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Metallocene catalysts on complex magnesium support modified by organoaluminum compounds

Summary — A $MgCl_2(THF)_2$ support modified by organoaluminum chloride or MAO enabled us to obtain specially active zirconocene catalyst systems for ethylene polymerization. The zirconocene system on the bimetallic support was found to be the more active than that on the monometallic support. Two kinds of catalytic active sites were found to exist in the supported zirconocene catalyst: unstable active sites that become deactivated during the polymerization of ethylene, and very stable catalytic centers created in the olefin environment. The kinetic investigations on the ethylene polymerization allowed to suggest the reason underlying the creation of the stable active sites.

Key words: low-pressure polymerization of ethylene, supported zirconocene catalyst, catalytic activity, kinetic polymerization.

In recent years metallocene catalysts have been developed, arousing an economic interest as it became clear that they can compete with Ziegler—Natta catalysts in industrial processes. However, they are more active than Ziegler—Natta catalysts only as the homogeneous metallocene systems, a fact that has essentially restricted their use to industrial polymerizations in the solution. Modern polymerizations are solvent-free slurry (with liquid monomer) or gas-phase processes. To be used in these processes, metallocene catalysts have to be converted into heterogeneous catalysts. However, activity problems have appeared with the supported metallocene catalysts, because the heterogeneous catalysts are much less active than Ziegler—Natta systems. Most reported solid systems have exhibited dramatically lower activities as compared with the corresponding metallocenes in the solution [1—3]. Thus, the development of a heterogeneous catalyst, with metallocene as the active component supported on the surface of a solid carrier, is the point of extreme interest [4, 5].

At the Institute of Chemistry, University of Opole, heterogenization of metallocene catalytic systems has been studied. The complex of magnesium dichloride with a Lewis base [$MgCl_2(THF)_2$] has been used as a support for the catalyst system [6]. With this support a zirconocene catalyst system was prepared that was relatively highly active in ethylene polymerization (110 kg PE/g Zr · h). The magnesium complex support $MgCl_2(THF)_2$ was previously used in our investigations during which active and stable titanium and vanadium Ziegler—Natta catalysts were obtained [7—10].

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. Bis(cyclopentadienyl)zirconium dichloride, Cp_2ZrCl_2 (Fluka), methylaluminoxane (MAO) (Witco's 10% solution in toluene) and $AlEt_2Cl$ (Schering) were used without further purification. $MgCl_2(THF)_2$ was prepared at the Institute of Chemistry, University of Opole.

Catalyst preparation

The bimetallic support was prepared by milling solid $MgCl_2(THF)_2$ with $AlEt_2Cl$ or MAO in a glass mill (capacity: 250 cm^3, 20 balls each 1 cm in diameter) in toluene solution at room temperature for 1 h by using the reactants in the equimolar ratio. To prepare the zirconium catalyst the resulting suspension of the bimetallic support was milled with Cp_2ZrCl_2 at room temperature for 24 h by using a mole ratio of Mg/Zr = 10/1.

Polymerization

Polymerization was carried out at 50°C in a 1-dm^3 reactor equipped with a stirrer, in hexane, at a constant

Table 1. The influence of the catalyst concentration and Al/Zr mole ratio on the activity of three investigated catalysts

No.	Concentration of catalyst $n_k \cdot 10^5$ mol Zr/dm^3	MAO:Zr mole ratio	Catalyst activity, kg PE/(g Zr · h)		
			Catalyst "A" $MgCl_2(THF)_2/Cp_2ZrCl_2$ + MAO	Catalyst "B" $MgCl_2(THF)_2/AlEt_2Cl/$ $/Cp_2ZrCl_2$ + MAO	Catalyst "C" $MgCl_2(THF)_2$/MAO/ $/Cp_2ZrCl_2$ + MAO
1	3.5	1180	15.23	—	—
2	3.5	1757	18.42	—	—
3	2.5	1172	5.89	—	—
4	2.5	1652	12.34	—	—
5	2.5	2000	—	28.18	—
6	2.5	2460	23.06	—	—
7	1.0	2000	—	38.85	53.90
8	1.0	4000	—	—	99.40
9	1.0	6150	54.82	—	—
10	0.5	2000	—	—	43.75
11	0.5	3000	—	—	79.40
12	0.5	3500	—	—	80.90
13	0.5	4000	—	77.60	157.20
14	0.5	8200	72.75	—	—
15	0.5	12 300	109.81	—	—

pressure of ethylene equal to 0.5 MPa. The zirconium catalyst and MAO used as cocatalyst in great excess were charged into the reactor and then ethylene was introduced. The reaction was terminated by adding methanol containing 5% by wt. of HCl. The polymer was filtered off, washed with methanol, and dried.

RESULTS

The subject of present investigations is heterogeneous zirconocene catalysts supported on $MgCl_2(THF)_2$ modified with an organoaluminum compound. The zirconocene catalysts were supported on the bimetallic carrier. $MgCl_2(THF)_2$ was made to react with $Al(C_2H_5)_2Cl$ or MAO (methylaluminoxane) to yield two bimetallic carriers: $MgCl_2(THF)_2/AlEt_2Cl$ and $MgCl_2(THF)_2$/MAO.

Metallocene compound Cp_2ZrCl_2 was supported on these carriers to obtain the heterogeneous zirconocene catalyst. After reactions with MAO used as cocatalyst in great excess, the activity of these two supported zirconocene systems in ethylene polymerization was studied. Results and comparison with the activities of the zirconocene catalysts supported on a monometallic complex $MgCl_2(THF)_2$ [6] are presented in Table 1. Catalyst concentration and the MAO-to-zirconium mole ratio are seen to affect the activity of each of the three catalysts in the ethylene polymerization process. This process was carried out in hexane suspension. According to our expectation, the activity of the catalytic systems rose as the catalyst concentration [Zr] was decreased. Again, the activity rose as the MAO-to-zirconium mole ratio was increased. With the catalyst on the monometallic support ("A"), the highest activity was obtained by using a very great amount of MAO. For the system ("B") on the support modified with diethylaluminum chloride, the same results were obtained by using MAO in an excess one-half as large. The modification of the support with methylaluminoxane ("C") resulted in the most active catalytic system.

Table 2. The activity of catalysts "B" [$MgCl_2(THF)_2/AlEt_2Cl/$ $/Cp_2ZrCl$ + MAO] on the polymerization of ethylene (catalyst concentration, $5 \cdot 10^{-6}$ mol/dm^3; MAO:Zr = 4000)

Time min	Yield g PE/dm^3	Activity kg PE/g Zr	Bulk density g/dm^3	Molecular weight $\overline{M}_n$ of PE
20	11.86	26.00	71	—
30	14.43	31.60	73	142 800
45	14.71	32.25	72	158 200
50	21.61	47.38	71	162 400
60	35.40	77.61	70	168 000
70	49.21	107.89	68	173 000
80	63.00	138.13	72	174 400
90	76.82	168.43	64	178 000
120	96.28	211.09	72	—

Results (Table 2) show the heterogeneous metallocene catalyst "B" to produce polymers having a relatively small molecular weight and bulk density. Figure 1 describes the PE yield as a function of the reaction time for the catalysts "A" and "B". These data allowed to calculate the ethylene polymerization rate as a function of the reaction time (Fig. 2). At the beginning of the process the polymerization rate decreased and, after some time, it attained a constant value. With the catalyst "A", the constant polymerization rate (Rp_A = 0.031 mol Et/dm^3 · min) was much lower than that with the catalyst "B" (Rp_B = 0.049 mol Et/dm^3 · min) (Fig. 2). Analysis of Figures 1 and 2 shows the two catalyst systems to have two kinds of active sites: stable and unsta-

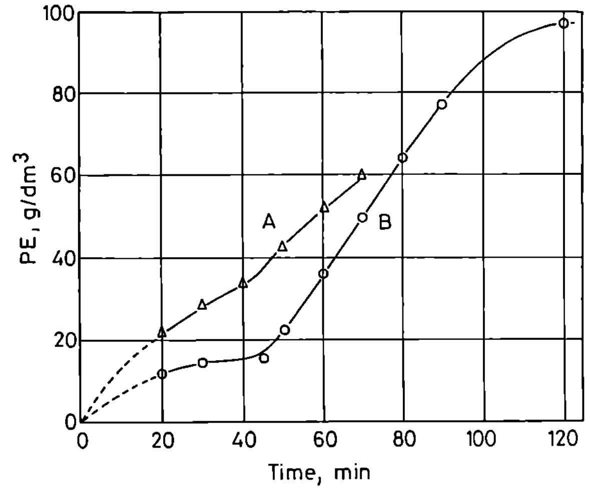

Fig. 1. Yield of PE as a function of polymerization time, [Zr] = 5 · 10^{-6}/dm^3: (A) catalyst on monometallic support [$MgCl_2(THF)_2$], mole ratio of MAO:Zr = 12 300; (B) catalyst on bimetallic support [$MgCl_2(THF)_2/AlEt_2Cl$], mole ratio of MAO:Zr = 4000

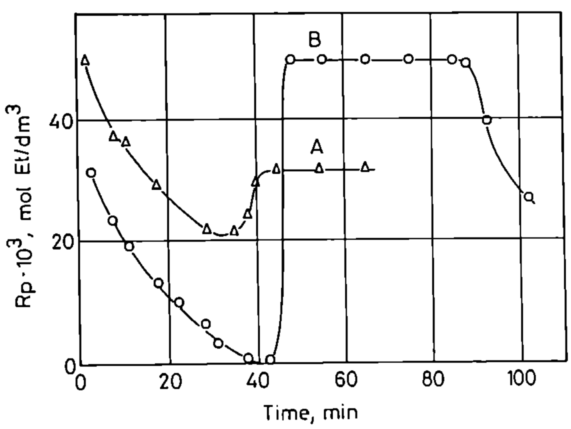

Fig. 2. Ethylene polymerization rate versus reaction time; for polymerization conditions see Fig. 1

ble. At the beginning, polymerization proceeds primarily on the unstable active sites, as confirmed by the decrease of the ethylene polymerization rate. With the catalyst "B" (on the bimetallic support), the polymerization rate fell almost to zero during the 40 minutes of the reaction. Hence, it can be concluded that there was a lack of stable active sites. After 40—45 minutes, the ethylene polymerization rate increased considerably to attain a value of 0.049 mol Et/dm^3 and remained uncharged during the next 50 minutes. The constant polymerization rate is undoubtedly the result of the constant concentration of the catalytic sites, which do not undergo deactivation, *i.e.* these are the stable sites. The decrease in the ethylene polymerization rate observed in 90 minutes is attributable to diffusion limitations caused through the PE powder in the reactor. This can be seen also by comparing the bulk density (g/dm^3) with the polymer yield (g PE/dm^3). The amount of the polymer obtained in 90 minutes is greater than the PE bulk density (Table 2).

The kinetic investigations on the range of the constant polymerization rate allowed us to evaluate the concentration of the stable active sites as well as the rate constant of the elementary reactions of ethylene polymerization over the catalyst "B" (Table 3). The concentration of the stable active sites was calculated by using the two kinetic models of polymerization proposed by Böhm [11] and Czaja [9]. The former assumes that, at any moment of ethylene polymerization, the reaction medium contains both the growing and the ready-built macromolecules. This assumption results in the following relationship:

Table 3. **Results of kinetic analysis**

Parameter	Catalyst "B": $MgCl_2(THF)_2$/ /$AlEt_2Cl$/ /Cp_2ZrCl_2 + MAO	Catalyst "A": $MgCl_2(THF)_2$/ /Cp_2ZrCl_2 + MAO
Ethylene polymerization rate on stable active sites, mol Et/dm^3 · min	0.0493	0.0310
Catalyst efficiency, n^*/n_k	0.77	0.49
k_p, propagation reaction rate constant, dm^3/mol · s	458	—
k_r the regeneration of active sites rate constant, dm^3/mol · s	0.069	—

$$PE/DP = n^* + 1/DP_\infty PE \qquad (1)$$

where: *PE — yield of polyethylene [mol Et/dm^3], DP — average polymerization degree of PE, DP_∞ — final average degree of polymerization of the product, n^* — concentration of active sites [mol/dm^3].*

With the PE = f(t) and DP = f(t) functions determined from the experimental values (yield of PE, molecular weight) for catalyst "B", equation (1) takes on the form:

$$PE/DP = 3.880 \cdot 10^{-6} + 1.5661 \cdot 10^{-4}\, PE \qquad (2)$$

The latter kinetic model [9] assumes that the rate of formation of the macromolecules is equal to the rate of the transfer reaction *i.e.* to the active site regeneration rate:

$$d(PE/DP)/dt = k_r \cdot n^* \cdot M \qquad (3)$$

For the stable active sites, the concentration n^* does not change during the polymerization of ethylene. Therefore, upon integration, equation (3) takes on the following form:

$$PE/DP = n^* + k_r \cdot M \cdot n^* \cdot t \qquad (4)$$

where: k_r — *transfer reaction rate constant [dm^3/mol · min], M — ethylene concentration [mol/dm^3].*

Thus, according to the experimental data, the function PE/DP = f(t) takes on the following form:

$$PE/DP = 3.875 \cdot 10^{-6} + 7.720 \cdot 10^{-6}\, t \qquad (5)$$

The regression ratio [*r*] for the equations (2) and (5) is 0.9998. The concentration of the active sites [n^*] determined on the basis of equations (2) and (5) is almost the same and equal to 3.88 · 10^{-6} mol/dm^3. Thus, the share of the active sites was calculated as $n^*/n_k = 0.77$ (n_k = catalyst concentration mol Zr/dm^3). The propagation rate constant [k_p] was calculated as:

$$Rp = k_p \cdot n^* \cdot M \qquad (6)$$

where: Rp — *polymerization rate [mol/dm^3 · min],* k_p — *propagation reaction rate constant [dm^3/mol · min].*

The comparison of equation (4) with (5) enabled us to determine the transfer reaction rate constant [k_r]. The final average polymerization degree of PE was calculated by using equations (1) and (2).

On the basis of our previous investigations [12] on the titanium catalysts supported on the monometallic [$MgCl_2(THF)_2$] and the bimetallic [$MgCl_2(THF)_2$/ /$Al(C_2H_5)_2Cl$] complexes we assumed that the elementary reaction rate constant of ethylene polymerization is not related to the modification of magnesium support by the organoaluminum compound. This assumption enabled us to determine the concentration of the stable active sites in the catalyst "A" by using equation (6) and the constant polymerization rate (Rp_A = 0.031 mol Et/dm^3 · min). According to our expectations, the share of the stable active sites catalyst "A" was much lower than that in catalyst "B" (Table 3).

DISCUSSION AND CONCLUSIONS

The $MgCl_2(THF)_2$ support modified with an organoaluminum or MAO enabled us to prepare a specially active zirconocene catalyst system for ethylene polymerization. The catalyst system on the bimetallic support is the more active than that on the monometallic support.

Two kinds of active sites were found to occur in the supported zirconocene catalyst:

— unstable active sites which are deactivated during polymerization of ethylene,

— very active and stable catalytic centers which are formed in the olefin environment.

With catalyst "B" prepared on the bimetallic support, the time formation of the stable and very active catalytic sites in the olefin environment is 40 to 45 minutes. Therefore, there is a need for shortening the formation time, *e.g.* by activation of the catalyst system in the olefin environment before polymerization of ethylene. For propylene polymerization such an activation of the catalyst is known as prepolymerization and it results in an active and stereoregular precatalyst [13]. It may be expected that modification of the zirconocene catalysts on the bimetallic support by olefin prepolymerization will minimize the time of formation of the active and stable sites and restrict the formation of the unstable active sites for the polymerization of ethylene.

The supported metallocene catalyst allows to prepare polyethylene with a relatively small molecular weight

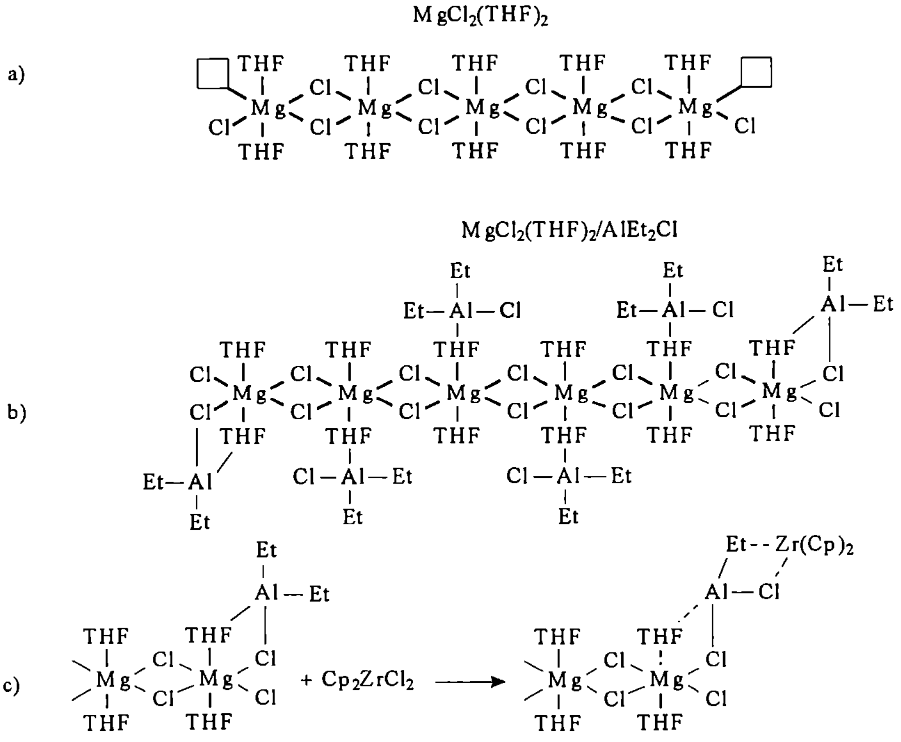

Fig. 3. The structure suggested for the magnesium support: (a) [$MgCl_2(THF)_2$] [8]; (b) proposed structure of bimetallic support [$MgCl_2(THF)_2/AlEt_2Cl$]; (c) proposed structure of zirconocene catalyst on the bimetallic support

and a very small bulk density. We expect that changing the kind and structure of the metallocene precursor will enable the properties of the polymer to be modified as is the case with homogeneous metallocene catalysts.

Our study has also contributed to the knowledge of the role of magnesium chloride and Lewis base in organometallic catalysts. The present results and analysis of literature data, allow to hypothesize on the reason for the formation of the two kinds of active sites. The bimetallic magnesium-aluminum complex used together with the Lewis base as a support for the metallocene as well as titanium precursor [12] gave the stable and highly active catalytic system for ethylene polymerization. The activity of this catalyst is superior to that offered by the catalyst on the monometallic support $MgCl_2(THF)_2$. Thus, the Lewis base plays an important role in the formation of the bimetallic support. This Lewis base is introduced into the system as a complex with magnesium dichloride. Its structure is presented in Fig. 3a [8]. The molecules contained in the complex split $MgCl_2$ agglomerates into small crystallites and prevent their reagglomeration. Thus, the role of THF is reduced to fill up all the coordination empty spaces in the magnesium dichloride structure, and also to form the bimetallic magnesium-aluminum complexes. The possibility of forming the bimetallic Mg-Al complexes in a Lewis base medium has already been reported by Karol [14] and Sobota [15].

However, the stable kind of these complexes will appear on empty coordination place. This can happen on terminal magnesium atoms in the linear structure of $MgCl_2(THF)_2$, as shown in Fig. 3b. The organoaluminum compound is strongly anchored to the structure of $MgCl_2$. The chloride atom of this compound is built into the $MgCl_2$ structure. Another kind of Mg-Al complex can be formed by THF — a bridge connection along the linear structure of $MgCl_2(THF)_2$. In this case, the molecule of the organoaluminum compound is very weakly anchored to $MgCl_2$. Therefore, during the reaction with transition compound, this bimetallic Mg-Al complex can be destroyed and form unstable active sites, which are not connected to the magnesium support. On the contrary, the organoaluminum compound of the stable Mg-Al complex forms the active organometallic site strongly connected to the support (Fig. 3c) and this active sites are very stable. This appears to be the reason for the formation of stable and active sites.

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