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## Magnesium chloride in zirconocene catalysts used for polymerization of ethylene

### RAPID COMMUNICATION

**Summary** — The activity and stability of zirconocene catalysts immobilized on magnesium chloride modified with an organoaluminum compound  $AlR_3$  ( $R = Me$  or  $Et$ ) were studied in the polymerization of ethylene (Tables 1, 2). An original method was used to introduce a Lewis internal base into the magnesium support. Trace amounts of water present in magnesium chloride were assumed to react with the organoaluminum compound to produce on the surface of the chloride an alkylaluminumoxane  $[R_2AlOAlR_2]$  with the basic centers functioning as a Lewis internal base. The resulting support was used to immobilize a zirconocene compound which, when activated with MAO, became a very active complex catalyzing the polymerization of ethylene at a constant rate (284 kg PE/g Zr · h). Catalytically active centers were found to occur in the solvent solution only (and not on the solid support surface) at a concentration found to be nearly equal to that of water in the magnesium chloride. The ethylene polymerization kinetics studied with two catalysts systems prepared and the physical and mechanical property data measured for the resulting PE (Table 2) allowed to infer the highly stable zirconocene homogeneous catalyst system to have magnesium atom incorporated into the following structure  $[ClMgOAlR_2/Cp_2ZrCl_2]$ . The modifier  $AlR_3$  was found to affect the physical and mechanical properties of the resulting PE (Table 2).

**Key words:** zirconocene catalysts, magnesium chloride, polymerization of ethylene, polymer property data.

Zirconocene catalysts have been successfully applied on the magnesium support modified by an organoaluminum compound  $AlEt_2Cl$  or MAO [1, 2]. These catalysts revealed a high activity in ethylene polymerization proceeding with yields of 77–274 kg PE/(g Zr · h). The modification of the magnesium support by organoaluminum compounds has also been known from studies on heterogeneous titanium Ziegler–Natta catalysts [3, 4].

In our previous research [2–4], the complex of magnesium chloride modified by the organoaluminum compound having an internal donor, *viz.*, tetrahydrofuran (THF),  $MgCl_2(THF)_2/AlEt_2Cl$  or MAO, was used to synthesize the supported catalysts.

In the present investigation, the magnesium complex modified by organoaluminum compounds  $AlR_3$  ( $R = Me$  or  $Et$ ) (with no internal Lewis base) was applied to synthesize the zirconocene catalyst. The organoaluminum compounds reacting with a small amount of water contained in magnesium chloride produce, on its surface, an alkylaluminumoxane which performs the donor function. The complex of magnesium chloride with alkylaluminumoxane is also the reducing agent for the transition metal contained in the zirconocene compound ( $Cp_2ZrCl_2$ ).

### 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 4 Å molecular sieves. Toluene (POCH, Gliwice) was distilled over sodium metal and stored over 4 Å molecular sieves. Bis(cyclopentadienyl)zirconium dichloride  $Cp_2ZrCl_2$  (Fluka), methylaluminumoxane MAO (Witco's 10% solution in toluene), triethylaluminum  $AlEt_3$  (Schering), and  $AlMe_3$  (Schering) were used without further purification. Magnesium chloride (98%) (Fluka) dried for 2 hours at 393 K contained 0.38%  $H_2O$  (determined by thermal analysis TG).

#### Modification of $MgCl_2$ with an organoaluminum compound: $AlR_3$ ( $R = Me$ or $Et$ )

A solution of  $AlR_3$  in toluene (10–14 wt. %) was added dropwise for 1 hour at 273 K to a vigorously stirred suspension of magnesium chloride in toluene (6.3 wt. %) to achieve an Al/Mg mole ratio 4/1 in the mixture. After that, the mixture was heated for 5 hours at 331–333 K. Each operation was carried out in an argon atmosphere.

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## Synthesis of catalysts I and II

The suspension of the modified magnesium chloride  $[\text{MgCl}_2/\text{AlR}_3]$  in toluene was mixed with  $\text{Cp}_2\text{ZrCl}_2$  in a glass mill (capacity: 250 cm<sup>3</sup>, 20 balls, each 1 cm in diameter) for 24 hours at room temperature by using a mole ratio of  $\text{Mg}/\text{Zr} = 10/1$ .

## Polymerization

The polymerization reaction was carried out in a 1 dm<sup>3</sup> reactor equipped with a stirrer at 323 K in hexane at a constant pressure of ethylene equal to 0.5 MPa. The zirconium catalyst and a great excess of the cocatalyst MAO were charged into the reactor and then ethylene was introduced. The reaction was terminated by adding methanolic 5 wt. % HCl. The polymer was filtered off, washed with methanol, and dried.

## RESULTS AND DISCUSSION

The activity of two zirconocene catalysts supported on magnesium chloride was investigated in the polymerization reaction (Table 1), *viz.*,

I.  $[\text{MgCl}_2/\text{AlMe}_3/\text{Cp}_2\text{ZrCl}_2 + \text{MAO}]$

II.  $[\text{MgCl}_2/\text{AlEt}_3/\text{Cp}_2\text{ZrCl}_2 + \text{MAO}]$

Each catalyst was found to be very active in the ethylene polymerization (over 200 kg PE/g Zr · h) as compared with the metallocene catalyst systems containing  $\text{MgCl}_2$  [2, 5, 6].

The time course of the polymerization reaction (Fig. 1), confirmed the polymer yield to vary in direct relation to the reaction time. The polymerization reaction started in about 10 minutes — a fact suggesting these catalysts to need activation in the monomer environment. Apart from the activation period, the polymerization reaction rate was constant ( $R_p = 0.048 \text{ mol Et}/\text{dm}^3 \cdot \text{min}$  for catalyst I, and  $R_p = 0.014 \text{ mol Et}/\text{dm}^3 \cdot \text{min}$  for catalyst II). As can be seen, both catalysts are stable within the polymerization time.

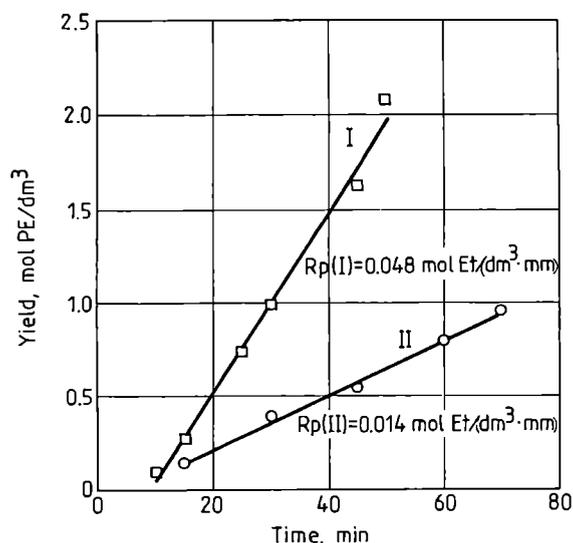


Fig. 1. The effect of polymerization time on the yield of polyethylene with the catalyst: I.  $[\text{MgCl}_2/\text{AlMe}_3/\text{Cp}_2\text{ZrCl}_2 + \text{MAO}]$ , II.  $[\text{MgCl}_2/\text{AlEt}_3/\text{Cp}_2\text{ZrCl}_2 + \text{MAO}]$  (for polymerization conditions see Table 1, items 1 and 2)

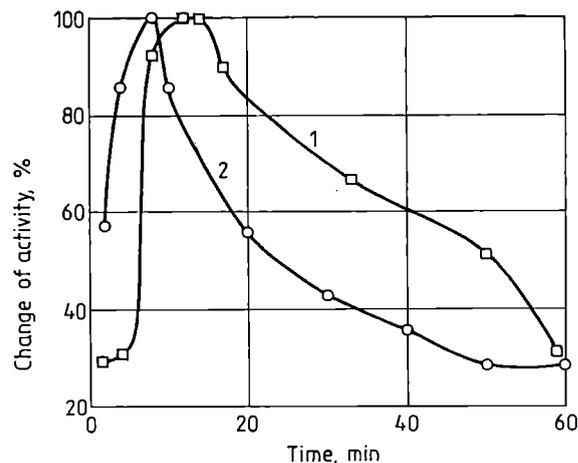


Fig. 2. The effect of polymerization time on the activity of homogeneous catalysts: 1 —  $[(\text{R-Cp})_2\text{ZrCl}_2]$ ,  $\text{R} = n\text{-Pr}$  [7]; 2 —  $[\text{Et}[\text{Ind}]_2\text{ZrCl}_2]$  [8]

It should be stressed that, in spite of their high activity, homogeneous metallocene catalysts are deactivated within the polymerization time [6–9]. The polymerization reaction rate on homogeneous metallocene catalysts decreases with the polymerization time (about 50% in 60 minutes) and reaches a maximum in several minutes of the polymerization reaction (Fig. 2) [7, 8]. On the contrary, for supported catalysts, and particularly with the magnesium support, the polymerization reaction rate is constant [2–5]. The stability of the present catalysts is characteristic for the supported systems.

Based on the kinetic model [10] as well as on the kinetic course of ethylene polymerization and on the average molecular weights of PE determined as a function of polymerization time, the concentration of active sites in catalyst I was determined to be  $n^* = 3.04 \cdot 10^7 \text{ mol}/\text{dm}^3$ . This value means about 15% of the transition metal had been used. For catalyst II, the share of active sites was slightly lower, about 13%. On the contrary, the share of active sites in a homogeneous metallocene catalyst is higher (50–100%) as compared with a magnesium supported catalyst (up to 10%) [11]. This value can also confirm our catalyst systems to be heterogeneous.

However, a very small bulk density of the polymer obtained (Table 1) is characteristic for the products obtained with nonsupported systems — a fact suggestive of the catalytic act to take place in the homogeneous phase. Therefore, a verifying polymerization of ethylene was carried out without the solid state of the catalyst II (Table 1, item 4).

Surprisingly, the activity of such a catalyst system was found to be almost identical with the activity of the systems involving the solid state, although the bulk densities of the polymers produced were slightly different (Table 1, items 3 and 4). Thus, in the systems investigated, active sites are unlikely to form on the magnesium chloride lattice.

By our assumption, the small amount of water included in magnesium chloride should give rise to a compound  $[\text{ClMgOAlR}_2]$  or  $[\text{Cl}_2\text{MgO}(\text{AlR}_2)_2]$  on the surface of  $\text{MgCl}_2$ . The former should be more stable than the latter. The latter can change into a typical alkylaluminumoxane  $\text{R}_2\text{AlOAlR}_2$  and  $\text{MgCl}_2$ . The donor included in

**Table 1.** Conditions and results of ethylene polymerization. Polymerization conditions: catalyst concn. =  $2 \cdot 10^{-6}$  mol/dm<sup>3</sup>, p = 0.5 MPa, T = 323 K, polymerization time = 60 min, polymerization medium, hexane

No.	Catalyst	Catalyst system	Mole ratio MAO/Zr	Activity kg PE/(g Zr · h)	Bulk density, g/dm <sup>3</sup>
1	I	[MgCl <sub>2</sub> /AlMe <sub>3</sub> /Cp <sub>2</sub> ZrCl <sub>2</sub> + MAO]	5000	284	59
2	II	[MgCl <sub>2</sub> /AlEt <sub>3</sub> /Cp <sub>2</sub> ZrCl <sub>2</sub> + MAO]	5000	212	73
3	II	[MgCl <sub>2</sub> /AlEt <sub>3</sub> /Cp <sub>2</sub> ZrCl <sub>2</sub> + MAO]	3000	124	58
4	II <sup>a)</sup>	[MgCl <sub>2</sub> /AlEt <sub>3</sub> /Cp <sub>2</sub> ZrCl <sub>2</sub> + MAO]	3000	123	33

<sup>a)</sup> Catalyst without the presence of the solid state.

**Table 2.** Mechanical and other physical properties of PE

Properties	PE obtained on catalyst I	PE obtained on catalyst II	PE obtained on catalyst I <sup>a)</sup>
Molecular weight (GPC), $M_w \cdot 10^{-3}$ , g/mol	110	200	180
Melting point, K	413.9	410.5	412.8
Tensile strength, MPa	20.5	39.2	41.5
Elongation at break	214	543	568
Melt flow index (load = 10 kg), g/10 min	0.25 at temp. 463 K	not flow at temp. 473 K	0.06 at temp. 473 K
Density at temp. 294.5 K, g/dm <sup>3</sup>	0.938	0.929	0.928

<sup>a)</sup> Catalyst without the presence of the solid state.

compounds is responsible for dilution in toluene and detaching from the crystal structure of magnesium chloride. Catalytic active sites were thus supposed to occur only in the hydrocarbon solution, and their concentration should equal the concentration of water in the case of the former and to be twice as high in the case of the latter compound. The concentration of water, calculated on the basis of the amount of water included in magnesium chloride, was equal to  $4.02 \cdot 10^{-7}$  mol H<sub>2</sub>O/dm<sup>3</sup>, close to the concentration of active sites ( $n^* = 3.04 \cdot 10^{-7}$  mol/dm<sup>3</sup>) calculated on the basis of the kinetic analysis of the ethylene polymerization.

The present results allow to assume the active sites of the investigated catalysts formed in the solvent [ClMgOAlR<sub>2</sub>/Cp<sub>2</sub>ZrCl<sub>2</sub>] upon activation with the co-catalyst MAO to reveal a high activity in the polymerization of ethylene. As can be seen from Fig. 1, the catalyst systems investigated are very stable, presumably on account of the magnesium chloride present in the structure of the active site.

The physical and mechanical properties of the polymer products prepared on the present catalyst systems are given in Table 2. The change of the structure of the magnesium chloride modifier (AlR<sub>3</sub>) has a considerable influence on the properties of PE. The catalyst I with AlMe<sub>3</sub> was the most active and the PE produced had a relatively low molecular weight (about 10<sup>5</sup>) and a melt-flow index of 0.25 g. The catalyst II with AlEt<sub>3</sub> had a slightly lower activity but the polymer revealed mechanical properties twice as good, doubtlessly because of its molecular weight twice as high. The properties of the PE prepared on catalyst II and on the catalyst without the solid state, were very similar (Table 2), except for the bulk density. This fact confirms that the catalytic act takes place in the homogeneous phase.

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