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Abstract

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POLYMERIZATION OF ETHYLENE ON A CHLORINATED MIXTURE OF TITANIUM AND ALUMINUM METALS

The most active catalysts for the polymerization of ethylene at low pressure are systems formed by mixing aluminum alkyls with titanium chlorides. Each year more and more papers appear in the literature on the polymerization of ethylene in the presence of modified heterogeneous catalysts of the Ziegler type, in which at least one of the components has been replaced by a simpler and more readily available compound.

Working in this field, we obtained, in high yield, solid polyethylene having a flow temperature, determined from thermomechanical curves, of 120 to 135°, using for this purpose heterogeneous catalytic systems prepared from α-$TiCl_3$ + $AlCl_3$ + Al, α-$TiCl_3$ + (Al + HCl), and then also α-$TiCl_3$ + (Al + Cl_2). Naturally, the latter two systems, in which $AlCl_3$ is obtained directly in the chlorination or hydrochlorination of metallic aluminum, are the logical consequence of the activity of a catalytic system prepared on the basis of commercial $TiCl_3$, $AlCl_3$, and Al. It is interesting that in the absence of $AlCl_3$, solid polyethylene was obtained in very small amounts, while without $TiCl_3$ the catalytic system turned into an alkylating catalyst.

Developing these studies, we proposed that a mixture of Al + Ti metals, previously treated with chlorine or dry hydrogen chloride in a suitable solvent, should possess catalytic activity in the polymerization of ethylene. On treatment with Cl_2 or HCl, part of the metallic Al is converted into "yellow" $AlCl_3$ of defective structure, according to the well-known reaction of Razuvanova ([1]), while part of the metallic Ti is chlorinated to $TiCl_4$. The latter is reduced by aluminum to titanium chlorides of lower valence. Analysis showed that, in addition to metallic titanium, aluminum, and the aluminum chloride formed, the precipitate contained only traces of Ti^{3+}, while Ti^{4+} was not detected in the precipitate at all.

Indeed, when finely cut shavings or filings of a mixture of Ti and Al metals* were treated with Cl_2 or HCl, an effective catalyst for ethylene polymerization was obtained. The best results were obtained when the molar ratio of the initial metals Al : Ti = 1 : 1 was used. It is noteworthy that chlorination with Cl_2 or HCl of metallic aluminum alone led to the formation of an alkylating catalyst,

whereas upon treatment with Cl_2 or HCl of metallic titanium the resulting system was capable of polymerizing ethylene to solid products only when the corresponding metal alkyl was introduced.

The results of experiments on the polymerization of ethylene (60°, 10 ± 1 atm) in the presence of preliminarily chlorinated Al + Ti metals, carried out—

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* Chlorination of the metals was carried out at 50° for 10 h, with the gas passed through a suspension of metallic shavings or powder in the corresponding solvent at a rate of 3–4 l/h. During this time, approximately 17–26% of the initially charged aluminum ($Al_{initial}$) and up to 2–3% of titanium ($Ti_{initial}$) were converted into metal chlorides.

Table 1

Polymerization of ethylene in the presence of (Al + Ti + HCl) **and** (Al + Ti + Cl_2)

$Al_{initial}$, g	$Ti_{initial}$, g	Cl/Al	PhOH/Al	Temp., °C	Pressure, atm	Polyethylene yield, g	Hexane-soluble polyethylene yield, g	Limiting viscosity of polyethylene, $[\eta]$	Softening temperature of polyethylene, °C
System (Al + Ti + HCl)	**System (Al + Ti + HCl)**	**System (Al + Ti + HCl)**	**System (Al + Ti + HCl)**	**System (Al + Ti + HCl)**	**System (Al + Ti + HCl)**	**System (Al + Ti + HCl)**	**System (Al + Ti + HCl)**	**System (Al + Ti + HCl)**	**System (Al + Ti + HCl)**
11,5	20,4	2,55	0,1	60	10	106	–	0,51	115
5,75	10,2	2,4	–	60	10	59	–	0,36	117
5,75	10,2	2,82	0,15	60	10	3	31	–	–
5,75	10,2	2,83	0,5	60	10	19	7	0,92	–
5,75	10,2	2,43	0,1	60	10	50	–	0,82	128
5,75	10,2	2,64	0,22	60	10	43	–	–	–
5,75	10,2	2,74	0,02	75	10	45	–	0,03	–
5,75	10,2	1,74	0,07	90	10	24	–	0,3	–
5,75	10,2	3	0,2	60	10	19	20	0,3	–
5,75	10,2	2,2	0,49	60	10	59	–	–	–
5,75	10,2	2,2	0,06	60	5	22	–	0,22	–
5,75	10,2	2,88	0,2	60	14	19	6	–	–
11,5	5,1	2,38	–	60	10	15	–	–	–
2,88	20,4	2,3	0,57	60	10	very little	–	–	–

Al_initial, g	Ti_initial, g	Cl/Al	PhOH/Al	Temp., °C	Pressure, atm	Polyethylene yield, g	Hexane yield, g	Limiting viscosity of polyethylene, [η]	Softening temperature of polyethylene, °C
System (Al + Ti + Cl_2)	**System (Al + Ti + Cl_2)**	**System (Al + Ti + Cl_2)**	**System (Al + Ti + Cl_2)**	**System (Al + Ti + Cl_2)**	**System (Al + Ti + Cl_2)**	**System (Al + Ti + Cl_2)**	**System (Al + Ti + Cl_2)**	**System (Al + Ti + Cl_2)**	**System (Al + Ti + Cl_2)**
5,75	10,2	2,8	–	60	10	44	9,5	0,22	120
5,75	10,2	2,24	0,04	60	10	40	–	–	–
11,5	5,1	1,3	0,05	60	10	70	–	–	119
11,5	5,1	2,84	0,004	60	10	20	10	–	–
11,5*	5,1	2,66	0,02	60	10	–	–	–	–
5,75	10,2	–	–	60	10	20,5	–	0,32	122
5,75	10,2	3,3	0,08	60	40	–	92	–	–

* Aluminum and titanium were treated with chlorine separately.

carried out by the procedure described in work ([2]), are summarized in Table 1. The polyethylene obtained was characterized by a high degree of crystallinity, as is seen from the electron diffraction pattern shown (Fig. 1) (see insert).

The kinetics of the ethylene polymerization process was characterized by the graphical dependences given in Fig. 2. Three periods are clearly distinguished.

Fig. 2. Rate of ethylene absorption in the course of polymerization ((Al + Ti + HCl), benzene).
1 –10 kg/cm^2 at 30°; 2 –10 kg/cm^2 at 40°; 3 –10 kg/cm^2 at 60°; 4 –10 kg/cm^2 at 75°; 5 –5 kg/cm^2 at 60°; 6 –14 kg/cm^2 at 60°.

Immediately after introduction of the monomer into the reaction zone, an increase in the polymerization rate takes place over a short interval of time, evidently associated with the formation of a stationary number of active centers (the first period). Consequently, the active centers, in all probability, are formed with the participation of the monomer, as has already been observed, for example, when using alfin catalysts ([3]). Having reached a maximum, the polymerization rate remains constant for a considerable time (the second period, steady state). Finally, the third period is associated with a decrease in the overall rate of ethylene polymerization, evidently due to the blocking of part of the active centers by the polymer formed.

To the article by K. S. Minsker, G. T. Fedoseeva, N. A. Vorob' eva, G. A. Razuvaev, p. 1351

Figure 1

Figure 1: Figure 1

Figure 1

Figure 2: Figure 1

Fig. 1. Electronogram of polyethylene obtained in the presence of $(Al + Ti + Cl_2)$

To the article by Ya. A. Ugai, E. M. Averbakh, Yu. Ya. Gukovoi, V. V. Lavrov, p. 1387

Fig. 1. Microstructure of the compound Zn_4Sb_3, obtained by rapid cooling. 600×

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Figures 3 and 4 show the change in the kinetic characteristics of the process in the region of constant rate as a function of the ethylene pressure in the reactor and the process temperature.

From the temperature dependence, the total apparent activation energy of the ethylene polymerization process was calculated; it proved to be 12.8 kcal/mole. It should be especially noted that the direction of the ethylene-conversion reaction depends to a substantial degree on the molar ratio Cl/Al in the heterogeneous phase of the catalyst (see Table 1).

Fig. 3. Change in the rate of ethylene absorption as a function of pressure in the region of constant rate $(Al + Ti + HCl)$, benzene, 60°.

Fig. 4. Temperature dependence of ethylene polymerization in the region of constant rate in the presence of $(Al + Ti + HCl)$, benzene, 10 kg/cm^2.

At a Cl : Al ratio below 2.8, the polymerization reaction proceeds predominantly, and the catalyst has anionic activity. At a Cl : Al ratio above 2.8, cationic activity of the catalyst begins to appear. In this case, instead of polymerization, deep alkylation of benzene by ethylene is observed. After treatment of the precipitate with air, besides aluminum, titanium, and chlorine, phenol was detected in varying amounts (the molar content PhOH/Al ranged from tenths to thousandths). The different phenol content in the catalyst did not affect its activity in the polymerization reaction (at one and the same Cl/Al ratio). This experimental fact permits the conclusion that the polymerization activity of the catalyst is not directly associated with the carbanion $C_6H_5^-$. However, in the

Figure 3 and Figure 4: kinetic plots

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process of catalyst formation, benzene (or another solvent of aromatic character closely related to it) is necessary. When benzene was replaced at this stage by an inert solvent of the saturated-hydrocarbon type, the process of ethylene polymerization to solid products did not occur.

On the basis of the facts set forth above, it should be considered that, in the process of treating a mixture of the metals Al + Ti with hydrogen chloride or chlorine in benzene, an active catalyst for ethylene polymerization of a new type is formed, the structure of which most closely corresponds to the formula $[Ti^{2+}Al_2Cl_8] \cdot C_6H_6$ (4). In this connection, the formation of phenol is due not to oxidation of the aryl metal Me—Ph by oxygen, but to oxidation of benzene in the presence of $AlCl_3$ and titanium chlorides.

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