FEATURES OF THE CATALYSIS OF ETHYLENE POLYMERIZATION ON THE SYSTEM $(\mathrm{C}_5\mathrm{H}_5)_2 – $\mathrm{Et}_2\mathrm{AlCl}$ AND $(\mathrm{C}_5\mathrm{H}_5)_2 – $\mathrm{Et}_3\mathrm{Al}$ IN AN ALKYL CHLORIDE MEDIUM

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Abstract

Full Text

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É. A. FUSHMAN, V. I. TSVETKOVA, N. M. CHIRKOV

FEATURES OF THE CATALYSIS OF ETHYLENE POLYMERIZATION ON THE SYSTEM $(C_5H_5)_2TiCl_2$—Et_2AlCl AND $(C_5H_5)_2TiCl_2$—Et_3Al IN AN ALKYL CHLORIDE MEDIUM

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A number of data obtained in studying the kinetics of ethylene polymerization in various solvents using the homogeneous catalytic systems $(C_5H_5)_2TiCl_2$—Et_2AlCl and $(C_5H_5)_2TiCl_2$—Et_3Al indicate that in solvents with a mobile chlorine atom, such as 1,2-dichloroethane, ethyl chloride, and methylene chloride, reactions occur that lead to activation of the complexes of trivalent titanium, which are practically inactive in polymerization (^{1,3}),

Fig. 1. Kinetic curves of ethylene polymerization on the system $(C_5H_5)_2TiCl_2$—Et_2AlCl in different solvents (the polymerization rate is referred to unit ethylene concentration). $T = 20°$; $P_{C_2H_4} = 390$ mm Hg; $[(C_5H_5)_2TiCl_2] = 1.2 \cdot 10^{-3}$, $[Et_2AlCl] = 12 \cdot 10^{-3}$ mol/l.
1—benzene, 2—chlorobenzene, 3—methylene chloride, 4—dichloroethane, 5—ethyl chloride

Fig. 2. Kinetic curves of ethylene polymerization in dichloroethane at various temperatures. $P_{C_2H_4} = 390$ mm Hg; $[(C_2H_5)_2TiCl_2] = 1.2 \cdot 10^{-3}$ mol/l, $[Et_2AlCl] = 12 \cdot 10^{-3}$ mol/l. Temperature: 1—20°, 2—30°, 3—40°, 4—after 3 hours at 40°, an additional $0.4 \cdot 10^{-3}$ mol/l Et_2AlCl was introduced

trivalent titanium $(C_5H_5)_2TiCl \cdot Et_2AlCl$ (I), $(C_5H_5)_2TiCl \cdot EtAlCl_2$ (II).

This explains the significant increase in the lifetime of the indicated catalytic systems when polymerization is carried out in an alkyl chloride medium (^{2}).

Figure 1 presents kinetic curves of ethylene polymerization in various solvents on the system $(C_5H_5)_2TiCl_2$—Et_2AlCl under identical conditions. It is seen from the figure that in benzene and chlorobenzene (curves 1 and 2) already one hour

Fig. 3

Figure 2: Fig. 3

after mixing the catalyst components the system is practically inactive; this is due to reduction of tetravalent titanium, which forms active centers, to trivalent titanium ([1,3]). Under the same conditions in alkyl chlorides the activity of the system is maintained for a long time (Fig. 1, curves 3, 4, 5), and the yield of polyethylene is considerably higher (see Table 1).

For this system, in contrast to ordinary Ziegler—Natta catalysts ([4]), when alkyl chlorides are used there is no substantial change in molecular weight (Table 1), and low branching is retained—

···of polyethylene (polyethylene contains less than one CH_3 group per 1000 carbon atoms). The polymer has high physico-mechanical properties ([2],[5]).

The decrease in the lifetime of the system observed upon lowering the molar ratio Al : Ti and upon raising the temperature (Fig. 2) is due to consumption of the aluminum alkyl (the activity increases when a new portion of Et_2AlCl is added, Fig. 2, 4). Thus, the cause of deactivation here is different from that in aromatic solvents. As is known ([1]), with Et_3Al the reduction of titanium proceeds very rapidly, and in inert solvents the system $(C_5H_5)_2TiCl_2$—Et_3Al practically does not polymerize ethylene.

Fig. 3. Change with time in the catalytic activity of the system $(C_5H_5)_2TiCl_2$ —Et_3Al (1, 2) and of complex II (3) in dichloroethane.
1 —20°, $P_{C_2H_4} = 390$ mm Hg; $[(C_5H_5)_2TiCl_2] = 1.2 \cdot 10^{-3}$ mol/l, $[Et_3Al] = 3.6 \cdot 10^{-3}$ mol/l;
2a —activity of the system after 7 days; 2 —after addition of $1 \cdot 10^{-3}$ mol/l Et_3Al;
3 —conditions of preparation of complex II: solvent 40 ml, $[(C_5H_5)_2TiCl_2] = 2 \cdot 10^{-3}$, $[Et_3Al] = 4 \cdot 10^{-3}$ mol/l; after removal of heptane and excess Et_3Al, 40 ml of dichloroethane was added. Polymerization conditions: 20°; $P_{C_2H_4} = 390$ mm Hg.

In an alkyl chloride medium the polymerization rate at the initial moment is low, but gradually the activity of the system increases (Fig. 3, 1), and at low molar ratios $Et_3Al : (C_5H_5)_2TiCl_2$ the maximum activity is close to the activity of the system $(C_5H_5)_2TiCl_2$—Et_2AlCl. The decrease in activity in this case too is associated with consumption of the aluminum alkyl: upon addition of Et_3Al, even after the deactivated system has been aged for 7 days, polymerization proceeds at a high rate (Fig. 3, 2).

Table 1

Effect of the solvent on the rate of ethylene polymerization and the properties of polyethylene.

System $(C_5H_5)_2TiCl_2$—Et_2AlCl; $T = 20°$; $P_{ethylene} = 390$ mm Hg.
$[(C_5H_5)_2TiCl_2] = 1.2 \cdot 10^{-3}$; $[Et_2AlCl] = 12 \cdot 10^{-3}$ mol/l

Solvent	Solubility of ethylene at 20°, mol/l • atm	Yield of polyethylene in 3 h, g/l	Characteristic viscosity of polyethylene $[\eta] \cdot 100$ ml/g*	Mol. wt.**
Benzene	0.12	9	0.8	26000
Chlorobenzene	0.17	15	0.16	3000
Dichloroethane	0.11	50	0.68	22000
Ethyl chloride	0.25	100	1.42	53600
Methyl chloride	0.22	31	0.23	4600

* Determined at 130° in tetralin.
** Calculated by the formula $[\eta] = 5.1 \cdot 10^{-4} M^{0.725}$.

The nature of the kinetic curves for ethylene polymerization on the system $(C_5H_5)_2TiCl_2$—Et_3Al indicates the conversion of complex II into a new, active form.

Indeed, when dichloroethane is added to complex II (inactive in benzene, toluene, chlorobenzene, heptane), intensive polymerization of ethylene is observed (Fig. 3, 3).

The interaction of trivalent titanium complexes with alkyl chlorides is indicated by the change with time in the EPR spectra of complexes I and II (Fig. 4), as well as of the visible and IR spectra.

The amount of reduced titanium at different stages of the interaction of $(C_5H_5)_2TiCl_2$ and $AlEt_2Cl$ in dichloroethane, as shown by titration with $FeCl_3$* (^{6}), passes through a maximum (Table 2). Thus, along with reduction of titanium in the system, its oxidation occurs; moreover, since each oxidation-reduction cycle is associated with consumption of the organometallic component, its amount in the system gradually decreases to zero.

Indeed, in the IR spectra of the final product of the interaction of complexes I and II with dichloroethane, absorption bands characteristic of the Al—C bond (615; 543; 419; 470 cm^{-1}) (^{7}) are absent.

The spectrum of the final product in the region 700-400 cm^{-1} is identical to the spectrum of the complexes $(C_5H_5)_2TiCl_2 \cdot AlCl_3$ and $C_5H_5TiCl_3 \cdot AlCl_3$, which also indicates the occurrence of oxidative processes.

Fig. 4. Change with time in EPR spectra. System $(C_5H_5)_2TiCl_2$—Et_2AlCl in dichloroethane. $[(C_5H_5)_2TiCl_2] = 1.2 \cdot 10^{-3}$, $[Et_2AlCl] = 12 \cdot 10^{-3}$ mol/l.

Fig. 4. Change with time in EPR spectra. System $(C_5H_5)_2TiCl_2$—Et_2AlCl in dichloroethane. $[(C_5H_5)_2TiCl_2] = 1.2 \cdot 10^{-3}$, $[Et_2AlCl] = 12 \cdot 10^{-3}$ mol/l. The numbers indicate the time, in minutes, elapsed after mixing the catalyst components.

Figure 3: Fig. 4. Change with time in EPR spectra. System $(C_5H_5)_2TiCl_2$—Et_2AlCl in dichloroethane. $[(C_5H_5)_2TiCl_2] = 1.2 \cdot 10^{-3}$, $[Et_2AlCl] = 12 \cdot 10^{-3}$ mol/l. The numbers indicate the time, in minutes, elapsed after mixing the catalyst components.

The numbers indicate the time, in minutes, elapsed after mixing the catalyst components.

In studying the transformations of the system in solvents with a labile chlorine atom, the formation of monocyclopentadienyl compounds was also detected**. This is evidenced by the following.

If the interaction of the catalyst components is carried out in benzene, heptane, or chlorobenzene, the titration results using $FeCl_3$ (^{7}) and $K_2Cr_2O_7$ coincide, whereas in the case of dichloroethane (see Table 2), titration of the same solution consumes a significantly larger amount of $K_2Cr_2O_7$. Special experiments showed that this is due—

Table 2

Amount of reduced titanium according to the results of titration with ferric chloride as a function of the time elapsed after mixing the catalyst components. Results of titration with dichromate. Solvent—dichloroethane.
$T = 20°$; A—$[(C_5H_5)_2TiCl_2] = 1.2 \cdot 10^{-3}$ mol/l; $Et_2Al : (C_5H_5)_2TiCl_2 = 15 : 1$; B—$[(C_5H_5)_2TiCl_2] = 1.5 \cdot 10^{-2}$ mol/l; $Et_2AlCl : (C_5H_5)_2TiCl_2 = 2.5 : 1$

Time after mixing $(C_5H_5)_2TiCl_2$ and Et_2AlCl	A: oxidant consumption (per 1 l of solution), $FeCl_3$, g-equiv$\cdot 10^3$	A: oxidant consumption (per 1 l of solution), $K_2Cr_2O_7$, g-equiv$\cdot 10^3$	A: amount of reduced Ti (in % of initial), by $FeCl_3$ consumption	B: oxidant consumption (per 1 l of solution), $FeCl_3$, g-equiv$\cdot 10^2$	B: oxidant consumption (per 1 l of solution), $K_2Cr_2O_7$, g-equiv$\cdot 10^2$	B: amount of reduced Ti (in % of initial), by $FeCl_3$ consumption
0	0	0	0	0	0	0
0.5 h	0.8	1	67	0.33	0.25	23
1.5 h	1	1.1	83	0.45	1.37	30
3 h	1	1.75	83	0.75	2.4	50
1 day	—	—	—	0.95	3	64
3 days	1.1	2.5	92	0.62	2.5	43

Time after mixing $(C_5H_5)_2TiCl_2$ and Et_2AlCl	A: oxidant consumption (per 1 l of solution), $FeCl_3$, g-equiv·10^3	A: oxidant consumption (per 1 l of solution), $K_2Cr_2O_7$, g-equiv·10^3	A: amount of reduced Ti (in % of initial), by $FeCl_3$ consumption	B: oxidant consumption (per 1 l of solution), $FeCl_3$, g-equiv·10^2	B: oxidant consumption (per 1 l of solution), $K_2Cr_2O_7$, g-equiv·10^2	B: amount of reduced Ti (in % of initial), by $FeCl_3$ consumption
30 days	0.25	1.75	21	0.125	1.9	8.4

is due to the presence in the titrated solution of cyclopentadiene or its derivatives, which do not react with $FeCl_3$ but do react with $K_2Cr_2O_7$.

Figure 4 shows the change in the ESR signal during the interaction of $(C_5H_5)_2TiCl_2$ with Et_2AlCl in dichloroethane medium. The spectrum 3 hours after mixing the catalyst components (Fig. 4) is identical to the spectrum of the product of the interaction of $C_5H_5TiCl_3$ with Et_2AlCl in benzene.

The formation of monocyclopentadienyl compounds is significantly accelerated in the presence of ethylene.

It was of interest to compare the catalytic activity of mono- and biscyclopentadienyl titanium derivatives. It turned out that $C_5H_5TiCl_3$, in combination with $AlEt_2Cl$, practically does not catalyze the polymerization of ethylene in benzene and alkyl chloride media. The question of the role of the monocyclopentadienyl compounds formed *in situ* remains open.*

Apparently, the specific action of alkyl chlorides is due to oxidation processes of complexes I and II, leading to regeneration of active particles, although the available data do not yet allow this to be judged unambiguously. Further investigation of the catalytic system carried out in the presence of ethylene will make it possible to give a more precise answer.

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* Before titration, to decompose organoaluminum compounds, a solution of H_2SO_4 (1:6) was added to the sample.

** The occurrence of processes of this type was shown by G. A. Razuvaev and co-workers ([8]) in studying the interaction of $(C_5H_5)_2TiR_2$ and $(C_5H_5)Ti$ with chlorine-containing compounds: CCl_4; $(C_6H_5)_3CCl$, etc.

Institute of Chemical Physics
Academy of Sciences of the USSR

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* The discrepancy between our results and the literature data (9) on the activity of $C_5H_5TiCl_3$ is apparently explained by the following. The $C_5H_5TiCl_3$ used by us was obtained by the action of acetyl chloride on $C_5H_5Ti(OC_2H_5)_3$ (m.p. 205-209°) (10). The preparation method thus excluded the presence of $(C_5H_5)_2TiCl_2$. In previously published works, $C_5H_5TiCl_3$ was synthesized by the action on $TiCl_4$ of either $(C_5H_5)_2Mg$ or $(C_5H_5)_2TiCl_2$, and could contain an impurity of $(C_5H_5)_2TiCl_2$.

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

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