# The Roles for a Lewis Base and $MgCl_2$ in Third-Generation Ziegler-Natta Catalysts

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**ABSTRACT:** Activity of a titanium catalyst supported on a bimetallic magnesium−aluminium system, involving a Lewis base $[MgCl_2(THF)_2/Al(C_2H_5)_2Cl]$, was studied in ethylene polymerization, and the effect of the catalyst composition on the properties of the final polymer produced was investigated. Analysis and discussion of the findings covering also some part of the kinetic study, resulted in defining the roles for $MgCl_2$ and a Lewis base in the third-generation Ziegler-Natta catalysts. $MgCl_2$ forms a bimetallic complex with an organoaluminium compound, which involves also a Lewis base. Its reaction with $TiCl_4$ yields a very active catalyst wherein the Mg : Ti molar ratio is close to 1. This means that $MgCl_2$ is involved in creating catalytic active sites. The structure of these catalytic sites were suggested. Hence, the role for $MgCl_2$ can be twofold: it is a component of a catalytic active site, and it is a support if Mg : Ti $> 5$. It was found in the study that the catalytic function of $MgCl_2$ can be maintained while its supporting function can be omitted. Thus, $MgCl_2$ can be substituted for $Al_2O_3$ and the catalytic system obtained will have the same activity. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1005−1011, 1998

**Key words:** polymerization of olefins; Ziegler-Natta catalysts; $MgCl_2(THF)_2$; kinetics of polymerization of ethylene; properties of HDPE

## INTRODUCTION

Organometallic complexes produced from a titanium compound supported on $MgCl_2$ and an organoaluminium compound, modified with Lewis bases, were found to be the most active third-generation Ziegler-Natta catalysts for olefin polymerization.

Despite a respectively wide use of this type catalysts in the industry, the present opinions that can be found in available literature on the role for $MgCl_2$ and a Lewis base differ significantly from one another, and neither of them has been confirmed experimentally. This situation results from the difficulties faced by scientists when investigating such a heterogeneous system with catalytic active sites located on its surface. Hence, our study was intended to evaluate the role for the $MgCl_2$ support and of a Lewis base in the formation of catalytic active sites.

We found in our earlier work[1−3] that introducing a Lewis base in the form bound with a magnesium support $[MgCl_2(THF)_2]$ into a catalytic system yields a very stable and active titanium catalyst, applicable in ethylene polymerization. The optimum composition of this catalyst $(A)^2$ differs significantly from an average composition of a third-generation titanium catalyst(s) employed commercially $(B).^4$

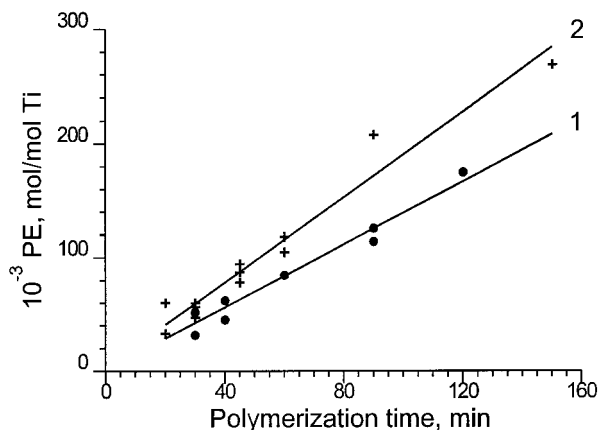| Catalyst | A<br>$MgCl_2(THF)_2/TiCl_4$ | B<br>$MgCl_2/TiCl_4/LB$ |
|---|---|---|
| Mg/Ti | $5 − 12$ | $6 − 50$ |
| LB/Ti | $10 − 24$ | $0.3 − 1.6$ |
| LB/Mg | 2 | $0.04 − 0.22$ |
| LB—Lewis base | | |

**Figure 1**  Productivity of PE as a function of polymerization time. Ti concentration—$4{,}5 \cdot 10^{-5}$ mol/dm$^3$; concentration of cocatalyst $[Al(C_2H_5)_2Cl]$—$3 \cdot 10^{-2}$ mol/dm$^3$; 1—Ti catalyst on a monometallic support $[MgCl_2(THF)_2/TiCl_4]$; and 2—Ti catalyst on a bimetallic support $[MgCl_2(THF)_2/Al(C_2H_5)_2Cl/TiCl_4]$.

High excess of LB over Ti in the catalyst A has no deactivating impact on this catalytic system; on the contrary, it offers stable efficiency in ethylene polymerization over a few hours. Ti catalysts (A and B) needed very high excess of a cocatalyst (organoaluminium compound) to be used. This encouraged us to set forth a hypothesis on a bimetallic complex $MgCl_2(THF)_2/Al(C_2H_5)_2Cl$ being formed that acts as a support.[2] And this means that immobilized $TiCl_4$ on such a support is isolated from contacting directly magnesium chloride. Consequently, there is no possibility for a titanium compound to be incorporated into the $MgCl_2$ structure.

It should be emphasized that the possibility of forming bimetallic Mg–Al complexes in a Lewis base medium was reported by Karol[5] and Sobota[6] in 1988–89.

The study presented here was intended primarily to confirm the above hypothesis. For this purpose, the bimetallic complex $MgCl_2(THF)_2/Al(C_2H_5)_2Cl$ was synthesized and then it was employed as a support for an ethylene polymerization catalytic system.

## RESULTS AND DISCUSSION

### Bimetallic Complex with a Lewis Base, Employed as a Support for a Titanium Catalyst

A reaction between solid $MgCl_2(THF)_2$ and diethylchloroaluminium was carried out in the hexane medium, with equimolar amounts of both re-actants. The reaction product—bimetallic complex $MgCl_2(THF)_2/Al(C_2H_5)_2Cl$—was employed as a support for a titanium catalyst. This catalyst was complexed with large excess of cocatalyst $[Al(C_2H_5)_2Cl]$. Catalytic activity of this obtained system in the polymerization of ethylene was evaluated as well as its influence on the properties of PE produced: molecular weight and grain size distribution.

The results shown in Figure 1, curve 2, confirm that the studied catalytic system is very active and stable. Thus, the catalytic system utilising a bimetallic support is similar to a system with a complex monometallic support (Fig. 1, curve 1), but its activity is higher of them.

Figure 2 presents that polymerization degree of PE obtained for both catalytic systems are not different from each other and they go up as polymerization time increases.

On the other hand, grain size distribution (Fig. 3) for PE produced on both catalytic systems studied is similar with one exception: the catalyst on a monometallic support produces high volumes (about 25%) of big granules that adversely affect the product bulk density. These findings suggest that active sites for the catalyst studied, employing a bimetallic support, are of the same type.

Activity of the catalyst tested were verified in a pilot plant (Table I).

For the needs of comparison, this table also provides the results obtained for the catalytic system on a monometallic support. These findings confirm that the catalyst on a bimetallic support is more active than the corresponding system on a monometallic support. Moreover, the study re-
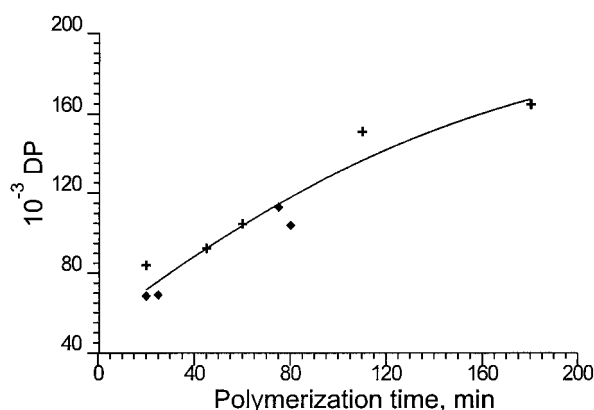


**Figure 2**  DP—Polymerization degree of PE as a function of polymerization time. ◆—catalyst on a monometallic support, +—catalyst on a bimetallic support; Ti concentration—$4{,}5 \cdot 10^{-5}$ mol/dm$^3$; and concentration of cocatalyst $[Al(C_2H_5)_2Cl]$—$3 \cdot 10^{-2}$ mol/dm$^3$.
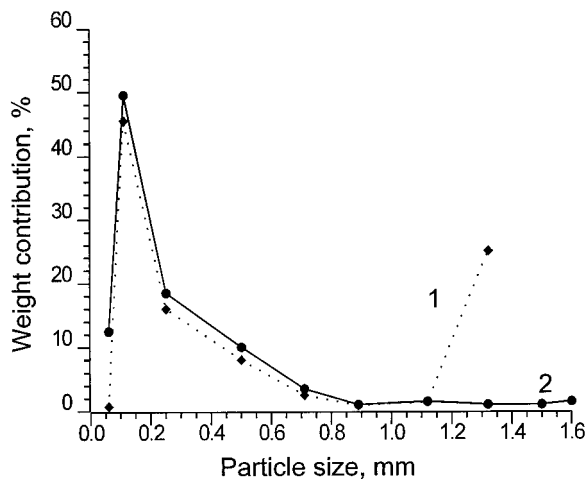
**Figure 3** Particle size distribution of PE obtained on the catalyst deposited on different supports. 1—monometallic, 2—bimetallic; polymerization time—60 min; Ti concentration—$4,5 \cdot 10^{-5}$ mol/dm$^3$; and concentration of cocatalyst $[Al(C_2H_5)_2Cl]$—$3 \cdot 10^{-2}$ mol/dm$^3$.

vealed a clear impact from the catalyst concentration on its activity.

## Ethylene Polymerization Rate vs. Catalyst Concentration

Availability of a pilot plant equipment made it possible to study the impact from the catalyst concentration on ethylene polymerization rate over a wide span of concentration ($1 \times 10^{-6}$ to $5 \times 10^{-5}$ mol Ti/dm$^3$). The results obtained were presented in Table II.

Based on these experimental results, it was found that the polymerization rate was not a linear function of the catalyst concentration.

Only a dual-logarithmic function becomes linear, as shown in Figure 4 and eq. (1):

$$\ln R_p = 3.07 + 0.49 \ln n_k \quad r = 0.989$$

$$r—\text{regression coefficient} \quad (1)$$

**Table II   The Influence of the Concentration of the Catalyst ($n_k$) on Its Activity ($A$) and the Polymerization Rate of Ethylene ($R_p$)**

| No. | $n_k$ (molTi/dm$^3$) | $A$ (kgPE/gTi·h) | $R_p$ (molEt/dm$^3$·min) |
|---|---|---|---|
| 1 | $0.10 \cdot 10^{-5}$ | 870 | 0.0248 |
| 2 | $0.24 \cdot 10^{-5}$ | 609 | 0.0417 |
| 3 | $0.52 \cdot 10^{-5}$ | 321 | 0.0476 |
| 4 | $0.50 \cdot 10^{-5}$ | 452 | 0.0644 |
| 5 | $4.50 \cdot 10^{-5}$ | 124 | 0.1584 |
| 6 | $4.50 \cdot 10^{-5}$ | 132 | 0.1694 |

Parameters: pressure of ethylene—1 MPa, concentration of ethylene: Et = 0.942 mol/dm$^3$.

Hence, polymerization rate takes the form of:

$$R_p = 21.5 \times (n_k)^{0.5} \quad (2)$$

or:

$$R_p = 21.5 \times e_k^{-0.5} \times (n^*)^{0.5} \quad (3)$$

where: $n_k$ is the catalyst concentration, mol Ti/dm$^3$, $n^*$ is the concentration of active sites, mol/dm$^3$, and $e_k$ is the share of active sites in the catalyst, $n^*/n_k$.

As the ethylene polymerization rate was found to be constant for a bimetallic-supported catalyst (Fig. 1, curve 2), the share of active sites in the catalyst remains unchanged ($e_k$ = const). Concentration of active sites also is unchanged:

$$n^* = \text{const} = n_0^*$$

where $n_0^*$ is the initial concentration of active sites.

Hence, the polymerization reaction rate of ethylene is directly proportional to $(n_0^*)^{0.5}$. Thus, the reaction order was found to be "0.5" for the concentration of catalytic active sites, and the kinetic

**Table I   Parameters and Results of Polymerization of Ethylene Catalyzed by Ti–Al-Supported Systems in the Pilot Plant**

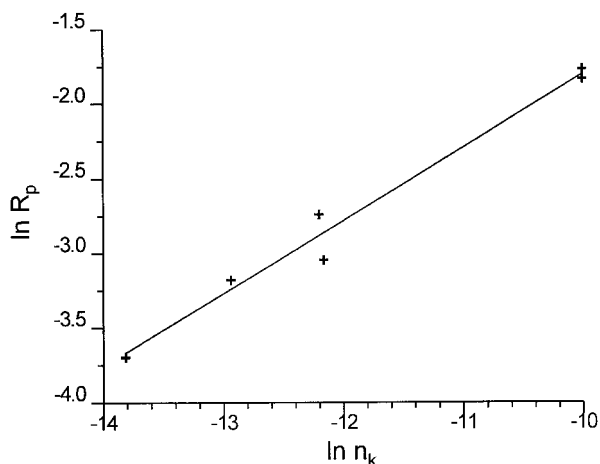| Conditions and Results of Polymerization | Monometallic Support | | Bimetallic Support | |
|---|---|---|---|---|
| Concentration of Ti·$10^5$ (mol/dm$^3$) | 5.0 | 1.0–1.5 | 0.5 | 0.1 |
| Molar ratio of Al/Ti (mol/mol) | 120 | 360 | 550 | 1500 |
| Pressure of ethylene (MPa) | 0.7–1.0 | 1.0 | 1.1–1.2 | 1.0 |
| Polymerization temperature (°C) | 50–62 | 58–62 | 55–58 | 50–55 |
| Activity (kgPE/(gTi·h)) | 105 | 358 | 520 | 1120 |

**Figure 4**   The influence of the concentration of the catalyst on the polymerization rate.

equation for ethylene polymerization involving a stable and active catalyst on a bimetallic support is as follows:

$$R_p = k_p \times (n_0^*)^{0.5} \times Et \qquad (4)$$

Utilizing experimental data for the functions of PE = $f(t)$ (Fig. 1, curve 2) and DP = $f(t)$ (Fig. 2) and employing the polymerization kinetic model as suggested by Böhm,[7] from the function of PE/DP = $f$(PE) the share of active sites was calculated: $e_k = n_0^*/n_k = 0.47$. And then, comparison of ethylene polymerization rate as per eqs. (3) and (4) made it possible to determine the chain propagation rate constant: $k_p = 0.55$ dm$^3$/(mol $\times$ $s$).

To verify the experimentally found polymerization reaction order of "0.5" for the concentration of active sites, kinetic findings from the laboratory and pilot plant runs were analyzed with the use of a different kinetic model. This model, suggested by Czaja,[8] assumes that the rate of creating macromolecules is equal to the rate of the transfer reaction, i.e., to the active site regeneration rate. Our analysis utilized the experimentally defined reaction order of "0.5" for the concentration of active sites:

$$dc_p/dt = k_r \times (n_0^*)^{0.5} \times Et \qquad (5)$$

where $c_p$ is the concentration of macromolecules = PE/DP, mol/dm$^3$.

The kinetic analysis of the experimental findings was based on eqs. (4) and (5), and the results were provided in Table III.

The values of $k_p$ and $k_r$ determined for the system studied, with a bimetallic support, in a labo-

ratory and in a pilot plant are close to each other and also to corresponding rate constants for a catalyst on a monometallic support. This confirms that the kinetic eqs. (4) and (5) were derived properly. Both these catalyst apparently differ only in their shares of active sites: the catalyst on a bimetallic support is superior. Its values of $e_k$, as found from the models developed by Böhm and Czaja, are similar (0.47; 0.49). This suggests that the mechanisms of ethylene polymerization reactions over monometallic and bimetallic complexes are similar. In both cases the bimetallic complex MgCl$_2$(THF)$_2$/Al(C$_2$H$_5$)$_2$Cl is no doubt an important component of the catalytic system. In the case of a monometallic support MgCl$_2$(THF)$_2$ a bimetallic complex is formed only after complexing the titanium catalyst [MgCl$_2$(THF)$_2$/TiCl$_4$] with much excess of an organoaluminium compound. This causes that the share of active sites for this system is a bit lower (0.35) compared to a catalyst wherein a previously obtained bimetallic complex is employed as a catalyst support.

## Polyethylene Properties vs. Composition of Catalyst Studied

Two titanium catalyst on a bimetallic support MgCl$_2$(THF)$_2$/Al(C$_2$H$_5$)$_2$Cl/TiCl$_4$ with different Mg : Ti molar ratios were synthesized. After their complexing with a cocatalyst [Al(C$_2$H$_5$)$_2$Cl], their catalytic activity in the ethylene polymerization process was observed. The results were provided in Table IV.

They suggest that the activity is similar for the both systems. It should be stressed that the composition of one of the catalysts investigated (Mg : Ti = 2 : 1) is clearly different from the data available elsewhere for this type of catalysts; literature reports that the Mg : Ti molar ratio must be higher than 5 : 1.[2,5] This suggests that magnesium chloride could participate in creating active sites, what in turn, means that MgCl$_2$ does not have to be solely a catalytic support. It was found, however, that in such a case PE obtained offers increased bulk density what results from unfavourable morphology of PE produced (Fig. 5).

For Mg : Ti = 10, PE granules were in fact fine balls, while the ratio of Mg : Ti = 2 yielded PE in the form of hard flakes. Other properties of polyethylene were similar in both catalytic conditions (Table IV). As can be seen, polyethylene had very high molecular weight and good mechanical properties.

The results (Table IV, Fig. 5) show that the use of a support is needed to obtain the required

**Table III   Kinetic Parameters of Polymerization of Ethylene**

| Kinetic Parameters | Catalytic System | | |
| --- | --- | --- | --- |
| | $MgCl_2(THF)_2/TiCl_4$ + $Al(C_2H_5)_2Cl$ | $MgCl_2(THF)_2/Al(C_2H_5)_2Cl/$ $TiCl_4$ + $Al(C_2H_5)_2Cl$ | |
| | Laboratory Scale | Laboratory Scale | Pilot Plant |
| $n_k \cdot 10^5$ (mol Ti/dm$^3$) | 4.5 | 4.5 | 0.5 |
| $p_{Et}$ (MPa) | 0.5 | 0.5 | 1.2 |
| $A$ [molEt/(mol Ti·min)] | 1379 | 1868 | 13,230 |
| $k_p$ (dm$^3$/(mol·s)) | 0.57 | 0.64 | 0.61 |
| $k_r \cdot 10^6$ [cm$^3$/(mol·s)] | 2.95 | 3.29 | 3.28 |
| $n^*/n_k$ (mol/mol) | 0.35 | 0.49 | 0.51 |

morphology of polyethylene produced (ball-shaped granules). We assumed that the support employed does not necessarily have to be $MgCl_2$, but it can be substituted by some other neutral support(s), for example, alumina. So, a new magnesium–aluminium–titanium catalyst was synthesized with the use of equimolar amounts of components: $MgCl_2(THF)_2$ : $Al(C_2H_5)_2Cl$ : $TiCl_4$ = 1 : 1 : 1. This product was supported on alumina of diameter 0.18–0.25 mm previously calcinated at 1100°C. Such obtained supported Ti catalyst after the reaction with cocatalyst gave the catalytic system, which was very active in ethylene polymerization: it was comparable with the system supported on $MgCl_2(THF)_2$, and what is most important, it yielded PE in the required granular form. Patent application was filed to protect the method of producing this new Ti–Mg–Al catalytic system on an oxide-type support.[9] This new oxide-supported Ti–Mg catalytic system minimizes the use of magnesium chloride. Thus, PE produced over this catalyst is not contaminated with any residual $MgCl_2$ from the catalyst support and can contain neutral $Al_2O_3$ that is environmentally friendly.

## CONCLUSIONS

This study contributed to the knowledge on the role for the magnesium dichloride and a Lewis base in third-generation Ziegler-Natta catalysts.

Utilization of a bimetallic magnesium–aluminium complex with a Lewis base [$MgCl_2(THF)_2/$ $Al(C_2H_5)_2Cl$] as a support for the titanium catalyst gave a stable and high-activity titanium–aluminium catalytic system for ethylene polymerization. Activity of this catalyst is superior to that offered by the catalyst on a monometallic support [$MgCl_2(THF)_2$]. This confirms our earlier suggestion[2] that isolation of titanium atoms from direct contact with the magnesium dichloride surface is a desirable situation. And this means that the supported titanium compound is not built into the crystal structure of $MgCl_2$, as has been believed so far.

What should be stressed is that there is considerable excess of a Lewis base over magnesium and titanium in the catalyst studied, which is unusual for available literature reports.[4] Thus, a Lewis base plays an important role in creating bimetal-

**Table IV   The Influence of the Composition of the Titanium Catalyst on Bimetallic Support on Its Activity and Properties of Obtained PE**
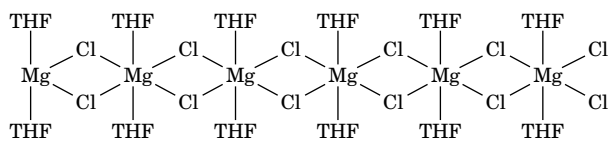
| Mg : Ti (mol/mol) | PE (kg/(gTi·h)) | $d_b$ (g/dm$^3$) | $m_\eta$ | $d$ [g/cm$^3$] | Crystallinity (%) | $T_{mp}$ (°C) | Tensile Strength (MPa) | Elongation (%) |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 10 | 70.0 | 93 | 4,459,200 | 0.962 | 67.0 | 138.8 | 36.1 | 295 |
| 2 | 66.2 | 149 | 3,156,600 | 0.951 | 55.7 | 141.0 | 36.5 | 325 |

$d_b$—bulk density of obtained PE.
$d$—density of PE.
$T_{mp}$—melting point.

lic complexes. This base is introduced to the system in the form of a complex with magnesium dichloride. Its probable structure is as follows:

THF   THF   THF   THF   THF   THF
 |  Cl  |  Cl  |  Cl  |  Cl  |  Cl  |  Cl
Mg    Mg    Mg    Mg    Mg    Mg
 |  Cl  |  Cl  |  Cl  |  Cl  |  Cl  |  Cl
THF   THF   THF   THF   THF   THF

A similar structure was reported in 1992[10] in the study of magnesium dichloride complexes with other Lewis bases. Hence, THF molecules contained in the complex split $MgCl_2$ agglomerates into small crystallites and prevent their reagglomeration. So, the suspension of the $MgCl_2$-$(THF)_2$ complex in hexane is composed of finely broken up particles that do not undergo settling down, which we have found experimentally. Thus, the role for THF is reduced to filling up all the coordination empty spaces in the magnesium dichloride structure, and also to form bimetallic magnesium–aluminium complexes that interact with a titanium compound to create ethylene polymerization active sites. This means that magnesium dichloride is involved in creating an active site.

The findings in the study on the influence from the catalyst composition on the yield and properties of the obtained polyethylene confirmed this suggestion. This means that magnesium dichloride does not have to be just a support. And this allowed for a structure of a magnesium–aluminium–titanium active site to be suggested:
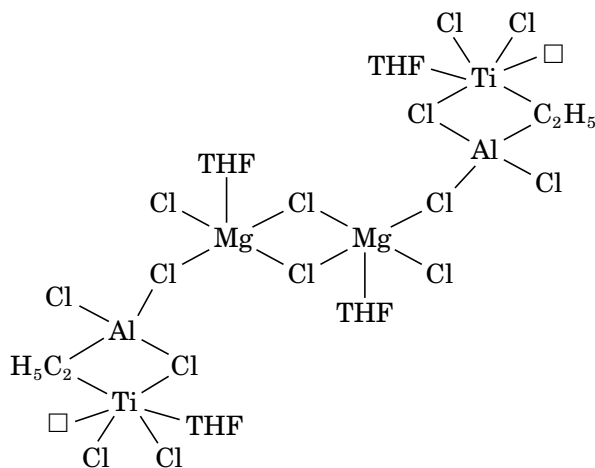
A labile donor (THF) can change its location. We think that this ligand is situated at the titanium atom and increases its electron density. In our earlier studies of ethylene polymerization on catalysts with alkoxy donor ligands we found that increase of electron density of Ti leads to the in-
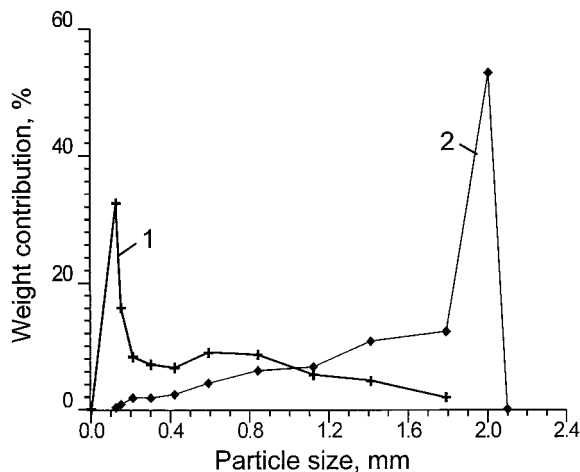


**Figure 5**    Particle size distribution of PE obtained on the catalyst deposited on bimetallic support. Polymerization time—60 min; Ti concentration—$4,5 \cdot 10^{-5}$ mol/$dm^3$; concentration of cocatalyst $[Al(C_2H_5)_2Cl]$—$3 \cdot 10^{-2}$ mol/$dm^3$; and 1—Mg/Ti = 10, 2—Mg/Ti = 2.

crease of molecular weight of PE.[12,13] The same phenomenon takes place in present work in which PE of very high molecular weight was obtained (Table IV).

We have found, however, in our study that PE obtained over a catalytic system that in practice has no support (Mg : Ti = 2 : 1) features unfavorable morphology. Instead of expected ball-shape granules, we produced the material in the form of hard and flat flakes. Thus, a supported catalyst is needed when PE with a required morphology is to be produced. Resulting from our investigation we learned that in this case magnesium chloride can be replaced with neutral alumina[9] that is environmentally friendly.

Moreover, in the course of this study we found that the polymerization reaction rate is a function of the catalyst concentration that was not reported in references on Ziegler-Natta catalysts, even on third-generation ones. Only Fischer,[11] in 1993, mentioned having observed the concentration impact in the case of very active metallocene catalysts on the rate of olefin polymerization reactions. Resulting from our experiments, this function was defined over a wide range of catalyst concentrations ($1 \times 10^{-6}$–$5 \times 10^{-5}$ mol Ti/$dm^3$). This function, as well as kinetic findings from ethylene polymerization involving the catalytic system studied, made it possible to derive a new kinetic equation. We have experimentally defined reaction order of "0.5" for the concentration of active sites.

## EXPERIMENTAL

### Chemicals

Ethylene (Petrochemia SA Płock, Poland) and pure argon (Polgaz, Poland) were used after passing through a column of metallic natrium supported on $Al_2O_3$. Titanium tetrachloride (Merck) and $(C_2H_5)_2AlCl$ (Schering) were used without further purification. $MgCl_2(THF)_2$ was prepared by the Institute of Chemistry, University of Wrocław (Poland).

### Catalyst Preparation

The bimetallic support was prepared by milling solid $MgCl_2(THF)_2$ with $(C_2H_5)_2AlCl$ in a glass mill (capacity: 250 $cm^3$, with 20 balls of 1-cm diameter) in hexan solution at the room temperature for 1 h using equimolar ratio of substrates. The titanium catalyst was prepared by milling the obtained suspension of bimetallic support with $TiCl_4$ at the room temperature for 24 h.

### Polymerization of Ethylene in a Laboratory Scale

The polymerization reaction was carried out at 50°C in 1 $dm^3$ reactor equipped with stirrer, in hexane, at a constant pressure of the ethylene. Assumed amounts of hexane (0.2 $dm^3$), Ti catalyst supported on the bimetallic (Mg–Al) complex and a great excess of the cocatalyst—$(C_2H_5)_2$-AlCl —were introduced into the reactor in an argon stream. All components were mixed for 15 min. Then 0.5 $dm^3$ of hexane was added and polymerization was started by ethylene introduction. The polymerization was stopped by methanol introduction. The polymer was filtered off, washed with methanol, and dried.

### Polymerization of Ethylene in a Pilot Plant Scale

The main elements of the pilot plant were: (1) a catalytic complex preparation reactor of 20 $dm^3$ volume, (2) a polymerization reactor of 80 $dm^3$ volume and working pressure up to 1.2 MPa, (3) a pump feeding the catalytic complex suspension to the polymerization reactor, and (4) a vessel for collecting samples during the polymerization process, equipped with all necessary measuring instruments.

The pilot plant was connected to a industrial polyprophylene plant in Płock.

### Measurements

The average molecular weight ($M_v$) of the produced polymers was determined by viscosity method in decalin at 135°C. Polymerization degree DP was calculated as a ratio of molecular weight of polyethylene and the monomer as DP $= M_v/28$.

Polymer melting points were measured with Unipan 605 calorimeter, at a heating rate of 5 K/min on samples that had been previously melted and recrystallized.

Granulometric distribution of polyethylene was determined on a Fritsch Vibratory Sieve Shaker "analysette 3." The samples of PE were shaken for 20 min on a set composed of 10 sieves of mesh width varying from 0.09 to 2.00 mm. Mass fraction of PE on each sieve was determined. The mean values of the partical size of the PE fraction was calculated according to the equation $a_{1/2} = (a_1 a_2)^{0.5}$, where $a_1$ is the mesh width for a higher sieve and $a_2$ is the mesh width for a lower sieve.

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