Ethylene polymerization with catalysts on the base of Zr-cenes and methylaluminoxanes synthesized on zeolite support

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Summary

The fixed aluminoxanes have been prepared on zeolite support Na-form of ZSM-5 (Si/Al=42) in reaction of partial hydrolysis of trimethylaluminium (TMA) with inside zeolite water. It was shown that aluminoxanes synthesized on zeolite surface form the heterogenized complexes with $Cp_2 ZrCl_2$ and $Et[Ind]_2 ZrCl_2$ which are active in ethylene polymerization without addition of other aluminiumorganic cocatalyst for a long time. The activation energy of ethylene polymerization in the presence of $ZSM-5(H_2O)/TMA$ - $Et[Ind]_2 ZrCl_2$ is equal to 32 kJ/mol. Molecular weight and melting point of polyethylene obtained with such zeolite supported Zr-cene catalysts are higher than those of polyethylene formed with appropriate homogeneous metallocene systems.

Introduction

Nowadays the actual problem of immobilization of soluble metallocene catalysts on solid supports is solved by many investigators by the several ways [1-7]. The main among them are: direct adsorption of the metallocene compound on inorganic supports: SiO_2, Al_2O_3, zeolite, $MgCl_2$, etc.; adsorption of the metallocene compound on support modified by AlR_3, MAO or other compounds; adsorption of the complexes of metallocene with MAO on silica or other carriers. All these methods require the introduction of the free MAO (or AlR_3) to supported catalyst for their activation in olefin polymerization.

Ealier we developed the method of metalorganic catalysts preparation on the surface of hydrated supports [8]. According to this method fixed alkylaluminoxanes are formed

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in the reaction of partial hydrolysis of aluminiumalkyl with the surface or inside support water and are used as cocatalyst for the ethylene polymerization without addition of other aluminiumorganic cocatalysts (AOC). The formation of alkylaluminoxanes in the system support(H_2O)/AOC was proved by the IR- spectroscopy investigation of the products of reaction of $AlEt_2Cl$ with water adsorbed on the KBr crystals [9,10]. Then it was confirmed by CP MAC^{13}C NMR investigation of the system $SiO_2(H_2O)$/TMA [7]. The aluminiumorganic compounds formed are predominantly bounded to the surface. According to the data of element analysis, Al content in the solution does not exceed 4-5wt % from the total quantity of Al introduced into reaction zone. The fixed AOC does not leach completely into solution even in the presence of the strong electron donors, for example, Et_3N.

The purpose of this work is to prepare the metallocene supported catalysts on the base of fixed MAO as the product of TMA partial hydrolysis with zeolite water by our method [8] and Cp_2ZrCl_2, $Et[Ind]_2ZrCl_2$. The ethylene polymerization on ZSM-5(H_2O)/TMA-Cp_2ZrCl_2 and ZSM-5(H_2O)/TMA-$Et[Ind]_2ZrCl_2$ systems was investigated and the properties of polyethylene obtained with these zeolite supported Zr-cene catalysts and appropriate homogeneous systems were compared.

Experimental

Materials

Na-form of ZSM-5 had the next characteristics: Si/Al=42, total volume of pores was equal to 0,287 cm^3/g, external surface (on benzene) - to 40 m^2/g, the inside water content - to 8,9 wt.% . Components of catalysts: Cp_2ZrCl_2 and $Et[Ind]_2$ $ZrCl_2$ were used as received from Aldrich C^{o}. TMA (from GNIIHTEOS, Moscow) and MAO (10 wt% in toluene solution, from Aldrich C^{o}) were used without further purification. TMA contained 37,2 wt.% of Al and 60,6 wt.% of Me. Toluene (from Aldrich C^{o}) was used as a solvent. Ethylene was of polymerization-grade purity.

Preparation of supported catalysts

The preparation of zeolite supported catalysts involved two steps: the preparation of the methylaluminoxanes anhored to zeolite by partial hydrolysis of TMA with inside zeolite water and the formation of heterogenized complexes from zirconocene and fixed

alkylaluminoxanes. The synthesis of fixed methylaluminoxanes and the preparation of zeolite supported Zr-cene catalysts were realized in 0,4 1 glass reactor equipped with stirrer and water jacket for thermostating. The reactor was evacuated and then filled in argon. Uncalcinated zeolite (1,3 g) contained 6.4 mmol of inside water was introduced into reactor. After the removal of argon from the reactor zeolite was suspended in 30 cm^3 of toluene. TMA (1.7 ml of 43 wt.% solution of TMA in toluene) was added dropwise to uncalcinated zeolite over an hour. The reaction of TMA with the zeolite water was carried out at 22 °C and intensive stirring of components. The end of the reaction of partial hydrolysis of TMA by the zeolite water was determined by the completion of the gaseous products (methane) evolution. After removal of methane from reaction zone 30 cm^3 of toluene solution of the zirconocene (Cp_2ZrCl_2 or $Et[Ind]_2 ZrCl_2$) was added. The quantity of Cp_2ZrCl_2 used for formation of catalytic complexes was varied from $2,5.10^{-6}$ moles to 40.10^{-6} moles, the quantity of $Et[Ind]_2 ZrCl_2$ - from $1,9.10^{-6}$ to 3.10^{-6} moles. Molar ratio of Al/Zr was changed from 4620 to 140 in the case of the system with Cp_2ZrCl_2 and from 4300 to 2440 - in the system with $Et[Ind]_2ZrCl_2$.

Polymerization of ethylene

Slurry ethylene polymerization was carried out in the same reactor where the catalytic complex has been prepared. The ethylene was introduced into the system immediately after Zr-cene addition. The ethylene pressure in reaction zone and polymerization temperature were held constant.

Characteristics of polyethylene

The molecular- weight characteristics of PE samples were measured by GPC (Waters, 150-C) in ortho-dichlorobenzene at 140° C. The PE melting point (T_m) was determined on a Dupont differential scanning calorimeter (DSC 910), with a heating rate of 10 K· min^{-1} from 295 to 425 K.

Results and discussion

The peculiarity of the zeolites is a very high mobility of the inside zeolite water. In contrast to the structure water of the other high hydrated supports such as aluminium hydroxide and kaolin the zeolite water is completely removed by the heating up to 800 - 1000 °C without the zeolite structure destruction and can be reabsorbed. It was shown

Table1.The consumption of AOC in dehydration of supports and the yield of RH.

Run	Support	H_2O in support, wt.%	AOC	AOC cosumption, mmol/g	RH	Yield of RH, mmol/g
1	Uncalcinated zeolite	8,9	$AlMe_3$	5,8	CH_4	6
2	Zeolite heated at 300^0C	5,4	$AlMe_3$	2,2	CH_4	2,25
3	Uncalcinated kaolin	13,8	$AlEt_2Cl$	0,1	C_2H_6	0,1
4	Uncalcinated $Al(OH)_3$	36,4	$AlEt_2Cl$	0,08	C_2H_6	0,08

that in the case of zeolite alyminiumalkyls react both with water adsorbed on the external surface of zeolite and with water from its chanels. As it is seen from the Table 1 data the consumption of AOC in dehydration process of zeolites as well as the gase (RH) evolution accompained this process are markedly higher (Tab. 1, runs 1,2) than in chemical dehydration of other inorganic supports by AOC (Tab. 1, runs 3,4).

We compared the sorption properties of zeolite (ZSM-5, previously heated in vacuo at 300 °C) with respect to TMA and water. According to the isotherms of adsorption obtained gaseous TMA (Fig. 1, curve 3) does not penetrate into the micropores of zeolite contrary to water (Fig. 1, curves 1,2). On the base of these sorption data we proposed that the fixed methylaluminoxanes (from TMA and zeolite water) and the Zr-cene complexes with fixed methylaluminoxanes can not be formed inside of the zeolite structure. Their formation proceeds in the secondary porous of zeolite structure and on its surface.

The high content of inside zeolite water (about 9 wt.%) and its mobility permit to form aluminoxanes on the zeolite surface in the amount enough for activation of Zr-cene component of catalyst. The ZSM-5(H_2O)/TMA-Cp_2ZrCl_2 (Fig.2) and ZSM-5(H_2O)/TMA-Et[Ind]$_2$ $ZrCl_2$ (Fig.3) systems are active in the ethylene polymerization without an addition of other cocatalysts for a long time (more than 100 hours). They give up to 1200 kgPE/molZr bar h (Tab.2, run 9).

By this means the investigated zeolite supported Zr-cene catalysts are significantly different from known catalysts [11] obtained by adsorption of zirconium compound on calcinated and treated by MAO zeolite. These zeolite/MAO/Cp_2ZrCl_2 catalysts [11] are inactive in ethylene polymerization. They are activated only by addition of free MAO into the reaction zone [11-13].
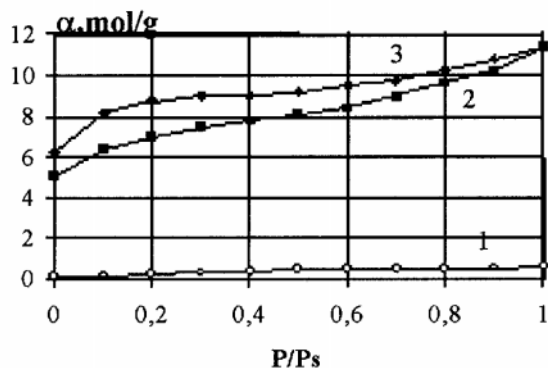

Fig.1. Isotherms of adsorption of $AlMe_3$ (1), adsorption (2) and desorption (3) of H_2O for zeolite heated in vacuo at $300^0 C$.
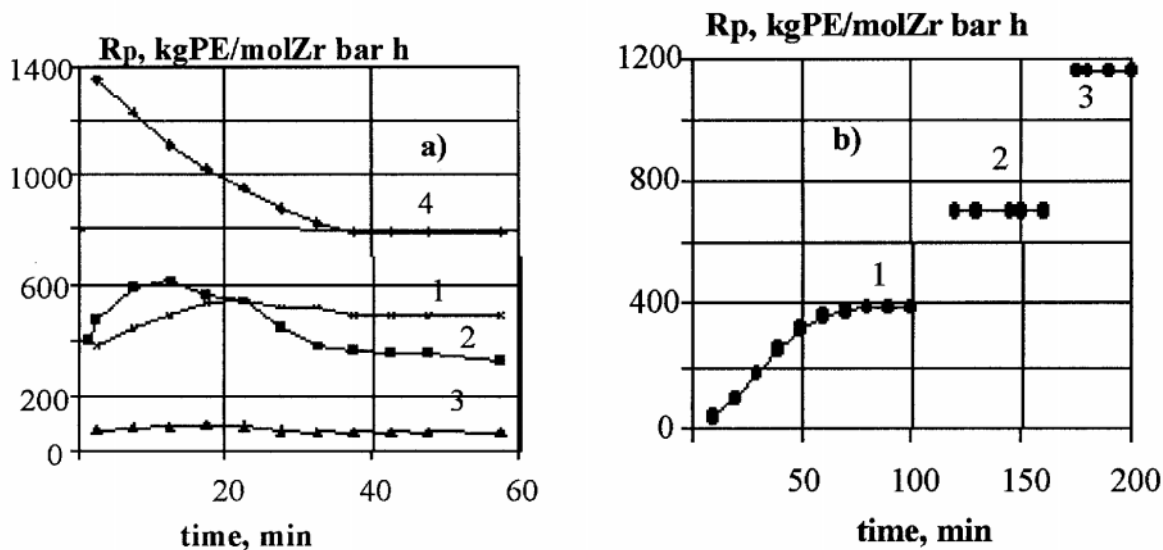

Fig.2. Rate - time profiles for ethylene polymerization with zeolite supported Zr-cene catalysts on the base of $Cp_2 ZrCl_2$ (a) and $Et[Ind]_2ZrCl_2$ (b).

a) ZSM-5(H_2O)/$AlMe_3$ -Cp_2ZrCl_2 (1,2,3), Cp_2ZrCl_2 - MAO (4); toluene;

0,46 bar; $34^0 C$; Zr, wt.%: 0,024 (1), 0,028 (2), 0,16 (3); [Zr] x 10^5, mol/l: 14 (4);

[AOC] x 10^3, mol/l: 68(1), 60 (2), 90 (3). 70 (4).

b) ZSM-5(H_2O)/$AlMe_3$ - $Et[Ind]_2ZrCl_2$;

toluene; 0,23 bar; 0,012 wt.% Zr; [Al]/[Zr]=4300; temperature,^{0}C: 34 (1), 50 (2), 70 (3).

Table 2 Ethylene polymerization with zeolite supported catalysts on the base of Cp_2ZrCl_2 and $Et[Ind]_2ZrCl_2$.

Run	Catalyst	Zr, wt.%	[Al]/[Zr]	t, °C	$P_{C_2H_4}$, bar	Activity, kgPE/molZr bar h	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.p., °C
1	ZSM-5(H$_2$O)/AlMe$_3$/Cp$_2$ZrCl$_2$	0,007	4620	34	0,46	80	202750	22	133,5
2	ZSM-5(H$_2$O)/AlMe$_3$/Cp$_2$ZrCl$_2$	0,024	1650	34	0,46	475	273810	10	132,5
3	ZSM-5(H$_2$O)/AlMe$_3$/Cp$_2$ZrCl$_2$	0,028	1090	34	0,46	460	280620	4,8	135
4	ZSM-5(H$_2$O)/AlMe$_3$/Cp$_2$ZrCl$_2$	0,300	140	34	0,46	80	n.d.	n.d.	n.d.
5	ZSM-5(H$_2$O)/AlMe$_3$/Cp$_2$ZrCl$_2$+ MAO	0,160	320[a]	34	0,23	500	52900	18	123,5
6	Cp$_2$ZrCl$_2$ + MAO[b]	0,140[b]	470	34	0,46	1000	133750	4,8	127
7	ZSM-5(H$_2$O)/AlMe$_3$/Et[Ind]$_2$ZrCl$_2$	0,012	4300	34	0,46	390	n.d.	n.d.	n.d.
8	ZSM-5(H$_2$O)/AlMe$_3$/Et[Ind]$_2$ZrCl$_2$	0,012	4300	50	0,40	700	n.d.	n.d.	n.d.
9	ZSM-5(H$_2$O)/AlMe$_3$/Et[Ind]$_2$ZrCl$_2$	0,012	4300	72	0,35	1165	n.d.	n.d.	n.d.
10	ZSM-5(H$_2$O)/AlMe$_3$/Et[Ind]$_2$ZrCl$_2$	0,018	4400	75	0,35	1200	173370	4	125
11	Et[Ind]$_2$ZrCl$_2$ + MAO[b]	0,028[b]	3200	75	0,35	4300	42000	2,5	125

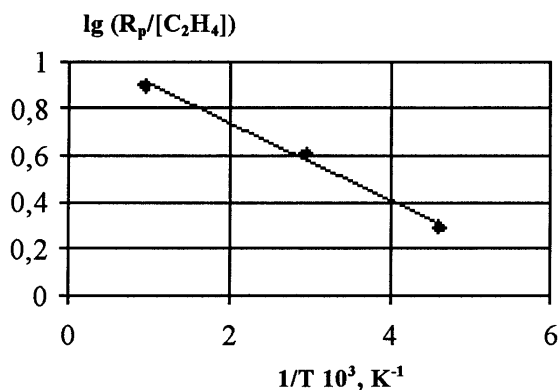a) Al:Zr = AlMe$_3$:Zr+MAO:Zr=160+160; b) homogeneous catalyst, [Zr], mmol/l,

Fig.3. $\lg(R_p/[C_2H_4])$ vs. $1/T$ with ZSM-5(H_2O)/AlMe$_3$ -Et[Ind]$_2$ZrCl$_2$ catalyst.

We investigated the influence of temperature on ethylene polymerization with ZSM-5(H_2O)/TMA-Et[Ind]$_2$ZrCl$_2$ catalyst and established that the rate of ethylene polymerization with this zeolite supported catalyst increases with increasing of temperature in the range of 34-73°C (Fig.3). The energy of activation of ethylene polymerization is equal to 32 kJ/mol (Fig.4). At the same time it is known that the rate of ethylene polymerization in the presence of homogeneous Zr-cene systems reaches a maximum values in the range of 45 - 50 ° C and decreases with a further increase of temperature [14].

The properties of polyethylene obtained with zeolite supported Zr-cene catalyst are presented in the Table 2. It is seen that the molecular weight and the melting point of polyethylene formed with ZSM-5(H_2O)/AlMe$_3$-Cp$_2$ZrCl$_2$ catalyst are higher (Tab.2, runs 1-3) than those of polyethylene obtained with homogeneous Cp$_2$ZrCl$_2$ - MAO catalyst (Tab.2, run 6). The tendency for an increase of molecular weight and the melting point of polyolefins in the case of catalyst immobilization on the support is a typical for metallocomplex catalysis. The addition of MAO to ZSM-5(H_2O)/AlMe$_3$-Cp$_2$ZrCl$_2$ catalyst increases its activity but decreases the molecular weight and the melting point of polyethylene formed (Tab.2, run 5). It is possible that the part of active centeres of zeolite supported catalyst transfer to solution from the surface after introduction a free MAO into the reaction zone.

Conclusion

The use of the heterogenized Zr-cene catalysts on the base of fixed aluminoxanes as a products of partial hydrolysis of AOC with inside zeolite water allows to replace

MAO by TMA and exclude the addition of the free MAO for formation of the zeolite supported Zr-cene complexes. We suppose that the synthesis of MAO directly on the zeolite support and the absence of free MAO may be one of the way of the reduction of supported Zr-cene catalyst leaching. In this case the appearance of homogeneous active centres in reaction zone has been made less possible. The positive temperature coefficiency of polymerization rate as well as the increase of molecular weight and melting point of PE obtained with the zeolite supported Zr-cene catalyst developed in this work compared to PE produced by homogeneous Zr-cene system confirms this view.

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