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Partially Hydrolyzed Alkylaluminums as the Active Heterogenized Components of Metallocene Catalysts

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Abstract—The heterogenized reaction products of the partial hydrolysis of the organoaluminum compounds $AlMe_3$ and $Al(i\text{-}Bu)_3$ with water as a constituent of highly hydrated supports, zeolite (ZSM-5–H_2O) and montmorillonite (MMT–H_2O), have been synthesized. The thermal degradation of the resulting heterogenized methylalumoxane compound and methylalumoxane (MAO) in a solid state is studied by temperature-programmed desorption with the mass-spectrometric analysis of liberated gaseous products, and the structural identity of the above compounds is found. Alkylalumoxanes prepared immediately on the surface of a support form heterogenized complexes with the metallocenes Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$. These heterogenized complexes exhibit high activity in the reactions of ethylene and propylene polymerization. For this reason, MAO can be replaced by $AlMe_3$ or $Al(i\text{-}Bu)_3$ and the additional introduction of MAO or another alkylaluminum for zirconocene activation is unnecessary. It has been found that, upon the immobilization of commercial MAO on dehydrated SiO_2, the MAO molecule loses a portion of its most reactive methyl groups and, as a result of this, becomes incapable of activating metallocenes.

INTRODUCTION

The pretreatment of a dehydrated support (usually, SiO_2) with methylalumoxane (MAO) followed by the addition of a metallocene is the most frequently used procedure for the heterogenization of homogeneous zirconocene catalysts for olefin polymerization [1–12]. However, as a rule, surface-immobilized MAO becomes incapable of activating the metallocene and the resulting SiO_2/MAO/metalocene catalyst is inactive in the process of polymerization. The addition of MAO or another organoaluminum compound from the external to the solution is required for the activation of this catalyst.

Although a great number of publications are available, the nature of interactions in the SiO_2/MAO and SiO_2/MAO/metallocene systems is not fully understood. The problem is complicated by the fact that commercial oligimeric MAO, which is used for metallocene activation, is a complex product; it contains about 30% $AlMe_3$, which cannot be completely removed from MAO by evacuation. There are different opinions concerning which particular component, MAO itself or its $AlMe_3$ constituent, reacts with surface OH groups in the treatment of SiO_2 with MAO [13–15].

A recently developed method for metallocene heterogenization consists in the preparation of the partial hydrolysis products of alkylaluminums (alkylalumoxanes) immediately on the surface of supports by the reaction of constitution water with AlR_3 followed by supporting a metallocene [16–24]. An active cocatalyst for metallocenes was prepared for the first time in this manner [16] by the treatment of organic supports (starch, lignin, etc.) with trimethylaluminum. Previously [25–27], we proposed a method for the preparation of alkylalumoxanes immobilized on support surfaces by the partial hydrolysis of alkylaluminums with the constitution water of inorganic supports (kaolin, aluminum trihydrate, etc.). The formation of alkylalumoxanes on the support surfaces and the participation of alkylalumoxanes in the alkylation reactions of transition metal compounds were demonstrated using IR spectroscopy [26, 27].

The current applications of this method for metallocene heterogenization on hydrated supports, such as SiO_2, zeolites, and montmorillonite (MMT), resulted in the preparation of a number of highly active catalysts for ethylene and propylene polymerization. In some cases, these catalysts were highly competitive with homogeneous analogs in terms of activity [17–24].

In contrast to the SiO_2/MAO system prepared by supporting MAO from a solution in toluene onto the surface of dehydrated SiO_2, the partial hydrolysis products of AlR_3 (alkylalumoxanes) synthesized immediately on the support form a complex with a metallocene. This complex exhibits activity in polymerization reactions without the addition of external MAO or another organoaluminum compound. Thus, catalysts of this kind do not require the use of commercial MAO.

In this work, we studied the structures of organoaluminum components in the SiO_2/MAO and support(H_2O)/AlR_3 systems in a comparison with the

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structure of commercial MAO in a solid state in order to find reasons for the above difference. For this purpose, we used mass-spectrometric analysis of the products of temperature-programmed desorption (TPD–MS). In this work, we also report the results of a study of ethylene and propylene polymerization on catalysts prepared on the surfaces of hydrated supports (ZSM-5 zeolite and MMT) by the interaction of the constitution water of these supports with $AlMe_3$ or $Al(i\text{-}Bu)_3$ (ZSM-5$(H_2O)/AlR_3$ and MMT$(H_2O)/AlR_3$ systems) followed by the addition of the zirconocene Cp_2ZrCl_2 or $Et(Ind)_2ZrCl_2$.

EXPERIMENTAL

Materials. In this study, Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$ metallocenes, polymethylalumoxane as a 10% solution in toluene, $AlMe_3$ as a 2 M solution in toluene, and $Al(i\text{-}Bu)_3$ as a 1 M solution in toluene (all from Aldrich) were used. Spectroscopically pure toluene, which was kept with molecular sieves 5 Å and distilled from $LiAlH_4$ in an atmosphere of argon, was used as a solvent. Ethylene and propylene were of polymerization grade. All of the operations of catalyst preparation were performed in a vacuum or in argon, which was passed through columns with a Ni–Cr catalyst and molecular sieves 5 Å. The supports were the Na form of ZSM-5 zeolite and MMT (Cloisite^{R}Na$^+$) with the following characteristics: a SiO_2/Al_2O_3 ratio of 24, a constitution water content of 8.9 wt %, a total pore volume of 0.287 cm^3/g, and an outer surface area of 40 m^2/g (benzene) for the zeolite and a constitution water content of 9.6 wt %, an average particle size of 8 μm, and a cation-exchange capacity of 92.6 mg-equiv per 100 g for MMT.

Preparation of MAO immobilized on the support surface. To obtain a surface-immobilized alkylalumoxane, we performed the partial hydrolysis of $AlMe_3$ or $Al(i\text{-}Bu)_3$ by the constitutional water of the support. For this purpose, a suspension of the support in toluene was treated with a toluene solution of AlR_3 under vigorous stirring at 22°C. The reaction was performed using two procedures described below. The resulting ZSM-5$(H_2O)/AlR_3$ and MMT$(H_2O)/AlR_3$ systems were treated with the solutions of Cr_2ZrCl_2 or $Et(Ind)_2ZrCl_2$ in toluene; thereafter, the catalysts were used in polymerization.

The MMT$(H_2O)/AlMe_3$ samples for TPD–MS studies were dried in a vacuum at 22°C.

In addition, a sample (SiO_2/MAO) with commercial MAO supported onto the surface of dehydrated SiO_2 was prepared. For this purpose, SiO_2 heated at 300°C in a vacuum was treated with an MAO solution in toluene and vacuum dried at 22°C. This sample, as well as solid MAO, which was prepared by the evacuation of a toluene solution of commercial MAO at 22°C, was also studied by TPD–MS.

TPD–MS studies. The TPD–MS analysis [28, 29] of the samples of solid MAO, MMT$(H_2O)/AlMe_3$, and SiO_2/MAO was performed as follows: A sample was placed in a special cell, which was directly connected to the mass spectrometer through a heated admission system. The sample was pumped and then heated from room temperature to 500°C at a constant rate of 10 K/min. In this case, the desorption products were continuously analyzed on the mass spectrometer, which detected ions with m/z from 10 to 300.

Ethylene and propylene polymerization. The polymerization of olefins was performed in a glass jacketed reactor filled with toluene and equipped with an electromagnetic stirrer. In the course of experiments, the monomer pressure and the temperature were maintained constant. The experimental procedure was described in greater detail elsewhere [20]. To stop polymerization, a 5% HCl solution in ethanol was added to the reactor. The resulting polymer products were filtered off, washed with ethanol, and dried in a vacuum at 60°C.

Characterization of polymer products. The molecular-weight characteristics of polymers were determined by gel permeation chromatography (GPC) on a GPC Waters 150C instrument in *ortho*-dichlorobenzene at 140°C. Melting points were measured using a Dupont DSC 910 differential scanning calorimeter at a heating rate of 20 K/min.

RESULTS AND DISCUSSION

A specific feature of the zeolite and MMT used as supports is a considerable concentration of constitution water. Almost all surface water and water in the channels and interlayer spaces of these supports is capable of reacting with alkylaluminums.

The alkylalumoxane amount formed on the surface depends on the concentration of constitutional water, and it can be regulated by partial predrying of the support (Table 1).

The nature of the hydrated support and the procedure of its treatment with an alkylaluminum (the order and rate of component mixing) affect the interaction of the alkylaluminum with support water. In this study, we used two procedures for the treatment of supports with AlR_3.

Procedure 1 consisted in that an AlR_3 solution was added in drops to a support suspension in toluene. In this case, hydrolysis occurred under conditions of an excess of support water with respect to the alkylaluminum ($[H_2O] : [AlR_3] > 1$). In the course of the reaction, gaseous products were released. The supply of AlR_3 was stopped when this release terminated. The alkylaluminum amount consumed in the dehydration of the

Table 1. Consumption of AlR_3 and the yields of gaseous products in the interaction of AlR_3 with support water

R	Support treatment procedure	Support	Water content of the support, mmol/g	Consumption of AlR_3, mmol/g	Yield of RH, mmol/g	$[RH]/[AlR_3]$, mol/mol
CH_3	1	Zeolite	5.0	5.8	6.0	1.03
CH_3	1	Zeolite heated at 300°C	3.0	2.2	2.25	1.02
CH_3	1	MMT	5.0	2.8	5.0	1.79
CH_3	2	MMT	5.0	5.0	6.3	1.26
i-C_4H_9	2	MMT	5.0	5.0	6.75	1.35

support and the yield of gaseous reaction products were determined from gas evolution curves (Fig. 1, curve *1*).

Procedure 2 consisted in a single-step supply of AlR_3 in an equimolar amount to water as a constituent of the support ($[H_2O] : [AlR_3] = 1$). Table 1 summarizes the consumption of $AlMe_3$ and $Al(i\text{-}Bu)_3$ for the dehydration of the support and the amount of a released hydrocarbon (methane or isobutane) depending on the nature and water content of the support with the use of both of the procedures.

As can be seen in Table 1, the consumption of $AlMe_3$ for the dehydration of uncalcined ZSM-5 (5.0 mmol of H_2O per gram) and ZSM-5 calcined at 300°C (3.0 mmol of H_2O per gram) in procedure 1 corresponded to the initial water content of the support, whereas the number of moles of liberated methane corresponded to the number of moles of $AlMe_3$ added ($[CH_4] : [AlR_3] = 1 : 1.03$). The MAO synthesized on the surface of ZSM-5 proved to be an active cocatalyst for zirconocenes of olefin polymerization.

The use of procedure 1 for the treatment of MMT with an alkylaluminum gave other results. Figure 1 shows the dependence of the yield of methane on the amount of $AlMe_3$ introduced into an MMT suspension in toluene. It follows from Fig. 1 and Table 1 that the consumption of $AlMe_3$ for the dehydration of 1 g of MMT containing 5 mmol of H_2O was only 2.8 mmol; however, the methane amount released in this case was much greater (5.0 mmol); that is, $[CH_4]/[AlMe_3] = 1/79$. It is likely that water in the interlayer space of MMT is more mobile and more accessible to AlR_3 than the internal water in ZSM-5. Therefore, hydrolysis performed in accordance with procedure 1, that is, under conditions of an excess of MMT water, results in the formation of a large amount of the products of deep alkylaluminum hydrolysis in addition to MAO. Complexes formed by the products of reactions of MMT with alkylaluminums in accordance with procedure 1 exhibit low activity in the processes of olefin polymerization.

Procedure 2 provided milder conditions for the hydrolysis of AlR_3 with MMT water, as compared with procedure 1. In this case, the ratio between the initial components and gaseous reaction products was close to the reaction stoichiometry of the formation of oligomeric alkylalumoxanes:

$$(n+2)AlR_3 + (n+1)H_2O \longrightarrow R_2Al\text{–}[\text{–}O\text{–}Al(R)\text{–}]_n\text{–}O\text{–}AlR_2 + 2(n+1)RH, \quad \text{where } n \geq 10. \tag{I}$$

The treatment of 1 g of MMT, which contained 5 mmol of H_2O according to thermogravimetric data, with an equimolar amount of $AlMe_3$ or $Al(i\text{-}Bu)_3$ with respect to the amount of water was accompanied by the release of 6.3 mmol of methane or 6.75 mmol of isobutane, respectively (Table 1). That is, the $[H_2O] : [AlR_3] : [RH]$ molar ratio was 1 : 1 : (1.26–1.35).

MAO and isobutylalumoxane prepared on the surface of MMT by procedure 2 were found to be active cocatalysts for zirconocene systems in olefin polymerization.

The general reaction scheme of the formation of an immobilized alkylalumoxane by the interaction of sup-

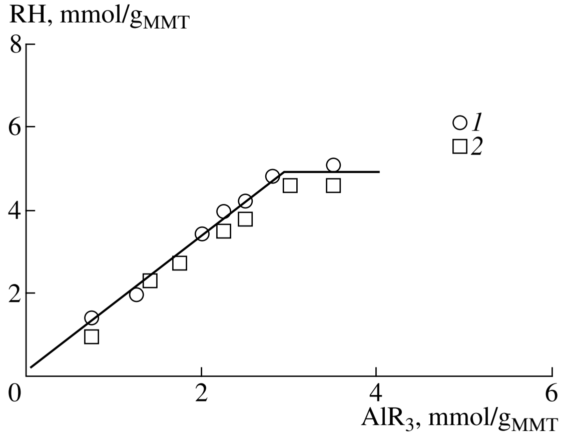


Fig. 1. Dependence of the amount of released RH (methane or isobutane) on the amount of introduced AlR_3 in the treatment of hydrated MMT in accordance with procedures (*1*) 1 and (*2*) 2.

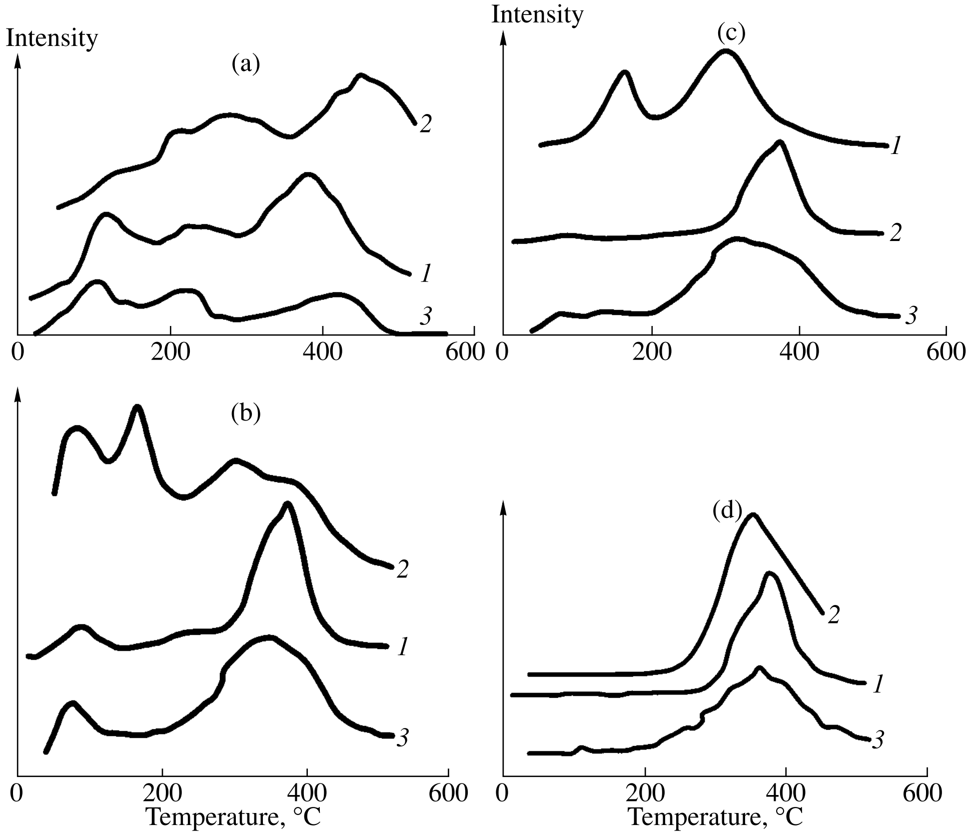
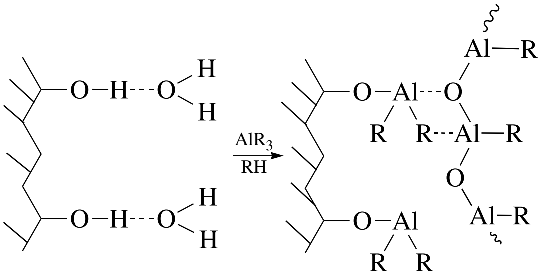


Fig. 2. TPD curves for fragments with m/z = (a) 15, (b) 57, (c) 70, and (d) 145 obtained in the analysis of (*1*) MAO in a solid state, (*2*) the product of the treatment of dehydrated silica gel with a MAO solution, and (*3*) alkylalumoxane synthesized on the surface of MMT.

port water with an alkylaluminum can be represented in the following form:



Scheme 1.

MAO synthesized on the support surface of MMT, as well as commercial solid MAO or the product prepared by the treatment of SiO_2 dehydrated at 300°C with an MAO solution in toluene, was studied by TPD–MS. In all of the three cases studied, the compositions of products formed by the thermal decomposition of organoaluminum components were found to be identical. The most intense lines in mass spectra were assigned to the following fragments of oligomeric MAO molecules: $Al(Me)_2$, Al_2O, OAlMe, $OAlMe_2$, O_2AlMe, Al_3O_3, and OAl_3O_3. These fragments are consistent with the three-dimensional structure of the MAO molecule, which was described previously [30, 31]. Note that, in principle, the large Al_3O_3 and OAl_3O_3 fragments can belong to both cyclic and linear structures. The mass spectra also indicated an intensive release of methane due to the elimination of CH_3 groups from the tested compounds.

Figure 2 shows the TPD curves for products with m/z of 15, 57, 70, and 145 (CH_3, $Al(Me)_2$, Al_2O, and OAl_3O_3 fragments, respectively) from all of the three samples. These curves indicate at which temperatures each of the fragments was eliminated from the MAO molecule in the course of thermal degradation under conditions of the linear heating of the sample.

The experimental data indicate that solid commercial MAO and MAO in the $MMT(H_2O)/AlMe_3$ sample (surface synthesis) were identical in composition to thermal desorption products. Moreover, the TPD spectra of the same fragments were also similar (Fig. 2, curves *1*, *3*). In both cases, the most intensive release of fragments with mass numbers of 70 and 145, that is, the decomposition of MAO with the formation of >Al–O–Al< and $–O–Al_3O_3–$, occurred at 350–380°C (Figs. 2c and 2d, curves *1*–*3*).

In both cases, the TPD spectra of fragments with m/z 57, that is, $–Al(CH_3)_2$, exhibited less intense peaks at low temperatures (~80°C) along with the main peak at 350–380°C (Fig. 2b, curves *1*, *3*). This low-temperature peak was due to the elimination of the $Al(CH_3)_2$ fragment in the decomposition of $Al(CH_3)_3$, which was present in both samples. It is obvious that the complex shape of spectra in Fig. 2a (curves *1*, *3*) (maximums at 120, 220–250, and 420–440°C) is due to the elimination of a CH_3 group from various MAO fragments with different thermal stabilities of the Al–C bond.

Note that the detected methyl groups resulted from the thermal decomposition of MAO rather than $Al(CH_3)_3$, which was also present in both samples, because the liberation of methyl groups was not detected by mass spectrometry upon the decomposition of $Al(CH_3)_3$ [32].

The above results led us to conclude that the resulting MAO immobilized on MMT was structurally very similar to commercial MAO.

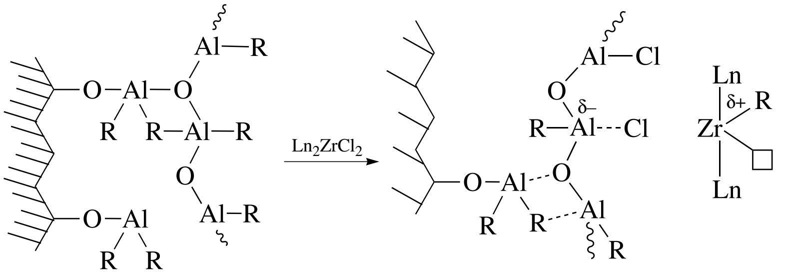
At the same time, the sample prepared by supporting commercial MAO on dehydrated SiO_2 exhibited special properties (Fig. 2, curve *2*). Thus, a low-temperature peak (about 120°C) was practically absent from the TPD curve for *m*/*z* 15 (Fig. 2a, curve *2*), whereas the other two curves exhibited this peak.

These data indicate that alumoxane molecules likely lost at least a portion of the most active methyl groups in the course of MAO immobilization on the surface of dehydrated SiO_2. On the treatment of dehydrated SiO_2 with a MAO solution, not only $Al(CH_3)_3$, which was contained in MAO, but also a portion of the most reactive methyl groups of MAO reacted with the reactive surface OH groups of silica gel. Evidently, because of the loss of these CH_3 groups, MAO molecules lose their alkylating ability upon supporting onto SiO_2, and they cannot form metallocene complexes, which are active in polymerization.

Moreover, as can be seen in Figs. 2b and 2c (curves *2*), the thermal decomposition of MAO supported on SiO_2, which was accompanied by the elimination of fragments, began at lower temperatures than in commercial MAO or in MAO synthesized on the surface. Thus, an additional peak at 160°C appeared in the TPD curves corresponding to the elimination of $–Al(CH_3)_2$ and –Al–O–Al– fragments (*m*/*z* 57 and 70, respectively) in the thermal decomposition of SiO_2/MAO (curves *2*), whereas this peak was absent from the spectra of the other two samples.

Evidently, a three-dimensional MAO molecule rigidly fixed on the surface of a dehydrated support became more strained; because of this, decomposition processes occurred more readily in this case. In the synthesis of MAO immediately on the surface by the interaction of internal support water with AlR_3, this rigid fixation of MAO on the surface did not occur. Note that the three-dimensional molecular structure of MAO was retained upon the fixation on the surface of SiO_2. The elimination of large fragments like $–O–Al_3O_3$ (Fig. 2d, curves *1–3*) occurred at 340–370°C in the thermal decomposition of all of the tested samples.

Alumoxanes that were synthesized immediately on the support surface by the interaction of internal support water with AlR_3 formed heterogenized metallocene complexes, which are active in the polymerization reactions of ethylene and propylene (Scheme 2).



Scheme 2.

Tables 2 and 3 summarize data on the activity of $MMT(H_2O)/AlR_3$/zirconocene (R = $AlMe_3$ or $Al(i\text{-}Bu)_3$; zirconocene = Cp_2ZrCl_2 or $Et[Ind]_2ZrCl_2$) catalysts in ethylene polymerization and of a $ZSM\text{-}5(H_2O)/AlMe_3/Et(Ind)_2ZrCl_2$ catalyst in propylene polymerization, respectively.

As can be seen in Table 2, the activity of $MMT(H_2O)/AlR_3$/zirconocene catalysts in the reaction of ethylene polymerization depends on the conditions of alkylalumoxane synthesis on the surface of MMT. Thus, the yields of polyethylene (PE) at 40°C in the presence of catalysts based on Cr_2ZrCl_2 and the reaction products of support water with $AlMe_3$, which were prepared in accordance with procedures 1 and 2, were 1050 and 10 000 kg PE (mol Zr)$^{-1}$ $[C_2H_4]^{-1}$ h^{-1}, respectively (Table 2, experiments 3 and 2). Isobutylalumoxane, which was synthesized in accordance with procedure 1, in combination with $Et(Ind)_2ZrCl_2$ also exhibited low activity, as compared with isobutylalumoxane synthesized on MMT in accordance with procedure 2 (Table 2, experiments 9 and 8). This was likely due to the formation of a large amount of deep hydrolysis products of AlR_3 on the treatment of MMT with an alkylaluminum in accordance with procedure 1, that is, under conditions unfavorable for the synthesis of alkyl-

Table 2. Ethylene polymerization on $MMT(H_2O)/AlR_3$/zirconocene supported catalysts ($[C_2H_4] = 3.4 \times 10^{-2}$ mol/l)

Experiment no.	Catalyst	Support treatment procedure	Zirconium content $Q_{Zr} \times 10^6$, mol/g_{MMT}	$\frac{[Al]}{[Zr]}$	Reaction temperature, °C	Activity, kg PE $(mol\ Zr)^{-1}$ $[C_2H_4]^{-1}$ h^{-1}	$\overline{M}_w \times 10^{-3}$	$\frac{\overline{M}_W}{\overline{M}_n}$
1	Cp_2ZrCl_2-MAO (homogeneous)	–	(5.6×10^{-5} mol/l)	1000	40	20800	–	–
2	$MMT(H_2O)/AlMe_3/Cp_2ZrCl_2$	2	4.6	1100	40	10000	–	–
3	$MMT(H_2O)/AlMe_3/Cp_2ZrCl_2$	1	4.1	1000	40	1050	–	–
4	$Et(Ind)_2ZrCl_2$-MAO (homogeneous)	–	(4.0×10^{-5} mol/l)	1100	40	26000	180	3.3
5	$MMT(H_2O)/AlMe_3/Et(Ind)_2ZrCl_2$	2	2.4	2000	40	14700	220	3.3
6	$MMT(H_2O)/AlMe_3/Et(Ind)_2ZrCl_2$	2	2.4	2270	55	21450	85	4.2
7	$MMT(H_2O)/AlMe_3/Et(Ind)_2ZrCl_2$	2	2.4	2000	65	54850	–	–
8	$MMT(H_2O)/Al(i\text{-}Bu)_3/Et(Ind)_2ZrCl_2$	2	2.4	1400	65	17800	–	–
9	MMT-$H_2O/Al(i\text{-}Bu)_3/Et(Ind)_2ZrCl_2$	1	2.4	2300	40	1500	–	–

Table 3. Propylene polymerization on $ZSM\text{-}5(H_2O)/AlMe_3/Et(Ind)_2ZrCl_2$ catalysts ($ZSM\text{-}5(H_2O)/AlMe_3$ was prepared in accordance with procedure 1; the propylene pressure was 0.57 atm)

Experiment no.	Zirconium content $Q_{Zr} \times 10^6$, mol/g_{ZSM}	$\frac{[Al]}{[Zr]}$	Reaction temperature, °C	Activity, kg PP $(mol\ Zr)^{-1}$ $[C_3H_6]^{-1}$ h^{-1}	$\overline{M}_W \times 10^{-3}$	$\frac{\overline{M}_W}{\overline{M}_n}$	T_m, °C
1	1.4	5500	40	19800	40	13	124
2	1.6	4350	40	9170	43	8	123
3	2.0	5000	75	13160	1.5**	-	-
4*	(0.026×10^{-3} mol/l)	1720	75	25000	2.0**	-	-

* On the $Et(Ind)_2ZrCl_2$–MAO homogeneous catalyst.

** M_n was determined by the ozonolysis of terminal double bonds.

alumoxanes. As a result, the real alkylalumoxane amount was insufficient for the formation of an active catalytic system with a zirconium compound.

It can be seen in Tables 2 and 3 that the $MMT(H_2O)/AlR_3$/zirconocene (prepared using procedure 2) and $ZSM\text{-}5(H_2O)/AlMe_3/Et(Ind)_2ZrCl_2$ catalysts, which include the products of the mild hydrolysis of AlR_3 with support water, are similar in activity to their homogeneous analogues.

Catalyst heterogenization was favorable for an increase in the molecular weight of PE, as compared with the polymer prepared on a homogeneous catalyst (Table 2). The addition of external MAO to the reaction zone of ethylene polymerization on $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$ was accompanied by a decrease in the molecular weight of the polymer product. Figure 3 shows the molecular-weight distribution curves of PE formed on the heterogenized $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$ catalyst (curve *1*) and on this catalyst upon the addition of external MAO to the reaction zone a time after the onset of the reaction (curve *2*). The shape of curve *2* indicates that two polymer products with different molecular weights were formed in the system. By this is meant that, on the addition of external MAO, a portion of active centers passed from the surface into solution, and the resulting soluble catalytic complexes initiated the formation of a lower molecular weight polymer. Hence, it follows that active centers in supported $ZSM\text{-}5(H_2O)/AlR_3$/zirconocene catalysts are primarily localized on the support surface.

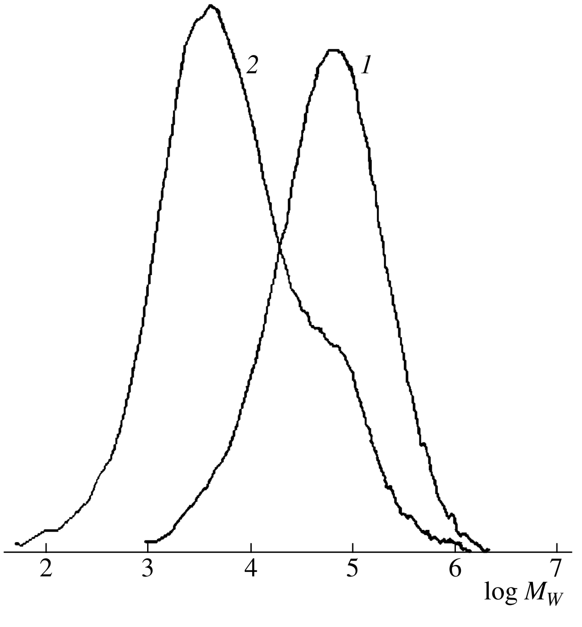


Fig. 3. Gel permeation chromatograms of PE prepared on (*1*) ZSM-5(H_2O)/$AlMe_3$/Cp_2ZrCl_2 and (*2*) ZSM-5(H_2O)/$AlMe_3$/Cp_2ZrCl_2 + MAO catalysts. Polymerization conditions: $T = 34°C$; $[C_2H_4] = 0.054$ mol/l; [Zr] = 0.16 wt %; [Al]/[Zr] molar ratios of (*1*) 160 and (*2*) 320.

In the polymerization of propylene on the ZSM-5(H_2O)/$AlMe_3$/Et$(Ind)_2ZrCl_2$ zirconocene catalyst supported on the zeolite surface, polypropylene (PP) with a wider molecular-weight distribution than that of ordinary polymer prepared on a corresponding homogeneous catalyst [33] was formed. An increase in the polydispersity of the product is characteristic of polymerization processes on heterogenized metallocene catalysts.

Thus, the use of catalysts of the support(H_2O)/AlR_3/zirconocene type (in this case, zeolite(H_2O)/AlR_3/zirconocene and MMT(H_2O)/AlR_3/zirconocene) allowed us to avoid using commercial MAO for metallocene activation. The mild conditions under which surface water of the support reacts with AlR_3 are responsible for the synthesis of alkylalumoxanes with the structure that gives rise to the formation of heterogenized zirconocene complexes active in the reactions of olefin polymerization.

The TPD–MS experiments demonstrated that the immobilization of commercial MAO on dehydrated SiO_2 results in the loss of a portion of the most reactive methyl groups from MAO due to their interaction with the OH groups of the support. Moreover, the three-dimensional structure of MAO becomes more strained after this immobilization. For this reason, immobilized MAO loses the ability to activate metallocenes, and an organoaluminum compound should be additionally introduced into the reaction zone in order to activate the catalyst.

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