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Kinetics of ethylene polymerization over titanium catalyst supported on bimetallic carrier $\text{MgCl}_2(\text{THF})_2/\text{AlEt}_2\text{Cl}$

RAPID COMMUNICATION

Summary — Ethylene polymerization kinetics over $\text{TiCl}_4/\text{Et}_3\text{Al}$ catalyst supported on $\text{MgCl}_2(\text{THF})_2/\text{AlEt}_2\text{Cl}$ was investigated. The investigated catalyst system shows the presence of two kinds of the active sites: the unstable, low active classic sites, and the high active sites, supported on the bimetallic complex. The former can be eliminated from the catalyst system by means of a prepolymerization reaction with 1-pentene. Kinetics analysis allowed to determine: overall concentration of active centers (n_k , stable + unstable centers), concentration of stable active centers (n^*), chain propagation rate constant (k_p), and chain transfer rate constant (k_{tr}). It was concluded that number of stable active centers in the primary catalyst (prior to prepolymerization) is much higher than the number of eliminated active unstable centers (73% compared with 27%).

Key words: ethylene polymerization, supported organometallic titanium catalyst, kinetic characteristics, stable and unstable active centers.

It was found in our groups' earlier work [1–3] that tetrahydrofuran introduced into the catalyst as a Lewis Base in the form bonded to the magnesium support $\text{MgCl}_2(\text{THF})_2$, yields a stable and active titanium catalyst system applicable in ethylene polymerization. This complex magnesium support is not only much better than MgCl_2 alone, but also necessary when the titanium/magnesium complexes with internal Lewis Base are used as titanium compounds [4].

It also yields very good activities when used as a support of the vanadium catalyst for ethylene polymerization [5–7]. In the successive studies the $\text{MgCl}_2(\text{THF})_2$ complex carrier was modified by AlEt_2Cl , what gave the bimetallic carrier [8, 9]. The titanium catalyst supported on this bimetallic carrier after activation by TEA (AlEt_3) revealed very high activity (about 700 kg PE/g Ti · h) [10].

The purpose of the present work comprised kinetic investigations conducted in order to determine active sites concentration and elementary ethylene polymerization reaction rate constants for reaction carried out using this titanium catalyst supported on the bimetallic carrier and activated by TEA.

EXPERIMENTAL

Materials

Ethylene (Petrochemia SA, Plock) 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, Plock) was refined with sulfuric acid, dried by refluxing in argon over sodium metal, and stored over 4 Å molecular sieves. Titanium tetrachloride — TiCl_4 (Merck), AlEt_2Cl (DEAC) and AlEt_3 (Schering), 1-pentene (Aldrich) were used as received. Tetrahydrofuran (Fluka) was purified according to standard method using NaOH, metallic Na and benzophenone as indicator. Magnesium chloride (98 wt. %) (Fluka) dried for 2 h at 393 K contained 0.38 wt. % H_2O (determined by thermal analysis TG).

Synthesis of the complex support $\text{MgCl}_2(\text{THF})_2$

Anhydrous commercial magnesium chloride was mixed with tetrahydrofuran in a glass mill (capacity: 250 cm³, 24 glass balls, each 0.5–0.7 cm in diameter) for 24 h at room temperature by using a mole ratio of $\text{THF}/\text{MgCl}_2 = 20$. The $\text{MgCl}_2(\text{THF})_2$ complex was precipitated by means of purified *n*-hexane, then filtered off,

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washed with *n*-hexane ($4 \cdot 150 \text{ dm}^3$) and dried. All steps were carried out in oxygen-free conditions using inert nitrogen atmosphere. The complex support obtained contained 9.39 wt. % Mg, as determined by AAS.

Bimetallic support preparation

Solid $\text{MgCl}_2(\text{THF})_2$ was mixed with AlEt_2Cl in a glass mill (capacity: 250 cm^3 , 20 balls, each 1 cm in diameter) in hexane for 1 h for solution at room temperature at equimolar ratio of the substrates.

Catalyst preparation

Suspension of the bimetallic support was mixed with TiCl_4 for 24 h at room temperature at mole ratio of $\text{Mg}/\text{Ti} = 10$.

Prepolymerization

Predetermined amounts of hexane, $[\text{MgCl}_2(\text{THF})_2/\text{AlEt}_2\text{Cl}/\text{TiCl}_4]$, AlEt_2Cl (AlEt_2Cl as cocatalyst, Al/Ti mole ratio = 100) and 1-pentene ($0.5 \text{ mol}/\text{dm}^3$) were added into 100 cm^3 glass reactor and nitrogen was bubbled through the mixture during 1 h at room temperature. Finally, the precatalyst obtained was stored for 24 hours.

Polymerization

Polymerization was carried out under nitrogen atmosphere in a 1 dm^3 stainless steel autoclave equipped with a stirrer. First, measured amounts of hexane, cocatalyst (AlEt_3), and catalyst were added successively into the reactor and, subsequently, ethylene was introduced at 50°C and subjected to polymerization under constant ethylene pressure of 5 atmospheres. Once polymerization was complete, reaction gases were slowly released, and the product was poured into a dilute solution of hydrochloric acid in methanol. The resulting polymer was filtered off, washed with methanol and dried.

Polymer characterization

The average molecular weight (M_η) of the received polyethylene was determined using the viscosity method and calculated from equation (1) [11] ($[\eta]$ in dm^3/g):

$$[\eta] = 4.75 \cdot 10^{-4} \cdot M_\eta^{0.725} \quad (1)$$

Intrinsic viscosity $[\eta]$ measurements were carried out at 135°C using a polymer concentration of about 0.05 g in 100 cm^3 of decaline and employing an Ubbelohde viscometer. Polymerization degree of polyethylene was calculated from the following equation: $DP_\eta = M_\eta/M_{\text{Et}}$ where M_{Et} is the molecular weight of ethylene.

Particle size analysis of the PE was performed using the vibrating screen sieve method (Frisch Company). Constant weight samples were shaken during 20 minutes using a set of sieves with the sieve mesh 0.09–2.0 mm. Weight of each fraction was recorded and weight percentages calculated. Average particle diameter $a_{1,2}$ was calculated as $a_{1,2} = (a_1 \cdot a_2)^{0.5}$, where a_1 and a_2 are the mesh diameters of the top and bottom sieves, respectively.

The FT-IR analysis was performed using Philips Analytical PU 9800 spectrometer, resolution $R = 2 \text{ cm}^{-1}$, bands 4000–400 cm^{-1} , in Nujol KBr/KBr.

The amount of magnesium in the support was determined by AAS (*Atomic Absorption Spectrometry*) by using the SOLAR 969 Unicam spectrometer.

Kinetics calculations

Böhm [12] and Czaja [5] kinetic models were applied in kinetic investigations. The former assumes that reaction medium at any moment of ethylene polymerization contains both growing and ready-built macromolecules. This assumption results in the following relationship:

$$\text{PE}/DP = [n^*] + \text{PE}/DP_{\text{max}} \quad (2)$$

where: PE — yield of polyethylene, $\text{mol Et}/\text{dm}^3$; DP — average polymerization degree of PE; DP_{max} — final average polymerization degree of the polyethylene obtained; $[n^*]$ — concentration of the active sites, $\text{mol Ti}/\text{dm}^3$.

The second kinetic model assumes that the rate of formation of macromolecules is equal to the rate of transfer reaction *i.e.* to the rate of active site regeneration:

$$d(\text{PE}/DP)/dt = k_{tr} \cdot [n^*] \cdot [M] \quad (3)$$

After integration:

$$\text{PE}/DP = (\text{PE}/DP)_0 + k_{tr} \cdot [n^*] \cdot [M] \cdot t \quad (4)$$

where: k_{tr} — transfer reaction rate constant, $\text{dm}^3/(\text{mol} \cdot \text{min})$; $[M]$ — ethylene concentration, $\text{mol Et}/\text{dm}^3$.

Because $(\text{PE}/DP)_0 = [n^*]_0$, and $[n^*]_0 = \text{const.} = [n^*]$, equation (4) changes to:

$$\text{PE}/DP = [n^*] + k_{tr} \cdot [n^*] \cdot [M] \cdot t \quad (5)$$

RESULTS AND DISCUSSION

The FT-IR spectra of the $\text{MgCl}_2(\text{THF})_2$ carrier, reveal band of tetrahydrofuran bonded to magnesium chloride at 1033 cm^{-1} , whereas band of free THF at 1080 cm^{-1} is not present. The complex support obtained has 9.39 wt. % Mg as was determined by AAS, corresponding with its molecular formula $\text{MgCl}_2(\text{THF})_2$. TiCl_4 immobilized on bimetallic carrier leads to formation of the titanium precatalyst $\text{MgCl}_2(\text{THF})_2/\text{AlEt}_2\text{Cl}/\text{TiCl}_4$ (I), which was applied to ethylene polymerization after activation by AlEt_3 as cocatalyst. Only very small quantities ($n_k =$

$2 \cdot 10^{-6}$ mol Ti/dm³) were used to carry out polymerization in the kinetic region determined in our previous work [10].

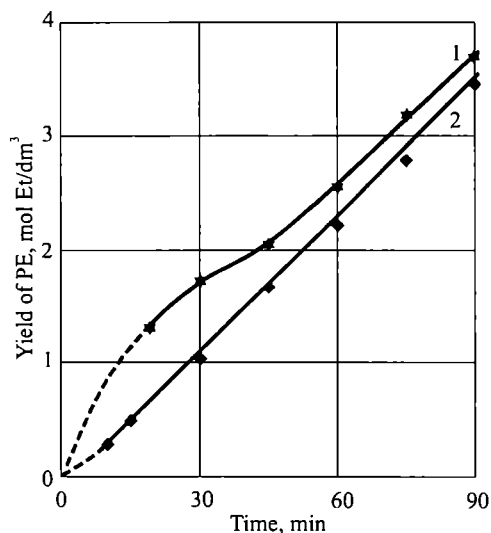


Fig. 1. Influence of polymerization time on the yield of PE obtained by using titanium catalyst $MgCl_2(THF)_2/AlEt_2Cl/TiCl_4$ (concentration = $2 \cdot 10^{-6}$ mol/dm³, mole ratio Mg/Ti = 10, $AlEt_3$ concentration = $3 \cdot 10^{-2}$ mol/dm³); 1 — catalyst system (I), 2 — catalyst system (II) modified by 1-pentene prepolymerization

Figure 1 (curve 1) shows that polymerization reaction rate is initially relatively fast, but decreases with time. A proportional increase of PE yield is observed after some 40 minutes of initiation. Such shape of the kinetic curve indicates that the catalyst system initially operates with two kinds of active sites. All unstable sites are eliminated after about 40 minutes. Thus, it is concluded that unstable active sites should be eliminated prior to catalyst activation by using an organoaluminum compound, e.g. catalyst prepolymerization by using higher olefin under moderate conditions. In our work, the titanium catalyst $MgCl_2(THF)_2/AlEt_2Cl/TiCl_4$ was modified by a prepolymerization reaction of 1-pentene leading to the titanium catalyst system (II). The resulting catalyst system (II) (curve 2 on Fig. 1) had only one kind of the active sites, giving constant reaction rates of the ethylene polymerization opposite to curve 1 on this figure.

Kinetic curve 2 is described by equation (6):

$$PE = -0.103 + 0.039 \cdot t \quad (6)$$

where: PE — yield of PE, mol Et/dm³; t — polymerization time, min; 0.039 (mol Et/dm³ · min) — ethylene polymerization rate (R_p).

The particle size distribution of the PE obtained (Fig. 2, curve 2) also points to presence of only one kind of the active sites.

Analysis of the polymerization reaction kinetic function (Fig. 1, curve 2) and effect of polymerization time

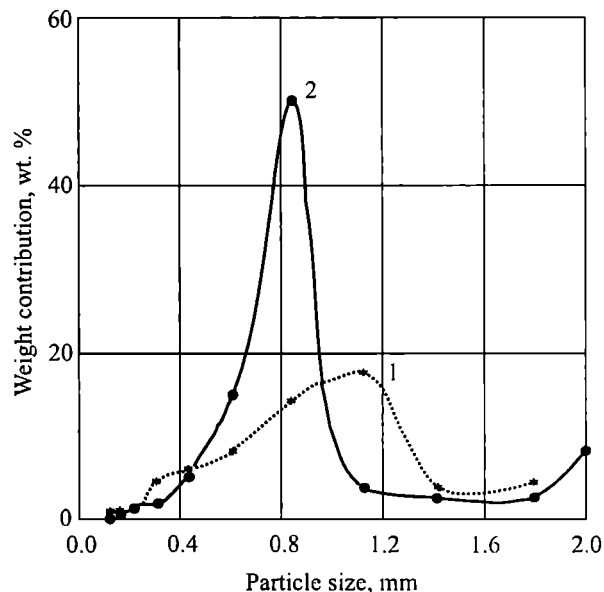


Fig. 2. Particle size distribution of PE obtained when using the $MgCl_2(THF)_2/AlEt_2Cl/TiCl_4$ titanium catalyst system: 1 — without prepolymerization, 2 — modified by 1-pentene prepolymerization

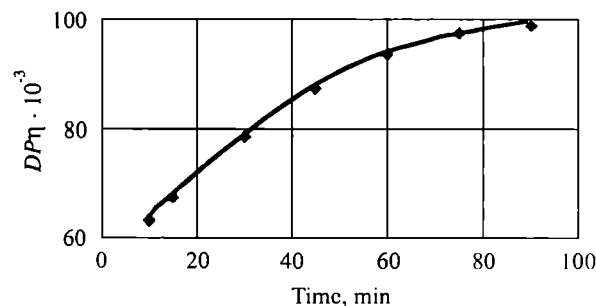


Fig. 3. Average polymerization degree (DP_n) of PE obtained on the catalyst system (II) as a function of polymerization time

on the average molecular weight of the PE (Fig. 3) enabled to determine concentration of the active sites and the elementary reaction rate constants for ethylene polymerization over the studied titanium catalyst system (II). Thus, $PE/DP = f(PE)$ and $PE/DP = f(t)$ were determined (Fig. 4) and concentrations of the active sites were calculated. Both kinetic models gave almost the identical active sites concentration values. Transfer reaction rate constant k_{tr} was determined using equation (5). Polymerization reaction rate (R_p) with active sites concentration allowed propagation reaction rate constant [k_p in dm³/(mol · min)] to be calculated from equation (7):

$$R_p = k_p \cdot [n^*] \cdot [M] \quad (7)$$

Results of kinetic analysis and selected properties of the studied catalyst system (II) and polyethylene obtained were as follows:

Mole ratio of Al/Ti, mol/mol — 15 000

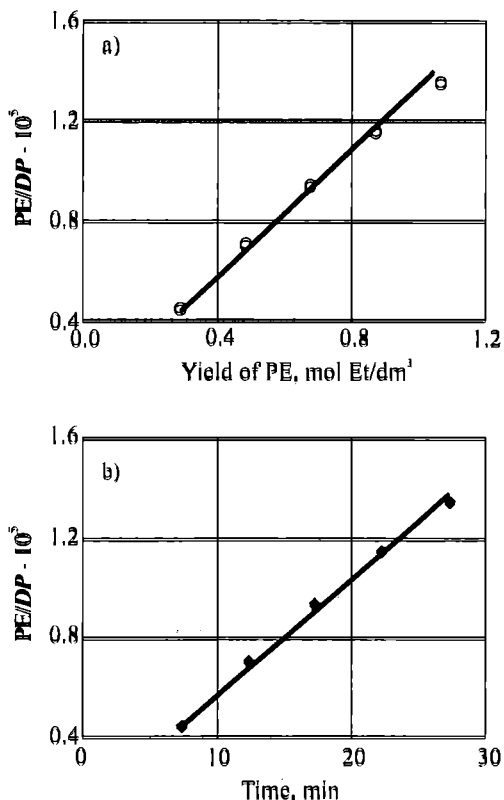


Fig. 4. Number of PE macromolecules obtained on the catalyst system (II) as a function of: (a) — yield of PE, (b) — polymerization time

Catalyst concentration n_k , mol Ti/dm ³	— $2 \cdot 10^{-6}$
Ethylene polymerization rate R_p , mol Et/(dm ³ · min)	— 0.039
Active sites concentration n , mol Ti/dm ³	— $1.44 \cdot 10^{-6} \pm 1.4\%$
Content of active sites in catalyst (n/n_k) · 100	— $73 \pm 1.4\%$
Catalyst A activity, kg PE/(g Ti · h)	— 687.43
Chain grow rate constant k_p , dm ³ /(mol · min)	— $57\,819 \pm 1.4\%$
Chain transfer reaction rate constant k_{tr} , dm ³ /(mol · min)	— $0.6642 \pm 1.4\%$
Molecular weight of PE M_v , g/mol	— $2\,544\,836 \pm 8.9\%$
Bulk density, g/dm ³	— 160.

CONCLUSIONS

Bimetallic magnesium support $MgCl_2(THF)_2/AlEt_2Cl$ applied to immobilized $TiCl_4$ gives a catalyst, which after reacting with triethylaluminum cocatalyst, forms an active catalyst system for ethylene polymerization. This catalyst system shows the presence of two kinds of the active sites at the beginning of the polymerization reaction: the unstable, low active classic sites and the very active sites on bimetallic support. Unstable active sites were eliminated from the catalyst system by means of the 1-pentene prepolymerization reaction. This permitted full characterization of this catalyst system to be elucidated, showing it to be very active and also stable ($n^* = const.$). High content of active sites (73%) allowed to conclude that content of unstable active sites deactivated in course of the prepolymerization reaction was very small.

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