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Bimetallic magnesium supported titanium catalyst for ethylene polymerization

Summary — Previously investigated Mg-Al-Ti catalyst has been modified by the application of $AlEt_3$ cocatalyst instead of $AlEt_2Cl$ and by the prepolymerization process. Both ways of modifications have increased considerably the activity of the catalyst system studied in ethylene polymerization process. The investigations of active titanium catalyst obtained activated with $AlEt_3$ have revealed the reason for non-linearity of the function of the ethylene polymerization reaction rate versus the catalyst concentration. Additionally, the application of the prepolymerization process has improved the morphology of PE obtained.

Key words: polymerization of ethylene, supported titanium catalyst, prepolymerization.

Previous investigations by the Opole team have revealed that the application of the magnesium support as a complex with Lewis base — $MgCl_2(THF)_2$ results in an active (50 kg PE/g Ti · h) and stable catalyst system $[MgCl_2(THF)_2/TiCl_4 + AlEt_2Cl]$ for ethylene polymerization [1]. The catalyst system obtained has been used with a great amount of the cocatalyst $AlEt_2Cl$ ($Al/Ti > 100$), what is typical for all supported titanium catalysts. Additionally, the studies by Karol [2] and Sobota [3] show that in presence of Lewis base, magnesium chloride creates bimetallic complexes with aluminum compounds. These two conclusions directed us towards the hypothesis that during the creation of the titanium-aluminum metalloorganic catalyst system, a reaction of the magnesium support $[MgCl_2(THF)_2]$ with diethylaluminum chloride $[Et_2AlCl]$ appears. In consequence, the bimetallic complex $[MgCl_2(THF)_2/Et_2AlCl]$ is created which isolates titanium compound from the crystal structure of magnesium chloride.

During investigations, this bimetallic complex was synthesized and applied as the support for the titanium catalyst which after activation with an excess of $AlEt_2Cl$ cocatalyst appeared to be more active in ethylene polymerization than the system on the monometallic support $[MgCl_2(THF)_2]$. Results obtained revealed that the reason for the higher activity of the bimetallic supported catalyst was the creation of greater amount of the active sites [4].

In this paper, further results of the modification of the titanium catalyst on the bimetallic support $[MgCl_2(THF)_2/AlEt_2Cl]$ are presented.

The modification of the catalyst system was carried out by two methods:

1. change of the cocatalyst — application of $AlEt_3$ instead of $AlEt_2Cl$ previously used,
2. prepolymerization of chosen olefin with the use of the titanium catalyst on the bimetallic support in mild conditions.

EXPERIMENTAL

Materials

Ethylene (Petrochemia SA, Płock) and pure argon (Polgaz) were used after having been passed through a column of sodium metal supported on Al_2O_3. Pure-grade hexane (Petrochemia SA, Płock) was refined with sulfuric acid, dried by refluxing in argon from sodium metal, and stored over 4A molecular sieves. Titanium tetrachloride (Merck) and $AlEt_2Cl$ and $AlEt_3$ (Schering) were used without further purification. $MgCl_2(THF)_2$ was prepared at the Institute of Chemistry, University of Opole (Poland).

Catalyst preparation

The bimetallic support has been prepared by milling solid $MgCl_2(THF)_2$ with $AlEt_2Cl$ in a glass mill (capacity: 250 cm^3, with 20 balls of 1-cm diameter) in hexane solution at room temperature for 1 h using equimolar ratio of the substrates. The titanium catalyst has been prepared by milling the resulting suspension of the bimetallic support with $TiCl_4$ at room temperature for 24h.

Polymerization

The polymerization reaction was carried out at 50°C in 1 dm^3 reactor equipped with stirrer, in hexane, at a constant pressure of ethylene. Assumed amounts of hexane (0.7 dm^3), Ti catalyst supported on the bimetallic (Mg-Al) complex and a great excess of the cocatalyst—$AlEt_3$ were charged into the reactor and then ethylene was introduced. The reaction was terminated by adding methanol containing 5 wt. % HCl. The polymer was filtered off, washed with methanol and dried.

Prepolymerization

Predetermined amounts of hexane, $[MgCl_2(THF)_2/ /AlEt_2Cl/TiCl_4]$, $AlEt_2Cl$ and chosen olefin were added into 100 cm^3 glass reactor and argon was bubbled through the mixture during 1 h. The prepolymerization conditions were: Al/Ti mole ratio, 100:1; temp. 25°C; atmospheric pressure. Finally, after 24 hours, the precatalyst obtained was used in the polymerization process.

RESULTS AND DISCUSSION

The change of the kind of the cocatalyst

It was found by K. Szczegot [5, 6] that the mixture of $AlEt_2Cl$ with $AlEt_3$ used as cocatalyst results in the most active titanium-aluminum catalyst system on $MgCl_2(THF)_2$ support.

In our investigations, the application of triethylaluminum as the cocatalyst to the titanium catalyst system on the bimetallic support $[MgCl_2(THF)_2/AlEt_2Cl]$ also leads to the increase of the activity of this catalyst (Tab. 1.). Replacement of $AlEt_2Cl$ cocatalyst by $AlEt_3$ results in the increase of the activity of the system about 30% (Tab. 1, item. 4, 5). Thus, the effect of the cocatalyst replacement is very active titanium catalyst on the bimetallic complex support. It means that in this catalytic system are both $AlEt_2Cl$ and $AlEt_3$. $AlEt_3$ is the best as the cocatalyst. $AlEt_2Cl$, as one of the compounds of the complex support, is responsible for isolation of the immobilized titanium compound from the crystal structure of magnesium chloride. Therefore, the results of our investigations show the reason for the greater activity of the system in which the mixture of the alkylaluminum compounds $[AlEt_2Cl + AlEt_3]$ was applied as the cocatalyst.

Table 1. The effect of the kind of the cocatalyst on the activity of the titanium catalyst system supported on the complex magnesium support in the ethylene polymerization. Polymerization conditions: p = 0.5 MPa, T = 323K

No	Catalyst conc. mol/dm^3 · 10^6	Carrier	Cocatalyst	Activity kg PE/ /g Ti · h	Ref.
1.	45	$MgCl_2(THF)_2$	$AlEt_2Cl$	50	1
2.	45	$MgCl_2(THF)_2$/ $Al(C_2H_5)_2Cl$	$AlEt_2Cl$	70	4
3.	45	$MgCl_2(THF)_2$/ $Al(C_2H_5)_2Cl$	$AlEt_3$	75	—
4.	2	$MgCl_2(THF)_2$	$AlEt_2Cl$	533	1
5.	2	$MgCl_2(THF)_2$/ $Al(C_2H_5)_2Cl$	$AlEt_3$	695	—

However, the results in Table 1 show that at higher concentrations of the titanium compound the catalyst activity decreases (item. 2, 3). On the basis of these results we decided to investigate the effect of the catalyst concentration n_k (in a wide scope from 2 · 10^{-6} mol Ti/dm^3 to 45 · 10^{-6} mol Ti/dm^3) on its activity and the polymerization rate (Tab. 2, Fig. 1, curve 1). It was found that the reaction ratio R_p of the ethylene polymerization with

Table 2. The effect of the catalyst concentration on its activity in the ethylene polymerization, and on the bulk density of PE obtained. Polymerization conditions: p = 0.5 MPa, T = 323 K, cocatalyst conc. C_{AlEt_3} = 30 · 10^{-3} mol/dm^3

No	Catalyst conc. mol/dm^3 · 10^6	Yield PE g/dm^3	Activity kg PE/g Ti · h	Bulk density g/dm^3
1.	2	68.9	696.5	131
2.	3	90.7	631.5	157
3.	5	118.0	460.0	138
4.	15	147.7	205.6	153
5.	25	165.5	138.2	152
6.	35	191.2	114.1	163
7.	45	137.1	63.5	157

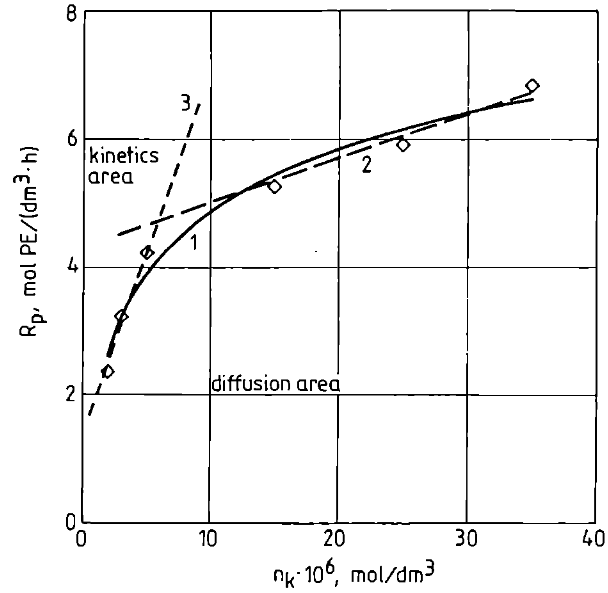

Fig. 1. The effect of the catalyst concentration on the reaction rate of ethylene polymerization (for curve symbols, see main text)

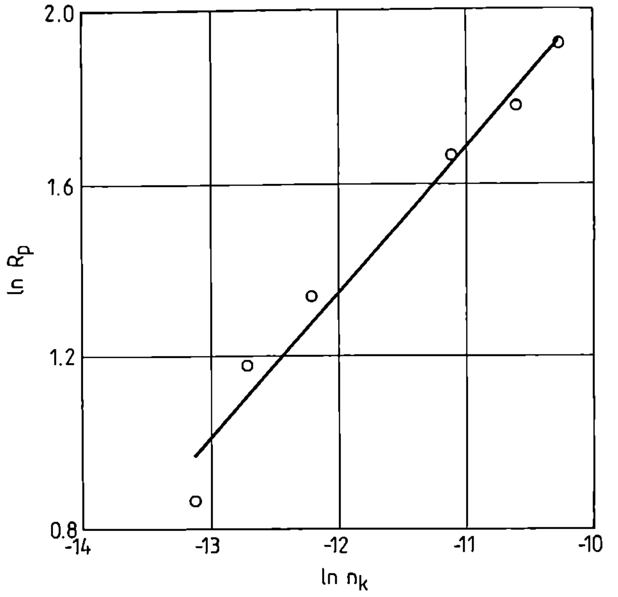

Fig. 2. Polymerization rate ln R_p versus catalyst concentration ln n_k

using the studied catalyst system on the bimetallic support [$MgCl_2(THF)_2/AlEt_2Cl$] with $AlEt_3$ as the cocatalyst was not directly proportional to the concentration of the catalyst (Fig. 1, curve 1). Only a bi-logarithmic function becomes linear, as shown in Fig. 2 and equation (1).

$$\ln R_p = 5.30 + 0.33 \ln n_k; \quad r = 0.972 \tag{1}$$

where: n_k — *catalyst concentration [mol/dm^3].*

Hence, the polymerization rate takes the form of:

$$R_p = 199.26\, n_k^{0.33} \tag{2}$$

Thus, for the catalyst concentration, the reaction order has been found to be about 0.33.

The similar reaction order (smaller than 1) for the catalyst concentration was confirmed earlier (in 1998) for the system on the same support but with $AlEt_2Cl$ as the cocatalyst [4].

However, for the catalyst concentration $35 \cdot 10^{-6} > n_k > 5 \cdot 10^{-6}$ mol Ti/dm^3 the yield of PE (g/dm^3) was much greater than the bulk density of the polymer obtained (Tab. 2). It shows that diffusion limitation take places. It indicates that for this catalyst concentration range the polymerization reaction takes place in the diffusion area, where the function $R_p = f(n_k)$ is linear (Fig. 1, curve 2):

$$R_p = 4.06 + 77\,700\, n_k; \quad r = 0.994 \tag{3}$$

On the contrary, we found that for the very low catalyst concentration $n_k \leq 5 \cdot 10^{-6}$ mol Ti/dm^3 the yield of PE is much lower than the bulk density of polyethylene obtained. In this case diffusion limitations were not observed. It means that only for the catalyst concentration $n_k \leq 5 \cdot 10^{-6}$ mol Ti/dm^3 the polymerization reaction of ethylene takes place in the kinetic area. In this range of the catalyst concentration the function $R_p = f(n_k)$ was also linear (Fig. 1, curve 3):

$$R_p = 1.40 + 570\,500\, n_k; \quad r = 0.992 \tag{4}$$

The comparison of the equations (3) and (4) shows that the polymerization reaction rate is almost 10 times greater in the kinetic than in the diffusion area.

Presented results of our investigations confirm that the function of the ethylene polymerization reaction rate versus the concentration of very active catalyst is nonlinear because the reaction runs through two areas:

— kinetic area, for very low catalyst concentrations, and

— diffusion area, for higher catalyst concentrations.

The borderline catalyst concentration depends on the activity of the catalyst system. The more active the catalyst system the lower the borderline catalyst concentration. For very active titanium catalyst system on the complex magnesium support [$MgCl_2(THF)_2/AlEt_2Cl$] with $AlEt_3$ as the cocatalyst, the value of the highest borderline catalyst concentration for the kinetic area was $5 \cdot 10^{-6}$ mol/dm^3.

Therefore, for the studied catalyst system, the influence of polymerization time on the yield of PE in the kinetic area has been investigated for the concentration of the titanium compound equal to $2 \cdot 10^{-6}$ mol/dm^3.

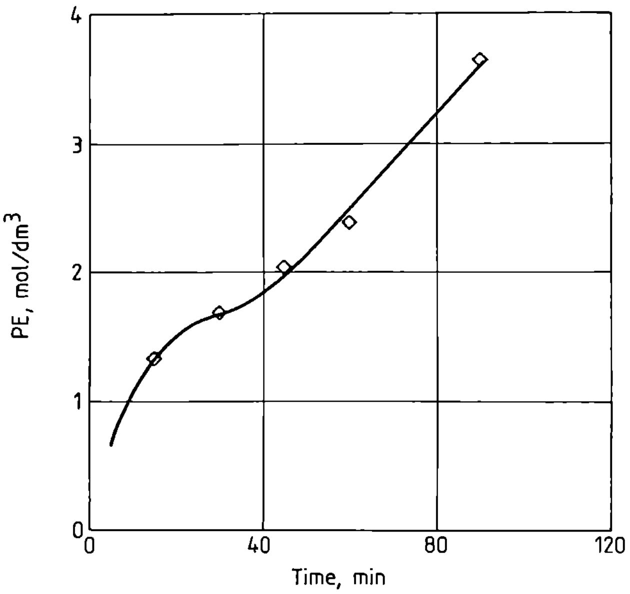

Fig. 3. PE yield versus polymerization time

As can be seen in Figure 3, at the beginning, the polymerization reaction rate is relatively fast but decreases with time. After 40 minutes a proportional increase of PE yield to the polymerization time can be observed. Such shape of the kinetic curve indicates that the catalyst system has two kinds of catalytic sites. Unstable sites catalyze the polymerization during first 40 minutes. Simultaneously with deactivation of the unstable sites, the stable active sites are created. After 40 minutes the amount of the stable ones does not change. This fact is confirmed by the polymerization reaction rate which is constant in further stage. It should be stressed that in this case the creation of the stable active sites is associated with the catalyst activation in olefin environment. On this basis we can deduce that the modification of the catalyst by so-called prepolymerization in mild conditions is necessary.

The modification of the studied catalyst system by prepolymerization

According to the new literature reports concerning the propylene prepolymerization [7—10] we decided to investigate the modification of our catalyst by various olefins prepolymerization to obtain very active and stable titanium catalyst. Moreover, we expected that the prepolymerization process could improve the morphological properties of PE obtained.

The prepolymerization conditions were fixed up on the basis of the results of the precatalyst synthesis for the propylene polymerization [11], that is: pressure 0.1 MPa, temperature 25°C, and Al/Ti mole ratio 100/1. Linear and branched olefins such as ethylene, pentene, octene, 4-methyl-l-pentene were applied to the prepolymerization reaction. After complexing with $AlEt_3$ cocatalyst, the activity of the precatalyst obtained has been investigated in the ethylene polymerization.

Table 3. The effect of the modification of the titanium catalyst by prepolymerization on the activity of the catalytic system in ethylene polymerization. Prepolymerization conditions: Al/Ti =100:1;T = 298 K, t = 24 h, p = 0.1 MPa. Polymerization conditions: C_{AlEt_3} = 0.03 mol/dm^3, C_{Ti} = 1 · 10^{-5} mol/dm^3

No	Monomer used in prepolymerization	Activity kg PE/ /g Ti · h	Bulk density g/dm^3	Comments
1.	—	139.43	133	without prepolymerization
2.	1-pentene	274.50	153	
3.	1-pentene	252.87	160	
4.	1-octene	234.62	130	
5.	1-pentene	49.83	116	prepolymerization with $AlEt_3$ as cocatalyst
6.	4-methyl-1-pentene	109.78	145	
7.	ethylene	562.48	163	cat. conc. = 0.5 · 10^{-5} mol/dm^3

Analysis of the results obtained (Tab. 3) shows that the modification of the catalyst by pentene prepolymerization increases its activity twice. Additionally, this precatalyst causes considerable increase of the bulk density of PE obtained (Tab. 3, items 1, 2 and 3). The application of a longer chain olefin, 1-octene, leads to the similar result but the increase of the catalyst activity is not associated with the increase of the bulk density of the polymer obtained (Tab. 3, item 4). The least favorable is the application of branched monomer, 4-methyl-1-pentene, into the prepolymerization process (Tab. 3, item 6).

The results of our investigations explicitly show that alkylaluminum chloride $AlEt_2Cl$ must be the cocatalyst in the prepolymerization process. Pentene prepolymerization with the use of $AlEt_3$ cocatalyst results in a drastic decrease of the catalyst activity and the bulk density of the polymer obtained (Tab. 3, compare items 2 and 5). The modification of the studied catalyst by ethylene prepolymerization leads to an increase of the catalyst activity and the bulk density of the polymer product (Tab. 2, item 3 and Tab. 3, item 7).

Generally it was found that both ethylene and pentene prepolymerization processes increase the activity of the supported titanium catalyst and the bulk density of polyethylene obtained. Higher bulk density is the effect of the change of PE morphology, which can be characterized by the particle size distribution, what was made for all samples of PE obtained. Figure 4 describes an exemplary effect of the modification of the catalyst by prepolymerization on the particle size distribution of PE. The maximal contribution of PE changes from PE of particle size Φ ≈ 1.2 mm (Fig. 4, curve 1) for unmodified catalyst system to the smaller particle sizes and narrower particle size distribution (Φ ≤ 0.8 mm) for the catalyst modified by ethylene or pentene prepolymerization (Fig. 4, curve 2). This advantageous effect was not found for the polymer obtained with 4-methyl-1-pentene as the precatalyst (Fig. 4, curve 3).

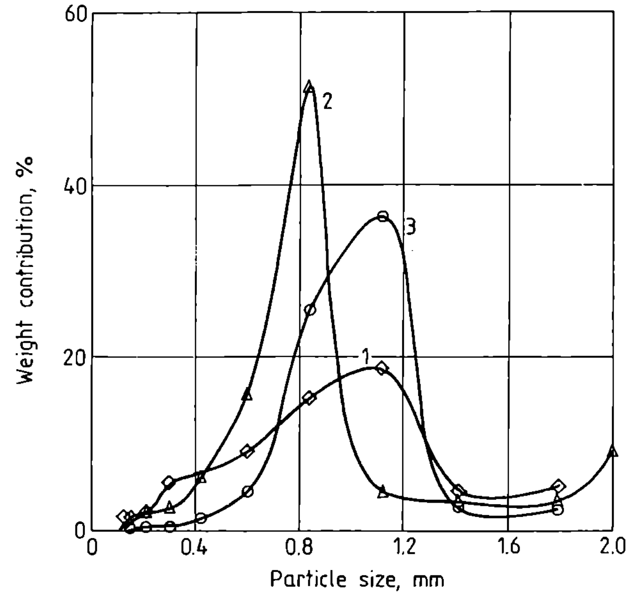

Fig. 4. Particle size distribution of PE obtained on Mg-Ti-Al catalyst: 1 — nonmodified by prepolymerization, 2 — modified by pentene prepolymerization, 3 — modified by 4-methyl-1-pentene

CONCLUSIONS

On the basis of the present investigations we can conclude:

The application of triethylaluminum as a cocatalyst led to obtaining a very active titanium catalyst system on the bimetallic support [$MgCl_2(THF)_2/AlEt_2Cl/TiCl_4$] for the ethylene polymerization.

For this catalyst system the polymerization rate as a function of the catalyst concentration is not linear because the reaction runs through kinetics and diffusion areas. The borderline catalyst concentration depends on the activity of the catalyst system. The more active the catalyst system the lower the borderline catalyst concentration. For the catalyst system on the bimetallic support the borderline catalyst concentration was $5 \cdot 10^{-6}$ mol Ti/dm^3.

The kinetics study of the ethylene polymerization with the catalyst system obtained indicates that there are unstable and stable active sites. The unstable active sites are deactivated at the beginning of the ethylene polymerization simultaneously with the creation of the stable ones. The results show that the modification of the elaborated catalyst system by prepolymerization process is necessary and should improve the morphology of PE.

The preliminary trials of the modification of the elaborated catalyst by the prepolymerization process reveal the need of the activation of the catalyst system in the olefin environment what results in following profitable changes:

— considerable increase of the catalyst system activity,

— advantageous modification of the morphology of the polyethylene obtained.

REFERENCES

1. Nowakowska M., Bosowska K.: *Makromol. Chem.* 1992, **193**, 889.
2. Karol F. J., Cann K. J., Wagner B. E.: "Transition Metals and Organometallic as Catalysts for Olefin Polymerization" (ed. Kaminsky W. and Sinn H), Springer, Berlin—Heidelberg 1988, p. 149—161.
3. Sobota P., Utko J., Lis T.: *J. Chem. Soc., Dalton Trans.* 1984, 2077.
4. Bosowska K., Nowakowska M.: *J. Appl. Polym. Sci.* 1998, **69**, 1005.
5. Szczegot K.: "Prekursory katalizatorów polimeryzacji etylenu" (Precursors of ethylene polymerization catalysts), Studia i monografie, Opole 1995.
6. Szczegot K., Sibelska-Wiercigroch I.: *Polimery* 1997, **42**, 610.
7. Wu Q., Wang H., Lin S.: *Macromol. Chem., Rapid Commun.*1992, **13**, 357.
8. Xu Z., Zhu Q., Freng L., Yang S.: *Macromol. C'hem., Rapid C'ommun.* 1990, **11**, 79.
9. Czaja K., Król B.: *Polimery* 1997, **42**, 497.
10. Król B., Maciejewska H.: *Polimery* 1991, **36**, 285.
11. Dawidowska-Marynowicz B., Nowakowska M., Pierz A.: *Polimery* 1999, **44**, 788.

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