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Titanium catalyst ($TiCl_4$) supported on $MgCl_2(THF)(AlEt_2Cl)_{0.34}$ for ethylene polymerization

Summary — Three titanium catalyst systems supported on the $MgCl_2(THF)(AlEt_2Cl)_{0.34}$ complex were synthesised by changing both the synthetic method and the precursor/support ratio. After activation by $AlEt_3$, the catalysts were applied for ethylene polymerization. All three systems proved to be single site catalysts regardless of the method of synthesis. This was confirmed by the kinetics curve character and the properties of the produced polyethylene. Due to the simultaneous reaction reduction and immobilization of $TiCl_4$ (at $AlEt_2Cl/TiCl_4$ molar ratio greater than 1) the actual time for the polymerization reaction to begin can be shortened to the minimum needed to only dissolve the ethylene in the reaction medium. Furthermore, the amount of the $AlEt_3$ activator ($AlEt_3/TiCl_4 < 1000$) is also considerably reduced when the high activity of the catalyst is maintained.

Key words: ethylene polymerization, supported titanium catalyst, magnesium carrier, polymer properties.

KATALIZATOR TYTANOWY ($TiCl_4$) NA NOŚNIKU $MgCl_2(THF)(AlEt_2Cl)_{0,34}$ DO POLIMERYZACJI ETYLENU

Streszczenie — Przedmiotem prezentowanej pracy jest zastosowanie kompleksowego nośnika $MgCl_2(THF)(AlEt_2Cl)_{0,34}$ do syntezy katalizatora tytanowego i zbadanie jego efektywności oraz jednorodności w polimeryzacji etylenu. Poprzez immobilizowanie $TiCl_4$ na wspomnianym nośniku, zmieniając zarówno metodę syntezy jak i stosunek molowy związku tytanu do nośnika (Ti/Mg), otrzymano trzy różne typy katalizatorów (tabela 1). Po uprzednim aktywowaniu otrzymanych katalizatorów trietyloglinem ($AlEt_3$) badano zachowanie się tych układów w reakcji polimeryzacji etylenu (rys. 1—3). Stwierdzono, że bez względu na sposób syntezy wszystkie trzy układy katalityczne tworzą centra aktywne jednego rodzaju. Potwierdza to liniowy przebieg krzywych kinetycznych (rys. 2) oraz właściwości otrzymanego polietylenu (PE) (rys. 4, tabela 2). Okazało się również, że dzięki redukcji $TiCl_4$ zachodzącej już w trakcie jego immobilizowania na kompleksowy nośnik (gdy stosunek molowy $AlEt_2Cl/TiCl_4 > 1$), można skrócić czas faktycznego rozpoczęcia reakcji polimeryzacji etylenu do minimum niezbędnego do rozpuszczenia etylenu w medium reakcyjnym (1,3 min). Zwiększenie stosunku molowego aktywatora $AlEt_3$ do katalizatora tytanowego ($AlEt_3/TiCl_4$) powoduje niewielki tylko wzrost masy molowej PE (tabela 2), przy czym aktywność układu katalitycznego maleje (rys. 3). Z badań wynika, że ilość niezbędnego aktywatora ($AlEt_2Cl/TiCl_4 < 1000$) można ograniczyć zachowując bardzo dużą aktywność układu katalitycznego oraz uzyskując dużą masę molową (M_w) PE wynoszącą od $8 \cdot 10^5$ do $11 \cdot 10^5$ g/mol.

Słowa kluczowe: polimeryzacja etylenu, nośnikowy katalizator tytanowy, nośnik magnezowy, właściwości polimeru.

In our earlier reports it was found that when anchored to the $MgCl_2(THF)_2$ support modified by $AlEt_2Cl$ (Al/Mg molar ratio = 1/1) and activated by $AlEt_3$ and methylaluminoxane (MAO) respectively, the titanium ($TiCl_4$) [1, 2] and zirconocene (Cp_2ZrCl_2) [3, 4] catalysts used in ethylene polymerization formed two kinds of active sites. The double site character of the studied catalysts was proven by the kinetics investigations of ethylene polymerization reaction and the properties of the polyethylene (PE) produced, *i.e.* the bimodal molecular weight distributions (MWDs) and particle size [1, 3, 4]. The undesirable active site was formed due to the presence of "free" $AlEt_2Cl$ unbounded to the $MgCl_2(THF)_2$ structure. Improvement in the support synthesis through the removal of free $AlEt_2Cl$ led to a bimetallic complex of the composition $MgCl_2(THF)(AlEt_2Cl)_{0.34}$. The zirconocene compound, Cp_2ZrCl_2, anchored on this complex support and activated by MAO turned out to be a heterogeneous single site catalyst as proved by both

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the kinetics investigations of the ethylene polymerization reaction and the physical and mechanical properties of PE produced [5].

In this work, we describe the titanium catalyst ($TiCl_4$) immobilized on the $MgCl_2(THF)(AlEt_2Cl)_{0.34}$ bimetallic complex support. This catalyst activated by $AlEt_3$ cocatalyst was used for the ethylene polymerization. The influence of the components and the synthesis method on catalyst activity, the character of the active site in the ethylene polymerization and the properties of PE produced have been analyzed.

EXPERIMENTAL

Materials

Ethylene from Petrochemia SA (Płock) and pure nitrogen from Polgaz were used after having been passed through a column of sodium metal supported on Al_2O_3. Pure-grade hexane delivered by Petrochemia SA was refined with sulfuric acid, dried by refluxing in argon from sodium metal, and stored over 4A molecular sieves. Toluene supplied by POCh (Gliwice) was distilled over sodium metal and also stored over 4A molecular sieves. Titanium tetrachloride ($TiCl_4$) purchased in Merck was used after distillation, triethylaluminium ($AlEt_3$) and diethylaluminium chloride ($AlEt_2Cl$) both from Aldrich were applied without additional purification. Tetrahydrofuran delivered by Fluka was purified according to the standard method using NaOH and metallic Na with benzophenone as an indicator. Magnesium (98 wt. %) also supplied by Fluka was dried for 2 h at 393 K.

Catalyst preparation

All steps were carried out in oxygen-free conditions using an inert nitrogen atmosphere. Both the complex support and catalyst preparation were carried out in a glass mill (capacity: 250 cm^3, 20 glass balls, each 0.5—0.7 cm in diameter).

The complex support $MgCl_2(THF)(AlEt_2Cl)_{0.34}$ was prepared by milling solid $MgCl_2(THF)_2$ with $AlEt_2Cl$ in equimolar ratio 1/1 in purified hexane solution at room temperature for 24 h. The solid product was filtered off, washed with hexane (2 × 20 cm^3), and dried as previously described [5].

An appropriate amount of the solid complex support (~1.5 g), 40 cm^3 of purified *n*-hexane, and $TiCl_4$ precursor were placed into a glass mill. The Mg/Ti molar ratio equal 10/1 was applied for catalyst A and 1/1 for catalyst B. After milling the mixture for 24 h at room temperature the solid product (catalyst A or B) was filtered off, washed thoroughly with *n*-hexane (2 × 20 cm^3), and dried. The solid catalyst, A or B, of known mass was placed into a glass mill with 40 cm^3 of hexane and then mixed for l h at room temperature. The obtained suspensions of the supported titanium catalyst were used for ethylene polymerization. The catalyst C was prepared using Mg/Ti molar ratio also equal 1/1, but after milling the mixture for 24 h at room temperature, in contrast to catalysts A and B, the obtained suspension of catalyst C was used for ethylene polymerization, without isolation of the solid catalyst (the washing step was omitted).

Polymerization procedure

Ethylene polymerization was conducted in 1 dm^3 stainless steel autoclave equipped with a stirrer. When measured amounts of *n*-hexane, $AlEt_3$, and the titanium catalyst, in the form of a hexane suspension, were added successively into the reactor under a nitrogen atmosphere, ethylene was introduced at 50 °C and subjected to polymerization while the pressure of ethylene was maintained at 0.5 MPa. The polymerization reaction was terminated by adding methanol containing hydrochloric acid. The polymer obtained was filtered off, washed with methanol, and dried. The reaction yield is described as the mass of PE obtained per volume of the reaction medium at a given catalyst concentration. The catalyst activity is described as the mass of PE obtained during 1 h of the polymerization reaction when 1 gram of the catalyst is used.

Methods of testing

Molecular weight and molecular weight distribution of each polymer sample were determined by gel permeation chromatography (GPC, Waters 150-CV) using 1,2,4-trichlorobenzene as a solvent at 142 °C. The data were analyzed using polystyrene calibration curves. The measuring error of the molecular weight equals about 11 %.

The amounts of Al, Mg, and Ti in the catalysts were measured by Atomic Absorption Spectrometry (AAS, Unicam SOLAR 969).

Bulk density of polyethylene was determined according to the Polish Standard PN-80/C-04532.

The degree of crystallinity and melting temperature of polyethylene were estimated using differential scanning calorimeter (DSC 2010 TA Instruments).

Polymer crystallinity (C) was calculated using the equation:

$$C = (\Delta h_f / \Delta h_{t,c}) \cdot 100\ \% \qquad (1)$$

where: Δh_f — *heat of fusion of polyethylene sample*, $\Delta h_{f,c}$ — *heat of fusion of standard*.

Tearing strength, elongation at break, and melt flow index were estimated using an Instron model 1112 testing machine according to the procedure outlined in the Polish Standard PN-81/C-89034.

Particle size distribution of PE was estimated by means of the sieve method using a vibrating screen and a set of sieves with the sieve mesh 0.09—2.0 mm.

RESULTS AND DISCUSSION

The bimetallic complex $MgCl_2(THF)/(AlEt_2Cl)_{0.34}$ was used as a support to immobilize $TiCl_4$ which, after activation by $AlEt_3$, was applied as a catalyst for ethylene polymerization. Three kinds of catalyst systems were investigated, denoted as A, B, and C, to determine the influence of both the amount of $TiCl_4$ and the synthetic method used on the performance of the catalysts. The compositions of catalysts A and B (Mg, Al, and Ti contents) determined by AAS method are listed in Table 1 together with composition of catalyst C.

Table 1. Compositions of catalysts A and B determined by AAS and of catalyst C calculated on the basis of the synthetic procedure

Catalyst	Metal content, wt. %			$AlEt_2Cl/TiCl_4$ molar ratio
	Mg	Al	Ti	
A	12.81±0,92	4.89±0.26	8.11±0.47	1.07
B	11.63±0.81	4.38±0.23	11.42±0.25	0.68
C	8.2	3.1	15.4	0.34

When investigating the behavior of a catalytic system in polymerization reaction, it is important to determine that the reaction conditions are kinetically controlled [1]. The reaction rates (R_p), defined as a slope of a straight line of the function of PE yield (in mol Et/dm^3) versus polymerization time (in h), were determined for given concentrations of catalyst [Ti]. Figure 1 presents the influence of [Ti] on R_p of ethylene polymerization. The function is linear for all the studied catalysts concentrations up to $1.9 \cdot 10^{-5}$ mol Ti/dm^3. This means that the polymerization reaction takes place in the kinetic area and the performed investigations are correct.

The influence of the polymerization reaction time on the yield of PE produced is presented in Figure 2. The dependence is also linear. The time needed to begin the polymerization reaction in the monomer environment called the activation time (t_0) is different. It equals 1.3, 17.1, and 11.1 min for the catalysts A, B, and C respectively and does not depend on catalyst concentration, as is shown for the catalyst A (Fig. 2, line A and A'). The influence of the activator/catalyst ($AlEt_3/TiCl_4$) molar ratio on the activity of the studied catalysts was evaluated (Fig. 3). As can be seen, the catalysts A, B and C behave in a very similar way. The greater the activator/catalyst molar ratio the lower the catalyst activity. The properties of PE produced are presented in Table 2 as well as shown by the particle size distribution in Fig. 4.

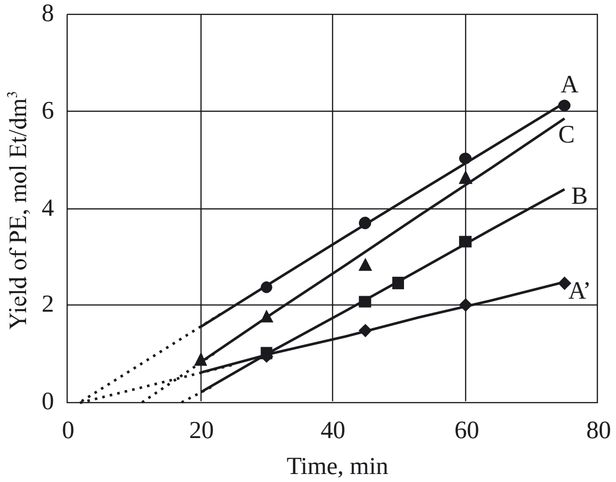


Fig. 2. Influence of the polymerization time on the yield of PE produced with the studied catalyst systems: A — [Ti] = $4.9 \cdot 10^{-6}$ mol/dm^3, A' — [Ti] = $2.5 \cdot 10^{-6}$ mol/dm^3, B — [Ti] = $4.7 \cdot 10^{-6}$ mol/dm^3, C — [Ti] = $5.4 \cdot 10^{-6}$ mol/dm^3; in all cases [$AlEt_3$] = $2 \cdot 10^{-3}$ mol/dm^3

The synthesis of magnesium-aluminium bimetallic complexes in the presence of a Lewis base was reported earlier [6, 7]. Our previous investigations [8, 9] of the role

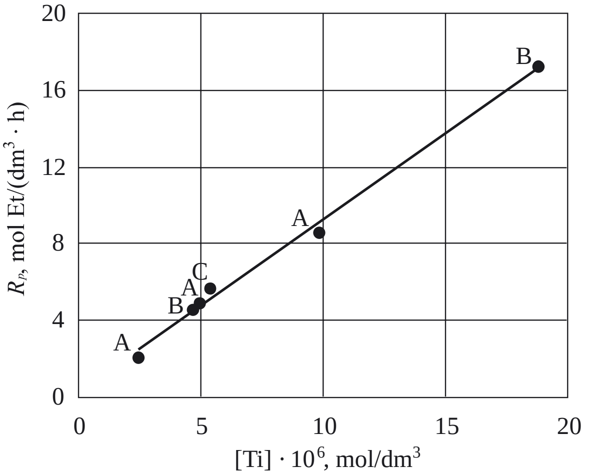


Fig. 1. Effect of the catalyst concentration [Ti] on the reaction rate [R_p] of ethylene polymerization

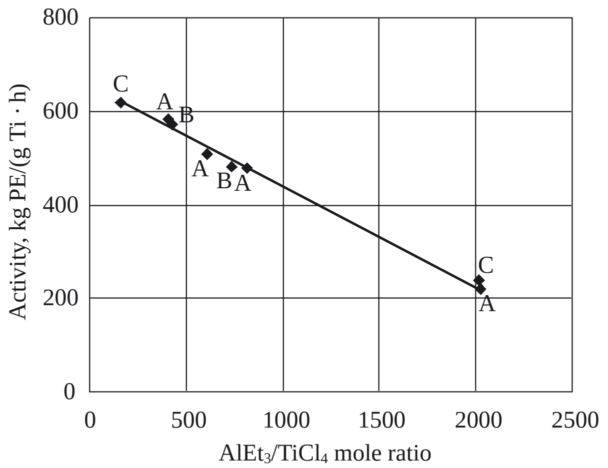


Fig. 3. Effect of $AlEt_3/TiCl_4$ molar ratio on the activity of the studied catalyst systems in ethylene polymerization; polymerization time equals 30 min

of $MgCl_2$ support and a Lewis base (THF) in Ziegler—Natta titanium catalysts proved that $AlEt_2Cl$ formed the bimetallic magnesium-aluminium complex on the surface of $MgCl_2(THF)_2$. The chlorine atom of $AlEt_2Cl$ is built into the empty coordination place (vacancy) of the magnesium support, which enables a strong anchorage of $AlEt_2Cl$ to the crystal lattice [formula (I)].

T a b l e 2. Conditions of polymerization reactions and selected properties of polyethylene produced

	Catalyst system	A	A′	B	C
Conditions of polymerization	Catalyst concentration $\cdot 10^6$, mol/dm^3	4.9	2.5	4.7	5.4
	$AlEt_3/TiCl_4$ molar ratio	507	813	425	200
	Catalyst activity, kg PE/(g Ti · h)	515.0	474.3	566.3	620.0
Polyethylene properties	melting temperature, °C	135.5	136.0	136.5	135.5
	crystallinity degree by DSC, %	57.4	57.8	55.7	68.0
	molecular weight $M_w \cdot 10^{-3}$, g/mol	961	1037	882	—
	molecular weight distribution (MWD)	5.1	4.6	4.6	—
	tearing strength, MPa	—	31.2	29.3	34.7
	elongation at break, %	—	266	290	365
	density, g/cm^3	—	0.929	0.928	0.932
	bulk density after 1 h polymerization time, g/dm^3	160	168	207	186

Therefore, according to the model of the crystal structure of Ziegler—Natta catalysts proposed by Natta, Patat and Sinn [10, 11], the studied $MgCl_2(THF)(AlEt_2Cl)_{0.34}$ complex support reduces immobilized $TiCl_4$ to $TiCl_3$ and forms bimetallic aluminium-titanium catalytic active sites [formula (II)]. Simultaneously, the binding of THF to the magnesium support weakens.

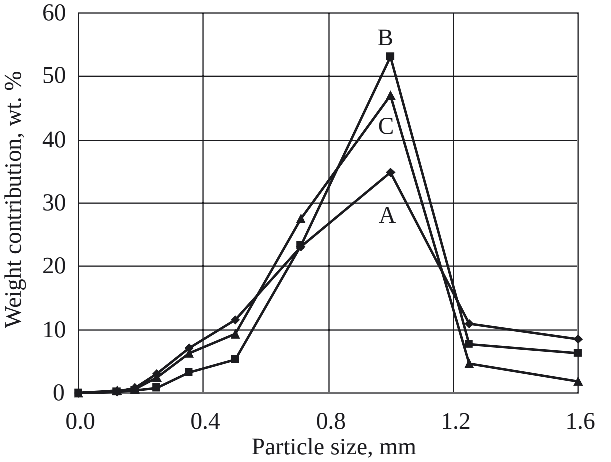
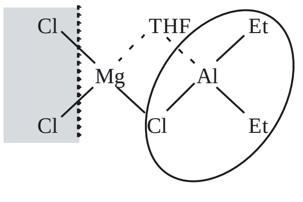
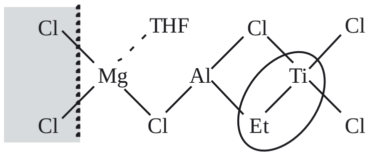


Fig. 4. Particle size distribution of PE polymers produced with the studied catalyst systems; polymerization time was 60 min, $[AlEt_3] = 2 \cdot 10^{-3}$ *mol/dm*^{3}*, denotations of curves as in Fig. 2*



(I)



(II)

The chlorine ligands and the terminal carbon atom of the growing polyethylene chain link the titanium and aluminium atoms through a double bridge thus representing the driving force to shift back the bridged alkyl group of the growing chain to its initial position after the migratory insertion step of the olefin molecule [12]. Based on the results of AAS analysis (Table 1), the mass balance, the proposed structure of active sites [formula (II)] and the composition of catalyst A can be determined as $MgCl_2(AlEtCl)_{0.34}(TiCl_3)_{0.32}$.

As can be seen, the weakly bounded THF can be completely detached from the support structure. For catalyst A, ethylene polymerization begins when $AlEt_3$ activator and ethylene were introduced into the reaction medium. Only a very short activation time (1.3 min) is required to saturate the hexane solution with ethylene up to the value about 0.47 mol Et/dm^3 at pressure 0.5 MPa. Catalyst A contains a greater amount of $AlEt_2Cl$ incorporated into the magnesium support than the amount of incorporated titanium compound ($AlEt_2/TiCl_4$ molar ratio equals 1.07, see Table 1). This means that during the immobilization process $TiCl_4$ is reduced to $TiCl_3$ by means of $AlEt_2Cl$ bounded to the support. As a consequence, Ti(III)-C bond (catalytic active site) responsible for the initiation of ethylene polymerization reaction is created. The results of the kinetics investigations of ethylene polymerization using catalyst A (Fig. 2, curves A and A′), *i.e.* a very short activation time and linear dependence, prove this conclusion.

Catalyst B obtained using an equimolar amount of $TiCl_4$ and magnesium support results in a much longer activation time (17.1 min). This means that $TiCl_4$ was not reduced completely during the immobilization process as $AlEt_2Cl/TiCl_4$ molar ratio was smaller than 1 ($AlEt_2Cl/TiCl_4 = 0.68$, see Table 1). The excess of non-reduced $TiCl_4$ adsorbed on the support surface blocks the access to the active sites already formed. It is known that $AlEt_3$ activator does not incorporate into the magnesium support structure [4] but undergoes the reaction with non-reduced $TiCl_4$ [13]:

$$2\,AlEt_3 + 2\,TiCl_4 \rightarrow 2(AlEt_2Cl \cdot TiCl_3) + C_2H_6 + C_2H_4 \quad (2)$$

The alkylaluminium compound $AlEt_2Cl$ produced in this reaction, due to the presence of the chlorine atom, can be strongly bound to $MgCl_2$ structure which thus creates active sites [formula (II)]. Simultaneously, the active sites previously formed are unblocked. This process requires some activation time of the catalyst system in the monomer environment.

Catalyst C obtained using Mg/Ti molar contents equal 1/1 had $AlEt_2Cl/TiCl_4$ molar ratio even smaller than that of catalyst B (0.34), while the activation time was shorter and equal 11.1 min. One possible explanation is that catalyst C was obtained in the form of a hexane suspension not as a solid. Thus, only a small amount of non-reduced $TiCl_4$ was adsorbed on the support. This made the access to the active sites created during the immobilization less difficult. The major amount of $TiCl_4$ remained in hexane. When $AlEt_3$ activator was introduced, the reaction described by eq. (1) occurred and the produced $AlEt_2Cl \cdot TiCl_3$ complex was built into the crystal lattice of the magnesium support structure. Thus, active sites similar to those of the catalysts A and B were created.

The various activation times of the studied catalysts in the ethylene environment show without doubt that $AlEt_3$ compound is not only the activator of the catalyst system but also the reductor of the titanium compound. The linear dependence of PE yield on the polymerization time for all the catalysts studied indicates that these catalysts are immobilized on the magnesium support, but not on the $TiCl_3$ crystal, as in the case of the low active classic Ziegler—Natta catalyst. The colinearity of the kinetics curves (Fig. 2) and the similar mechanical and physical properties of polyethylene polymers (Table 2) reveal a similarity of the catalytic sites of the studied catalysts and the same mechanism of the polymerization reaction. It is also confirmed by the molecular weight of PE samples ($M_w \approx 10^6$ g/mol). Small differences in M_w result from the conditions of the catalyst preparation and they are negligible. The increase in the activator/catalyst ($AlCl_3/TiCl_4$) molar ratio results in relatively small increase PE molecular weight (Table 2). Simultaneously, some decrease in the catalyst activity occurs (Fig. 3 and Table 2).

The monomodal particle size distribution of PE (Fig. 4) and the linear character of the kinetics curves (Fig. 2) prove that the immobilization of $TiCl_4$ on the bimetallic complex support $MgCl_2(THF)(AlEt_2Cl)_{0.34}$ lead to a titanium catalyst with only one kind of active site.

The comparison of catalysts A and B shows that there is no need to apply the $TiCl_4$ precursor in such excess during the synthesis of catalyst B, for which ten times greater amount of $TiCl_4$ was used than for catalyst A. Nevertheless, only a slightly greater amount of the titanium compound was incorporated into the support structure (Table 1). In contrast, the relatively small amount of the titanium compound used during the synthesis of catalyst A results in a very short activation time equal 1.3 min (Fig. 1). The important feature of the studied catalysts is the activator/catalyst molar ratio ($AlEt_3/TiCl_4 < 1000$, Table 2), smaller than those previously applied during investigations of the similar magnesium-aluminium complex support at the laboratory scale made catalysts (Al/Ti ≈ 2000—10 000) [1, 2, 9]. Therefore, there is no need to apply a great excess of the activator to maintain the high activity of the catalyst, which is an important economical factor.

It is worth comparing the titanium $TiCl_4$ catalyst (present work) and the zirconocene Cp_2ZrCl_2 catalyst [5] prepared in the same manner and anchored on the same support. The zirconocene catalyst yields 13 200 kg PE/mol Zr · h at the $Al_{(MAO)}/Zr$ molar ratio 11 000. The presented titanium catalyst yields 27 100 kg PE/mol Ti · h and the $AlEt_3/TiCl_4$ molar ratio equals only 425. This shows that the performance of the supported Ziegler—Natta catalysts still predominates those of the heterogeneous metallocene catalysts, which ensures large scale industrial application.

CONCLUSION

Application of the $MgCl_2(THF)(AlEt_2Cl)_{0.34}$ complex as a support of the $TiCl_4$ compound leads to the highly active single site titanium catalyst for the ethylene polymerization. The presence of only one kind of active site is confirmed both by the linear character of the kinetics curves and the properties of polyethylene produced. The method of the synthesis of the catalyst system (by removing an excess of $TiCl_4$) does not change the polymerization mechanism. However, due to the simultaneous reactions of immobilization and reduction of $TiCl_4$ at $AlEt_2Cl/TiCl_4$ molar ratio >1, it does reduce the activation time to the minimum necessary to dissolve the ethylene in the reaction medium. Furthermore, the needed amount of $AlEt_3$ activator is also considerably reduced ($AlEt_3/TiCl_4 < 1000$), while the high activity of the catalyst is maintained. The smaller amount of the activator needed should therefore be an important economical factor.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— Laserowe modyfikowanie materiałów polimerowych. Cz. I. Fizyczne podstawy działania i kryteria doboru laserów

— Reakcja utwardzania azometynowych epoksydowych ciekłych kryształów (*j. ang.*)

— Diagram sieciowania konwersja–temperatura–przemiana (CTT) układu epoksydowego EPY® (*j. ang.*)

— Wpływ promieniowania laserowego na cienkie błony kolagenowe. Cz. I. Mechanizm tworzenia struktury „mikropianki" i ablacja powierzchni kolagenu

— Modyfikacja kauczuku butadienowo-styrenowego polimetylosiloksanami. Cz. II. Układy napełnione krzemionką

— Badanie właściwości inkluzyjnych *p-tert*-butylokaliksarenów metodą inwersyjnej chromatografii gazowej

— Skurcz wtryskowy a zależność *p-v-T*

— Wpływ zawartości środka porującego na właściwości użytkowe zewnętrznych powłok kabli wytwarzanych z PVC metodą powlekającego wytłaczania porującego