.38 \cdot 10^{-2}$ and $0.18 \cdot 10^{-2}$ mol/l). These substances, with organoaluminum compounds, give colored complex compounds in the presence of $TiCl_4$ (red-yellow color of the filtrates).

Fig. 2. Kinetic curves of C_2H_4 polymerization in the presence of various catalysts and precipitate (1). $P_{C_2H_4}$ = 3.5 atm.; 30°C. Solvent: *n*-heptane. 1 –filtrate after separation of (1), diluted 11.7-fold with *n*-heptane (Ti content

Fig. 3. Kinetic polymerization curves

Figure 3: Fig. 3. Kinetic polymerization curves

1.77 g/l); 1a –the same + (1) (1.2 g/l), 2 –precipitate (1) (1.2 g/l) without cocatalyst, 3 –Et_2AlCl (0.5 g/l) and (1) (1.2 g/l), 4 –Et_2AlCl (0.45 g/l), $TiCl_4$ (0.7 g/l) + (1) (1.2 g/l).

The filtrate remaining after separation of precipitate (1) and containing a significant amount of these compounds was diluted with *n*-heptane (11.7-fold) in order to slow further transformations and was tested in the polymerization process. It turned out (see Fig. 2, 1) that at the initial moment the filtrate is inactive, but its activity increases with time. The time during which

the maximum rate is reached depends on the pressure of C_2H_4 and the temperature ([η] of the polyethylene obtained is $0.4 \cdot 100$ ml/g). The precipitate (1) suspended in *n*-heptane, in the absence of cocatalyst, is active only for several minutes after the introduction of ethylene; the polymerization rate is low (Fig. 2, 2). Precipitate (1) is practically inactive also in the presence of $TiCl_4$.

Fig. 3. Kinetic curves for the polymerization of C_2H_4 in the presence of various cocatalysts and precipitate (2), $P_{C_2H_4} = 3.5$ atm; 30 °C. Solvent: *n*-heptane. **1** –Et_2AlCl (0.5 g/l) and (2) (1.5 g/l); **2**–filtrate after separation of (1), diluted 11.7-fold with *n*-heptane, and precipitate (2) (precipitate concentration 1.5 g/l); **3**–Et_2AlCl (0.45 g); $TiCl_4$ (0.7 g/l) and (2) (1.5 g/l); **3a**–the same without precipitate.

For the system precipitate (1)–Et_2AlCl, the rate (see Fig. 2, 3) is at least 100 times lower than the value that could have been expected on the basis of the curve shown in Fig. 1, and the intrinsic viscosity is $[\eta] = 20 \cdot 100$ ml/g. Consequently, Et_2AlCl, as well as $EtAlCl_2$, which is still less active, is not the cocatalyst determining the rate of the process and the properties of the product in the $TiCl_4$–Et_2AlCl system. Such cocatalysts are evidently complex compounds formed in solutions containing $EtTiCl_3$, $TiCl_4$, and Et_2AlCl.

Indeed, if, instead of Et_2AlCl, the filtrate after separation of precipitate (1), diluted with *n*-heptane, is used as cocatalyst, the polymerization rate increases sharply (Fig. 2, 1a), while [η] of the polyethylene decreases to $1.7 \cdot 100$ ml/g. When this same filtrate is added to precipitate (2), which in the absence of cocatalyst is inactive, but with Et_2AlCl polymerizes C_2H_4 at a rate of 14 g/hour $\cdot$ atm $\cdot$ g, the rate increases approximately threefold (Fig. 3, 1 and 2). (With Et_2AlCl, [η]–14.6; with filtrate–$2.4 \cdot 100$ ml/g.) From these data it is seen that the decrease in the activity of the $TiCl_4$–Et_2AlCl system with time (Fig. 1) is due to a decrease in the concentration of active cocatalysts, which exist only in the presence of $TiCl_4$ in solution. The addition of small amounts of $TiCl_4$ to (1)–Et_2AlCl (Fig. 2, 4) and to (2)–Et_2AlCl (Fig. 3, 3) leads to a significant increase in the rate of the process. At the same time, [η] of the product decreases, respectively, to 1.7 and $2.4 \cdot 100$ ml/g.

Evidently, in the presence of $TiCl_4$, part of the precipitate dissolves and active complex cocatalysts are formed, in the presence of which lower-molecular-weight polyethylene is obtained. Probably, the sharp dependence of the rate of the process and of the molecular weight of the product on the concentration of cocatalysts and on the ratio between catalytic components, characteristic of systems containing $TiCl_4$, VCl_4 ([10,11,12]), as well as the change in the molecular weight of the product formed with time ([3,13]), are due to analogous phenomena.

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