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Synthesis and activity of zirconocene catalysts supported on silica-type sol-gel carrier for ethylene polymerization

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Summary

Synthesis and activity of bis(cyclopentadienyl)zirconium dichloride catalyst supported on unconventional silica-type material obtained in sol-gel process and activated by organoaluminium co-catalyst were studied.

The effect of support modification conditions (thermal dehydration and/or modification by organoaluminium compound) and a type of co-catalyst on an activity of the catalytic system in ethylene polymerization and properties of resulting polymers were investigated and compared with results obtained earlier for vanadium catalysts supported on mentioned sol-gel carrier. The most appropriate method of the sol-gel silica-type support preparation is thermal pre-treating (200°C) followed by modification with $AlEt_2Cl$. Metallocene catalyst supported on such sol-gel product and activated by MAO appeared to be most active among studied systems.

Studied Cp_2ZrCl_2/MAO supported on silica-type sol-gel carrier allow to obtain polyethylene (at 50°C polymerization temperature) with yield up to $30 \cdot 10^6$ g/($mol_{Zr} \cdot h$), molecular weight below 300 000 and MWD=2-4.

Introduction

For over 30 years, organometallic catalysts for olefin polymerization have been obtained using various supports, from which $MgCl_2$ allows to receive most active ones. However there is aspiration to reduce of $MgCl_2$ because received products contain unprofitable chloride quantity. Most of all oxide supports as alumina or silica are used [1].

Searching for other, non-chloride support, we applied a new silica-type material obtained in sol-gel process. Silicate gels are most often synthesized by hydrolyzing monomeric, tetrafunctional alkoxide precursors employing a mineral acid or base as a catalyst. Hydrolysis and condensation reactions can be described by following equations (Fig 1):

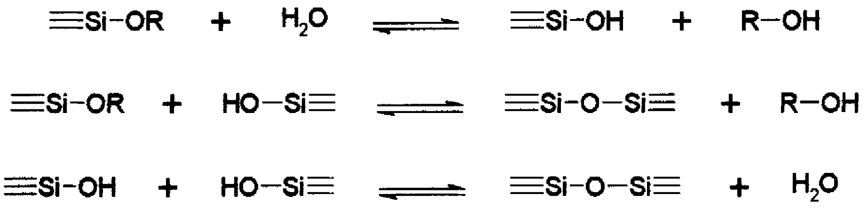

Fig 1. Hydrolysis and condensation of TEOS [2]

In this sol-gel process, depending on its conditions (molar ratio of reaction components, type of precursor, reaction pH and temperature), different products as bulk gels, films, fibers and powders can be obtained [2]. For application as organometallic catalyst support the most proper form of product is a sol-gel silica powder which we obtained employing hydrolysis and condensation of tetraethoxysilane (TEOS) catalyzed by ammonia [3].

It is known that surface properties of inorganic supports, predominantly oxides, influence the activity of supported catalyst and properties of polymer obtained. The morphology as well as the type, concentration and arrangement of ion sites over the oxide surface, inclusive of OH groups, can be changed by varying the conditions of their thermal pre-treating and by the chemical modification. Mentioned sol-gel silica powder, after annealing and modification by organoaluminium compound, was successfully used as a carrier for $VOCl_3/AlEt_2Cl$ catalyst [4,5]. Therefore it seems proper to estimate usefulness of this new carrier for heterogenization of high-active metallocene catalysts [6]. Because it should be stressed that homogeneous metallocene catalysts have to be heterogenized before application in modern gas-phase plant. Supported metallocene catalysts were first suggested by Sinn *et al.* [7] and Kaminsky *et al.* [8]. Many types of mentioned catalysts have been reported recently by Ribeiro *et al.* [9].

This report provides results from the study of the effect of calcination temperature and chemical modification by organoaluminium compound of the sol-gel silica powder as well as a type of co-catalyst on the activity of supported Cp_2ZrCl_2 system in slurry ethylene polymerization. Received results are compared with those obtained earlier for vanadium catalysts supported on mentioned sol-gel carrier [5].

Experimental

All operations, except for sol-gel support synthesis, were always performed under dry and oxygen-free argon.

Materials

Polymerization grade ethylene (Chemical Works "Blachownia" S.A.) and pure argon ("Praxair", K□dzierzyn-Ko□le, Poland) were purified by passing through a column of sodium metal supported on Al_2O_3. Toluene (POCh, Poland) was purified by distillation over sodium. Pure-grade hexane (ORLEN S.A., P□ock, Poland) was refined with sulfuric acid, dried with sodium hydroxide, rectified and then stored over 4Å molecular sieves. Tetraethoxysilane – TEOS (Fluka), Cp_2ZrCl_2 (Fluka), $AlEt_2Cl$ (Fluka), $AlEt_3$ (Fluka) and methylaluminoxane – MAO – (Witco) were used without further purification.

Synthesis of silica type sol-gel carrier and its modification

Silica-gel powder was produced in wet sol-gel process by hydrolysis and condensation of tetraethoxysilane (TEOS) in a mixture of water, ethyl alcohol and ammonia, which were used in following ratio [3]:

$$[\mathrm{TEOS}] : [C_2H_5OH] : [NH_3] : [H_2O] = 1 : 6 : 0.07 : 4.5$$

The final product was obtained by solvent evaporating from silica-gel suspension.
The sol-gel carrier was modified before supporting catalytic system. Two ways of modification were employed: thermal modification by annealing the support in the temperature from the range of 200–800°C for 3 hours in air atmosphere and then for 1 hour in argon or chemical modification by treating the support (previously calcined at 200°C) with $AlEt_2Cl$ or MAO solution.

Catalyst preparation

Supported catalysts were prepared by ball-milling of modified support with Cp_2ZrCl_2 precursor (0.5 mmol transition metal compound on 1 g of support) in toluene at room temperature for 24 hours. Then the precatalyst was activated by addition of organoaluminium co-catalyst.

Polymerization

The slurry polymerization of ethylene process was carried out in a 1.5 dm^3 Büchi glass-reactor equipped with a stirrer, in hexane, and under constant pressure of ethylene (0.5 MPa). Hexane (0.7 dm^3), cocatalyst and supported precatalyst were charged into the reactor and then ethylene was introduced. The reaction was terminated by addition of methanol containing 5 wt.% HCl. Obtained polymer was filtered off, washed with methanol and dried.

Measurements

Molecular weight and molecular weight distribution of investigated samples were determined by gel permeation chromatography (HT GPC Waters 150-C) at 142°C. Trichlorobenzene with stabilizer was used as a solvent.
Melting points and the degrees of crystallinity of polymers were measured by differential scanning calorimetry on TA Instruments 2010 DSC calorimeter at the heating rate 10 deg/min.

Results and discussion

Catalyst activity

The results presented in Table 1 reveal that sol-gel silica type powder used as a support of metallocene system leads to more active catalytic systems in ethylene polymerization according to vanadium counterparts. However it should be stressed that for vanadium catalysts typical organoaluminium compound ($AlEt_2Cl$) was applied as co-catalyst, whereas zirconocene catalytic systems were activated with methylaluminoxane (MAO).
The results also prove that increase of the calcination temperature of the sol-gel type support above 200°C caused some decrease of the activity of all catalysts studied (runs 1-2 and 3-5). Similar correlation between supports annealing temperature and catalyst activity for zirconocene system was obtained by Tait [10]. Cp_2ZrCl_2 catalyst immobilized on typical silica (MS 3040) calcined in 460°C offered over twice lower activity in comparison to system where temperature of 260°C was applied.

Table 1. Effect of thermal modification of sol-gel product on activity in ethylene polymerization of metallocene and vanadium catalysts.

run	support calcication temp. (°C)	transition metal comp.	co-catalyst	Al/M_t molar ratio	polym. Temp. (°C)	activity $kg_{PE}/(mol_{Mt} \cdot h)$
1	200	Cp_2ZrCl_2	MAO	2 000	50	6 900
2	800		MAO	2 000	50	4 000
3	200	$VOCl_3$	Et_2AlCl	167	45	1 100
4	500		Et_2AlCl	167	45	950
5	800		Et_2AlCl	125	45	850

Typical reactive surface functionalities of a oxide-type support are Brønsted acidic OH groups, Lewis basic oxide groups and Lewis acidic metal centers. The effect of the supports dehydration temperature on the activity of resulting catalysts is probably caused by differences in concentration of mentioned surface groups mainly hydroxyls (OH) and siloxanes (Si–O–Si).

It is known [2] that annealing of sol-gel materials up to about the temperature of 170°C eliminates from the gel structure rest of liquid reagents and physically adsorbed water, resulting in surface covered with hydroxyls, which are postulated to be vicinal, geminal or isolated (Fig 2). After that progressive removal of hydroxyls takes place. Heat treatment of silica gel at 170°C gaves a partially dehydroxylated silica as a result of removing vicinal OH groups through condensation reaction (Fig 2).

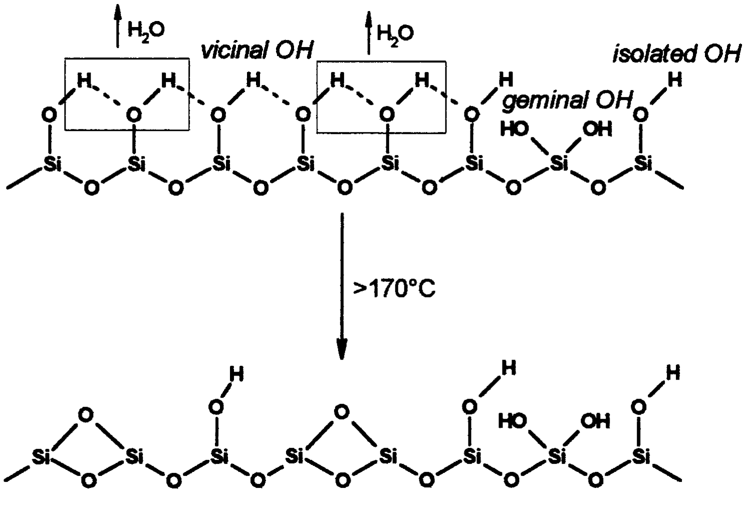

Fig 2. Dehydratation of silica type surface

In a range above 600°C, due to migration of individual hydroxyl groups further dehydratation is possible what results in almost fully dehydroxylated surface with remaining siloxane groups and not numerous geminal and isolated OHs [2].

Hydroxyls present on the support surface react with Cp_2ZrCl_2 and the reaction, dependently on the type of OH, may occur according to Fig 3.

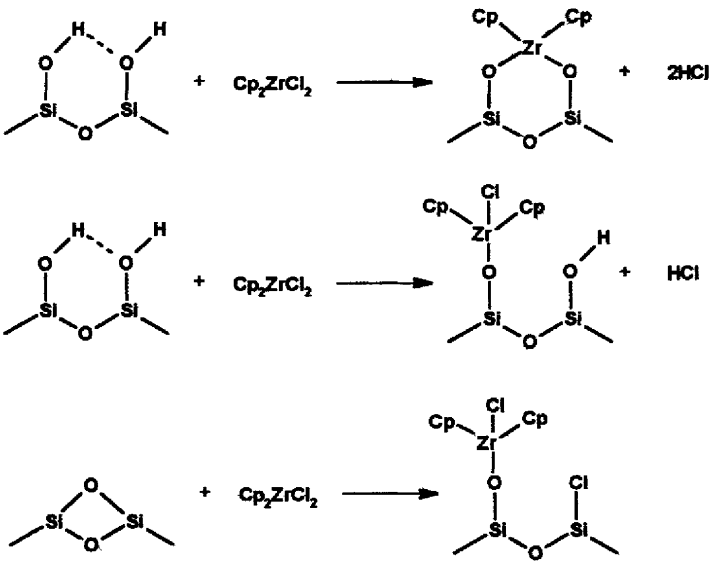

Fig 3. Reaction of Cp_2ZrCl_2 with silanol and siloxane groups

Received results of the influence of the supports calcination temperature on resulting catalyst activity obtained in this work indicate, that the support with large number of OH groups seems to be better than the support with fewer. It suggests that resulting zirconium active sites in the discussed systems should be attached mainly through the oxygen atom to the carrier surface.

One of the methods frequently employed in the process of supported metallocene catalysts preparation is adsorption of a transition metal compound on carrier modified in a reaction with organoaluminium compound [10-12]. Therefore on purpose to improve catalytic activity of systems studied, the chemical modification of the sol-gel silica-type powder with organoaluminium compounds was applied.

Our results presented in Table 2 indicate that utilization of MAO-modified sol-gel support allows to receive an active catalytic system, however with lower activity in comparison to appropriate catalyst supported on unmodified carrier (runs 6 and 1).

Results published by Soga [11] show, that pretreating SiO_2 with small amounts of MAO improves the metallocene catalyst activity and moreover allows to replace MAO (co-catalyst) with common alkylaluminiums. On the other hand there is a tendency to eliminate or limit MAO utilization in order to its undefined composition and high price.

However replacement of MAO as co-catalyst with $AlEt_2Cl$ or $AlEt_3$ in our catalytic system lead to activity lose (runs 7 and 8).

In further orders MAO as modifier was replaced by $AlEt_2Cl$, because the later one appeared to be profitable for earlier studied vanadium catalysts (runs 3 and 10) [5]. Also for zirconocene catalyst modification of sol-gel support by $AlEt_2Cl$ brought nearly double increase of activity (runs 1 and 9).

Utilization of $AlEt_2Cl$ as a supports modifier results in creation of superficial organoaluminium compounds, which are formed in reaction of $AlEt_2Cl$ with surface hydroxyl groups wherein the aluminium atom is fixed to the support through the oxygen. Replacing of surface OH groups by such superficial aluminium compounds eliminates a possibility of forming zirconium sites directly bounded with the support what seems to be profitable for catalysts activity.

Table 2. Effect of chemical modification of sol-gel product on activity in ethylene polymerization of metallocene and vanadium catalysts. Calcination temperature of supports – 200°C.

run	Support modificator	Transition metal comp.	co-catalyst	Al/M_t molar ratio	polym. Temp. (°C)	activity $kg_{PE}/(mol_{Mt} \cdot h)$
6	MAO	Cp_2ZrCl_2	MAO	2 000	50	5 000
7	MAO		$AlEt_3$	2 500	50	trace
8	MAO		$AlEt_2Cl$	2 500	50	trace
9	$AlEt_2Cl$		MAO	2 000	50	12 700
10	$AlEt_2Cl$	$VOCl_3$	$AlEt_2Cl$	500	45	1 850

Similar results were obtained in [13,14], where activity of titanium catalysts supported on magnesium carrier modified by $AlEt_2Cl$ appeared to be superior to that offered by the catalyst on unmodified support. These all results suggest that isolation of the transition metal atom from direct contact with supports surface enhances its utilization in creation of active sites.

Further polymerization studies were performed over [$sol\text{-}gel_{200°C}/AlEt_2Cl/Cp_2ZrCl_2+MAO$] – the most active catalyst among all systems studied.

The results of activity of this catalytic system in dependence on polymerization conditions are presented in Table 3. They show that with increase of MAO concentration in a polymerization feed an increase of catalytic activity was observed and that the activity of investigated catalyst in greater degree is dependent on quantities of added MAO than on Al/Zr molar ratio (runs 11-17).

Table 3. Results of ethylene polymerization over [$sol\text{-}gel_{200°C}/AlEt_2Cl/Cp_2ZrCl_2+MAO$] catalyst

run	polymerization time, (min)	c_{Zr} ($mmol/dm^3$)	C_{MAO} ($mmol/dm^3$)	Al/Zr molar ratio	polym. temp. (°C)	Activity $kg_{PE}/(mol_{Mt})$
11	30	0.01	6.67	2 000	50	6 350
12	30	0.005	3.33	2 000	50	3 800
13	30	0.005	6.67	4 000	50	6 900
14	15	0.005	13.33	8 000	50	9 700
15	30	0.0025	3.33	4 000	50	3 550
16	30	0.0025	6.67	8 000	50	5 700
17	30	0.0025	13.33	16 000	50	13 100
18	30	0.005	6.67	4 000	40	5 390
19	30	0.005	6.67	4 000	70	27 290

After that the studied catalyst gives quite good stability during the polymerization process (Fig 4) and shows also resistance on thermal deactivation (runs 18, 13, 19). It should be noticed, that increase of the polymerization temperature from 50 to 70°C allows to obtain more than triple growth of the polyethylene yield. Obtained data of polymerization rate in range 40–70°C (Fig 5) let to estimate the energy of activation of ethylene polymerization reaction, which equals 47.6 $kJ \cdot mol^{1}$.

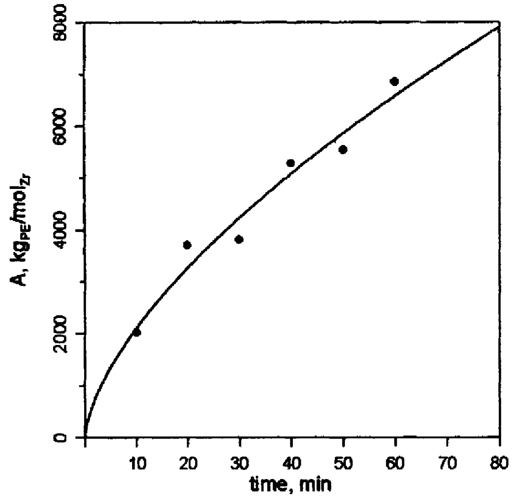

Fig 4. Catalyst activity versus polymerization time

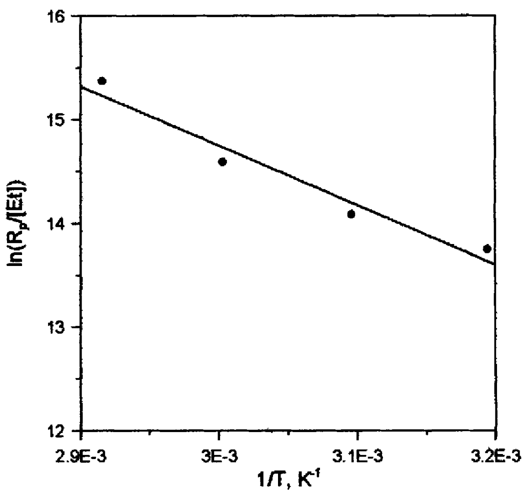

Fig 5. The effect of the temperature on polymerization rate according to Arrhenius eq.

Polymer properties

Table 3 shows selected properties of polymer products obtained with catalysts studied in comparison to properties of PE produced over vanadium one [5].

Table 3. Selected properties of polymers obtained over catalysts studied. M_v for PE obtained with vanadium system was determined by viscosity method.

Support	Precursor	Co-cat	M_n	M_v	M_w	MWD	Melting point °C	C_{DSC} %
sol-gel$_{200°C}$	Cp_2ZrCl_2	MAO	100 300	234 170	271 900	2.72	134.9	61.2
sol-gel$_{400°C}$		MAO	82 700	197 100	226 800	2.74	134.8	56.0
sol-gel$_{200°C}$/MAO		MAO	69 200	194 900	236 400	3.42	136.5	49.5
sol-gel$_{200°C}$/$AlEt_2Cl$		MAO	86 000	280 000	339 100	3.94	138.9	61.1
sol-gel$_{200°C}$	$VOCl_3$	$AlEt_2Cl$	-	$3.37 \cdot 10^6$	–	–	140.3	60.1
sol-gel$_{200°C}$/$AlEt_2Cl$		$AlEt_2Cl$	-	$2.86 \cdot 10^6$	–	–	143.0	64.3

It should be stressed that the molecular weights of the products obtained in polymerization of ethylene on the studied zirconocene catalysts are relatively low (M_v<300 000). Nevertheless, previous investigations into the corresponding vanadium catalysts resulted in polyethylene having very high molecular weights, about few million (Table 3) [5]. Differences in these results are confirmed by corresponding values of melting point and crystallinity. It indicates that in the case of the metallocene systems the ratio of chain transfer reaction rate to propagation reaction rate is much higher than for standard Ziegler-Natta catalysts.

Molecular weight distributions (MWD's) of the products obtained over zirconocene catalysts independently on support modification conditions are relatively narrow (MWD=2-4) and clearly narrower than for polymers obtained with typical heterogeneous, particularly supported, Ziegler-Natta systems. Narrow MWD is typical for homogeneous metallocene catalysts [15] what points on a uniformity of active sites. Thus the heterogenization of the metallocene catalyst on the sol-gel type support does not change considerably the homogeneous characteristics of the zirconium active sites. However chemical modification of the support results in some increase of catalyst heterogenity (higher MWD).

After all it should be noticed that Cp_2ZrCl_2 supported on sol-gel silica-type carrier modified by $AlEt_2Cl$ and activated by MAO yields polymer with the highest molecular weight, melting point and crystallinity among all studied zirconocene systems.

Conclusions

- Silica-gel powder obtained in wet sol-gel process, after thermal or/and chemical modification may be successfully used as a carrier of metallocene catalysts for ethylene polymerization.
- The most appropriate method of a sol-gel silica support preparation is dehydration at 200°C followed by chemical modification with organoaluminium compound mainly $AlEt_2Cl$.
- System [$\text{sol-gel}_{200°C}/AlEt_2Cl/Cp_2ZrCl_2+MAO$] appeared to be most active among all catalysts studied and it proves stable character during the polymerization process also in higher temperature.
- Products obtained over studied zirconocene catalysts on the contrary to vanadium counterparts show clearly lower molecular weights, narrower MWD's and lower melting points.

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