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Ethylene Polymerization and Ethylene–1-Hexene Copolymerization over Immobilized Metallocene Catalysts

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Abstract—Ethylene polymerization and ethylene–1-hexene copolymerization in the presence of metallocene catalysts based on Cp_2ZrCl_2, *rac*-Et(Ind)$_2$ZrCl$_2$, *rac*-Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$, and *rac*-Me$_2$Si(2-Me-4-Ph-Ind)$_2$HfCl$_2$ been investigated. The catalysts have been immobilized on montmorillonite (MMT) containing methylaluminoxanes (MMT-H_2O)/AlMe$_3$ or isobutylaluminoxanes (MMT-H_2O)/ Al*i*-Bu$_3$ synthesized directly on the support surface. The immobilized catalysts, with the general formula (MMT-H_2O)/AlR$_3$/Zr(Hf)-cene, show a high activity comparable with the activity of the respective homogeneous systems, which depends on the nature of the metal and on the metallocene composition and structure. The catalytic properties of the metallocene systems depend strongly on the nature of the activator as a component of the catalytic complex. (MMT-H_2O)/Al*i*-Bu$_3$ is a more effective activator of the hafnocene precatalyst in the polymerization processes than oligomeric methylaluminoxane or methylaluminoxane synthesized on the support. The immobilization of the metallocenes on (MMT-H_2O)/AlR$_3$ leads to an increase in the molar mass of polyethylene and ethylene–1-hexene copolymers relative to the molar mass of the polymers synthesized using the respective homogeneous systems. The immobilized metallocene catalysts display high selectivity toward the insertion of a higher α-olefin (1-hexene) into the polymer chain, retaining this important property of their homogeneous counterparts.

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Polyethylene (PE) and copolymers of ethylene with higher α-olefins are important industrial materials. The processing and performance characteristics of these polymers are largely determined by their molar mass and by the proportion and distribution uniformity of branches in the copolymer macromolecules [1, 2]. In addition to being extraordinarily active, the homogeneous single-site catalysts based on metallocene–methylaluminoxane (MAO) complexes provide means to control the molar mass and microstructure of polymer macromolecules via directed catalyst design]3–6]. There have been many publications on ethylene polymerization and ethylene copolymerization with higher α-olefins on homogeneous catalysts, including metallocenes with various compositions and structures. The authors of these publications consider the effects of the presence and structure of bridges and of the nature of η-bonded ligands and substituents therein on the performance of the catalysts, on the molar mass of the resulting polymers, on the composition of the copolymers, and on the copolymerization constants [2, 7–10]. A specific feature of metallocenes is that, in the processes in which they are involved, higher α-olefins differ in reactivity from ethylene and propylene to a much lesser extent than in the case of conventional Ziegler–Natta catalysts based on titanium or vanadium. This makes it possible to introduce a much larger proportion of a comonomer into the PE chain while conducting the copolymerization process, thus increasing the degree of branching and, accordingly, allowing the properties of the resulting low-density linear PE to be varied in wider ranges. The single-site nature of the metallocene catalysts provides means to synthesize polymers with a narrow molar mass distribution (MMD) and compositionally uniform polymers.

In order to adapt these unique catalytic systems to the existing industrial olefin production processes and technologies, which typically employ solid catalysts, it is necessary to immobilize these systems on a solid support without losing their advantages. Another challenging fundamental and applied problem is to find new metallocene activators that do not involve commercial MAO.

We have developed an immobilized catalyst preparation method in which metallocenes are activated by methylaluminoxanes or isobutylaluminoxanes synthesized just on the surface of a hydrated aluminosilicate, namely, montmorillonite (**MMT**-H_2O), and on the surface of various zeolites by partial hydrolysis of $AlMe_3$ and Al*i*-Bu$_3$, respectively, under the action of mobile water present in the support [11–16]. The composition and structure of the alkylaluminoxanes synthesized and immobilized on the support ((support–H_2O)/AlR_3) were determined by elemental analysis, IR spectroscopy [17, 18], and mass spectrometric analysis of the desorption products resulting from the temperature-programmed desorption of the alkyaluminoxanes [13, 14, 16]. The (support–H_2O)/AlR_3 system serves both as the support for metallocene immobilization and as the efficient metallocene activator. The (support–H_2O)/AlR_3/Zr-cene catalysts are as active in olefin homopolymerization as their homogeneous analogues in the absence of external MAO or another organoaluminum cocatalyst [11–16]. Our study of propylene polymerization demonstrated that the immobilization of metallocene precatalysts exerts an effect on the stereoregularity of the resulting polypropylene. This effect depends on the precatalyst composition and structure. The (MMT-H_2O)/AlR_3/Zr(Hf)-cene catalysts based on metallocenes with C_2 symmetry show good stereospecific properties comparable to the properties of the corresponding homogeneous systems [15, 16].

Here, we report ethylene polymerization and the copolymerization of ethylene with the higher olefin 1-hexene on a number of (MMT-H_2O)/AlR_3/Zr(Hf)-cene immobilized catalysts. The purpose of our study was to see how the polymerization kinetics, the performance of the catalyst, and the molar mass and structure of the resulting macromolecules depend on the kind of metal (Zr, Hf), on the composition and structure of the metallocene precatalyst, and on the nature of the activator/support as a component of the immobilized catalytic complexes. For this purpose, we examined the non-bridged zirconocene Cp_2ZrCl_2 (**1**), the *ansa*-zirconocenes *rac*-Et$(Ind)_2ZrCl_2$ (**2**) and *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2ZrCl_2$ (**3**), and the hafnium compound *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2HfCl_2$ (**4**), which is a structural analogue of **3**. The activator/support was MMT containing MAO ((MMT-H_2O)/$AlMe_3$) or isobutylaluminoxanes ((MMT-H_2O)/Al*i*-Bu_3) synthesized on its surface via an earlier developed procedure [13]. In order to understand how immobilization alters the performance of the catalytic complexes and the structure of the resulting polymer, we studied ethylene homopolymerization and ethylene copolymerization with 1-hexene in the presence of the homogeneous analogues of the immobilized metallocene systems under comparable conditions.

EXPERIMENTAL

The zirconium compounds Cp_2ZrCl_2 (**1**) and *rac*-Et$(Ind)_2ZrCl_2$ (**2**) were received from Aldrich. The metallocenes *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2ZrCl_2$ (**3**) and *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2HfCl_2$ (**4**) were synthesized via procedures described in [19, 20]. MAO was used as a 10% solution; $AlMe_3$, as a 2 M solution; Al*i*-Bu_3, as a 1 M solution (all received from Aldrich). The solvent was toluene (spectroscopic grade, Aldrich) additionally held over molecular sieve 5 Å and distilled from sodium wire in an argon atmosphere. Ethylene was polymer grade. 1-Hexene was dried over a molecular sieve and was distilled from sodium wire in an argon atmosphere. The C_6H_{12} fraction boiling at 64°C was collected.

All manipulations involved in catalyst synthesis and in the preparation of the solutions of catalyst components were performed in vacuo or in argon dried by passing it through chromium–nickel catalyst and molecular sieve 5 Å columns. The support was montmorillonite (Cloisite^{R}Na$^+$) with an internal water content of 9.6 wt %, a mean particle size of 8 μm, and a specific surface area of 220–270 m^2/g.

Methylaluminoxanes and isobutylaluminoxanes immobilized on the support surface were obtained by the partial hydrolysis of $AlMe_3$ and Al*i*-Bu_3, respectively, under the action of internal water of MMT at an equimolar AlR_3 : H_2O ratio and $T = 22$°C under vigorous stirring [13]. The products ((MMT-H_2O)/AlR_3) were treated with a solution of a metallocene compound in toluene, and the resulting catalysts were used in polymerization. The Zr and Hf concentrations on the support surface were 0.015–0.03 wt %, and the Al concentration was 14 wt %.

Ethylene polymerization and ethylene–1-hexene polymerization were carried out in toluene in a vigorously stirred, temperature-controlled, glass or steel reactor (0.4 l). The reactor was pumped and heated to the preset temperature and was then charged with the solvent and catalyst, and ethylene was then admitted into the system. For ethylene–1-hexene copolymerization, the appropriate amount of 1-hexene was introduced into the system prior to ethylene admission. The ratio of the molar concentrations of the comonomers, $f = [C_6H_{12}]/[C_2H_4]$, was varied between 0.5 and 8.0. The ethylene pressure and polymerization temperature during the run were maintained constant. In order to terminate polymerization, a 5% HCl solution in ethanol was introduced into the reactor. The resulting polymer product was filtered, washed with ethanol, and vacuum-dried at 60°C. Before determining the molar mass characteristics and composition of the polymer, it was freed from the support. To do this, PE and the ethylene–1-hexene copolymer were treated with HF, filtered, washed with water, and vacuum-dried at 60°C.

The molar mass characteristics of the polymers—M_w, M_n, and M_w/M_n—were determined by gel permeation chromatography on a GPC Waters 150°C chromatograph in 1,2,4-trichlorobenzene at 140°C. The viscosity-average molar mass M_η was determined in decalin at 135°C using the formula $[\eta] = (4.6 \times 10^{-4})M_\eta^{0.73}$.

The degree of branching ($\alpha = CH_3/1000C$) for ethylene–1-hexene copolymers was estimated by IR spectroscopy as the intensity of the 1378 cm^{-1} band [21]. IR spectra were recorded on a Beckman IR 4260 spectrometer. The concentration of 1-hexene units in

Table 1. Activity of the immobilized (MMT-H_2O)/AlR_3/M-cene catalysts and their homogeneous M-cene/MAO analogues in ethylene polymerization and the properties of the resulting PE

Entry	Precatalyst	Activator	Al : M	$[C_2H_4] \times 10^2$, mol/l	Reaction temperature, °C	$A \times 10^{-3}$, (kg PE) (mol M)$^{-1}$ $[C_2H_4]^{-1}$ h^{-1}	M_w, kg/mol	MMD
1	1'	MAO	1800	3.4	40	13.25	200	3.3
2	**1**	(MMT-H_2O)/AlMe	1130	5.9	40	10.0	145.2	5.0
3	**2'**	MAO	1100	3.4	40	26.0	180	3.0
4	**2**	(MMT-H_2O)/AlMe	2000	3.4	40	14.7	220	4.3
5	**2**	(MMT-H_2O)/AlMe	2300	3.4	55	21.4	85	4.2
6	**2**	(MMT-H_2O)/AlMe	2000	3.4	65	54.8	wax	–
7	**2**	(MMT-H_2O)/Al*i*-Bu_3	1700	3.4	40	10.1	260*	–
8	**2**	(MMT-H_2O)/Al*i*-Bu_3	1420	3.4	65	18.1	102*	–
9	**3'**	MAO	2400	4.0	30	32.5	176	3.0
10	**3**	(MMT-H_2O)/AlMe	4300	7.0	30	18.8	560	2.5
11	**3**	(MMT-H_2O)/Al*i*-Bu_3	4350	7.0	30	14.5	462.1	4.0
12	**4'**	MAO	2500	6.8	50	18.0	34	2.6
13	**4**	(MMT-H_2O)/AlMe	3500	6.8	50	3.3	421	4.7
14	**4**	(MMT-H_2O)/Al*i*-Bu_3	3000	6.8	50	33.3	520	3.1

Note: Zr or Hf content of the support, 0.015–0.03 wt %; Al content, 14 wt %. 1', 2', 3', and 4': the metallocene concentration is 5×10^{-5} mol/l. In entries 7 and 8, M_η is in units of kg/Da (starred).

the copolymers (mol %) was calculated as $C_{hex} = \alpha/2(500 - 2\alpha) \times 100$. The composition of the copolymers was also determined by ^{13}C NMR spectroscopy. The proton-decoupled ^{13}C NMR spectra of 10–15% copolymer solutions in *ortho*-dichlorobenzene were recorded at 393 K on an AM 400 WB spectrometer operating at 100.6 MHz using a special-purpose, high-temperature, high-resolution sensor having an external magnetic field stabilization channel.

RESULTS AND DISCUSSION

Table 1 presents data characterizing ethylene homopolymerization over the immobilized catalysts (MMT-H_2O)/AlR_3/**1**–**4** and, for comparison, the same data for the homogeneous systems **1**–**4**/MAO. All of these catalytic systems are very active; however, the immobilized zirconocenes **1**–**3** are somewhat less active than the corresponding homogeneous systems. As in the case of **1**–**3**/MAO, the PE yield with the immobilized catalysts depends on the composition and structure of the zirconium compound. The highest performance is shown by the catalysts based on **3**.

The rate of ethylene polymerization over the immobilized catalysts between 30 and 65°C is characterized by a positive temperature coefficient. The apparent activation energy of the reaction over (MMT-H_2O)/$AlMe_3$/**2**, as calculated from the Arrhenius dependence of the initial polymerization rate (reaction time of 1 min), is 13.3 kcal/mol.

The activity of metallocenes **2** and **3** depends insignificantly on the nature of the activator/support. Replacing a methyl group with an isobutyl group in the supported alkylaluminoxanes, which are the counterions in the cationic catalytic complexes, leads to a decrease in the activity of the immobilized catalysts: for the catalyst based on **3**, catalytic activity decreases from 18.8×10^3 to 14.5×10^3 (kg PE) (mol Zr)$^{-1}$ $[C_2H_4]^{-1}$ h^{-1} at 30°C (Table 1, entries 10, 12); for (MMT-H_2O)/AlR_3/**2**, from 14.7×10^3 to 10.1×10^3 (kg PE) (mol Zr)$^{-1}$ × $[C_2H_4]^{-1}$ h^{-1} at 40°C (Table 1, entries 4, 7; Fig. 1).

Using compound **3** and its structural analogue **4** as examples, we compared the zirconocene and hafnocene catalysts (Fig. 1). Hafnocenes of various compositions and structures are known to be less active activators of oligomeric MAO in olefin polymerization than the analogous zirconocenes [10, 15, 16, 22, 23]. This is also indicated by our data. The yield of PE synthesized over **3**/MAO and **4**/MAO is 81.5×10^3 (kg PE) (mol Zr)$^{-1}$ $[C_2H_4]^{-1}$ h^{-1} (at 30°C)

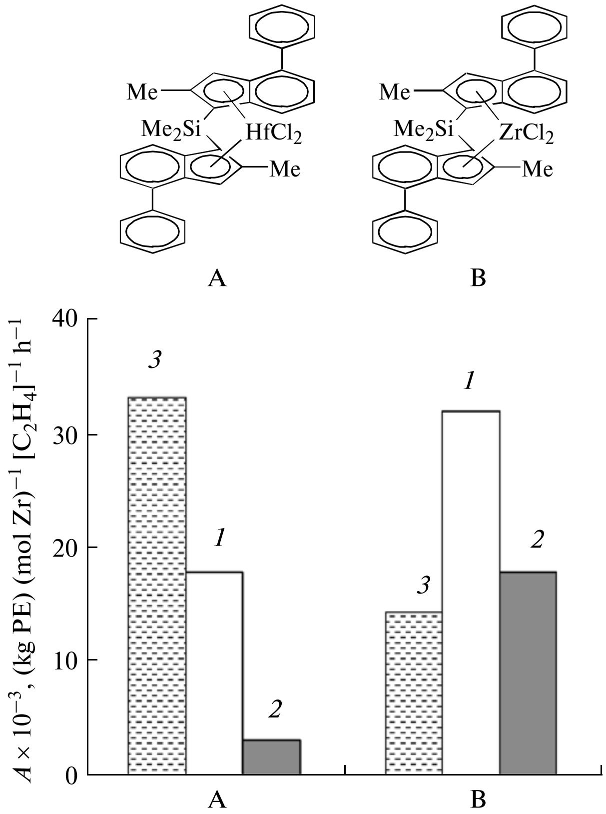

Fig. 1. Effect of the nature of the activator on the activity of (A) hafnocene **4** and (B) zirconocene **3** in ethylene polymerization: (*1*) MAO, (*2*) (MMT-H_2O)/$AlMe_3$, and (*3*) (MMT-H_2O)/Al*i*-Bu_3.

and 18.0×10^3 (kg PE) (mol Hf)$^{-1}$ [C_2H_4]$^{-1}$ h^{-1} (at 50°C), respectively (Table 1, entries 9, 12). This is due to the fact that, in the cationic complex of metallocene with MAO, the Hf–C bond is less polarized than the Zr–C bond. This leads to a higher activation energy for monomer insertion and to a lower polymer chain propagation rate.

The effect of the nature of the alkyl group (Me, *i*-Bu) on the activity of the heterogenized aluminoxanes as components of the catalytic complex is most pronounced in the case of **4**. Methylaluminoxane synthesized on the support is a less effective activator of **4** than oligomeric MAO (Table 1, entries 12, 13). At the same time, immobilization of **4** on MMT containing isobutylaluminoxane, which differs in electron donor and steric properties from MAO and heterogenized methylaluminoxane, affords high-performance catalytic complexes. The polymer yield with the (MMT-H_2O)/Al*i*-Bu_3/**4** catalyst at 50°C is 33.3×10^3 (kg PE) (mol Hf)$^{-1}$ [C_2H_4]$^{-1}$ h^{-1} (Table 1, entry 14), 10 times higher than in the case of (MMT-H_2O)/$AlMe_3$/**4**.

Polymerization activity (*A*) data for the catalysts based on **3** and **4** (Fig. 1) indicate that the performance of the metallocene catalysts depends both on the kind of metal (M) in the structurally and compositionally identical precatalysts and on the nature of the activator serving as the counterion in the cationic catalytic complexes. We demonstrated earlier that isobutylaluminoxanes synthesized on MMT, unlike MAO and (MMT-H_2O)/$AlMe_3$, are efficient activators of hafnocene compounds, including **4**, in propylene polymerization [15, 16].

Metallocene immobilization on (MMT-H_2O)/AlR_3 increases the molar mass of the polymer product. Polymerization over **3**/MAO, (MMT-H_2O)/$AlMe_3$/**3**, and (MMT-H_2O)/Al*i*-Bu_3/**3** at 30°C yields PE with M_w = 176, 560, and 462 kg/mol, respectively (Table 1, entries 9–11). Immobilization of **4** leads to a greater increase in the molar mass of PE at 50°C: M_w = 34 kg/mol for **4**/MAO, 421 kg/mol for (MMT-H_2O)/$AlMe_3$/**4**, and 520 kg/mol for (MMT-H_2O)/Al*i*-Bu_3/**4** (Table 1, entries 12–14). It is likely that the support surface on which the alkylaluminoxane anion–metallocene cation intimate pair is immobilized can sterically hinder β-agostic interaction and thereby hamper β-hydride elimination, which is the main reaction terminating the polymer chain in polymerization on homogeneous metallocene catalysts.

The fact that PE forming on the immobilized catalysts has a wider MMD than PE obtained in the presence of homogeneous systems may be due to active site nonuniformity. The surface of the support modified with synthesized alkylaluminoxanes obviously has coordination sites differing in energetic characteristics

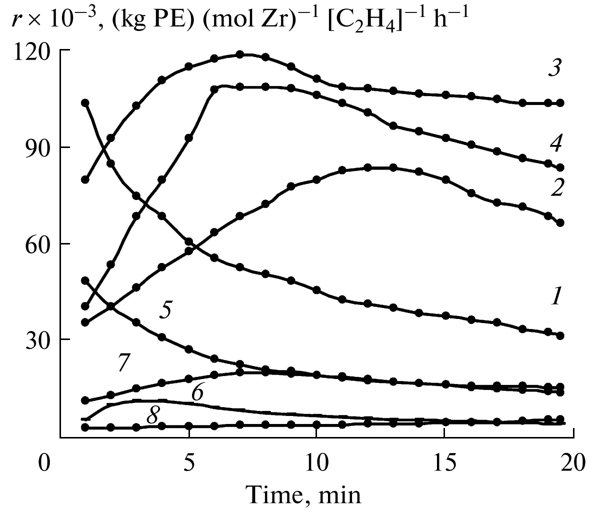

Fig. 2. Kinetics of ethylene–1-hexene copolymerization on the homogeneous and immobilized catalysts based on zirconocene **3** at 30°C and [C_2H_4] = 7.0×10^{-2} mol/l: (*1–4*) **3**/MAO at *f* = (*1*) 0, (*2*) 0.5, (*3*) 0.85, and (*4*) 1.6; (*5–8*) (MMT-H_2O)/Al*i*-Bu_3/**3** at *f* = (*5*) 0, (*6*) 1.55, (*7*) 2.6, and (*8*) 5.4.

and alkylaluminoxane structure. Interacting with a metallocene, these sites likely form active polymerization sites varying in properties. In our earlier study of the initial stages of gas-phase ethylene polymerization over (MMT-H_2O)/$AlMe_3$/Zr-cene immobilized catalysts, we indeed observed the energetic nonuniformity of active sites. This is evidence that the immobilized systems are multisite ones, which differentiates them from their single-site homogeneous analogues [24].

Using the catalysts based on zirconocene **2** as examples, we found out how the way the molar mass of PE varies with polymerization temperature depends on the nature of the activator/support. At 40°C, ethylene polymerization over (MMT-H_2O)/$AlMe_3$/**2** and (MMT-H_2O)/Al*i*-Bu_3/**2** yields PE with M_η = 220 and 260 kg/Da, respectively (Table 1, entries 4, 7). An increase in the polymerization temperature to 65°C leads to the formation of a liquid polymer product over (MMT-H_2O)/$AlMe_3$/**2** (Table 1, entry 6) and a PE powder with M_η = 102 kg/Da over (MMT-H_2O)/Al*i*-Bu_3/**2** (Table 1, entry 8).

The copolymerization of ethylene and 1-hexene was studied in the presence of the immobilized zirconocene catalysts based on **1** and **3**, their homogeneous analogues **1**/MAO and **3**/MAO, and the hafnocene catalyst (MMT-H_2O)/Al*i*-Bu_3/**4** in a wide range of comonomer concentration ratios (*f* = [C_6H_{12}]/[C_2H_4] (in the reaction zone. In order to avoid high 1-hexene conversion, which would have markedly decreased the *f* value by the end of the process, copolymerization was terminated in 15–20 min, when the 1-hexene conversion was at most 10 mol %.

As distinct from ethylene homopolymerization (*f* = 0), which starts at its highest rate and then slows down, copolymerization needs some time for active site formation (Figs. 2, 3). The copolymerization rate *r* expressed in terms of (kg PE) (mol Zr)$^{-1}$ [C_2H_4]$^{-1}$ h^{-1} gradually increases, passes through a maximum, and then decreases. For the homogeneous catalyst **3**/MAO, the time required to reach the maximum copolymerization rate r_{max} (τ) is 5 to 12 min (Fig. 2). For the immobilized catalyst **4**, active polymerization sites from less rapidly. At 30°C in the comonomer concentration ratio range examined, τ = 18–20 min (Fig. 3a). Raising the polymerization temperature markedly enhances the efficiency of the reaction and accelerates polymerization site formation (Fig. 3b). At 50°C, a smaller τ value of 2–6 min is observed at a similar *f* value.

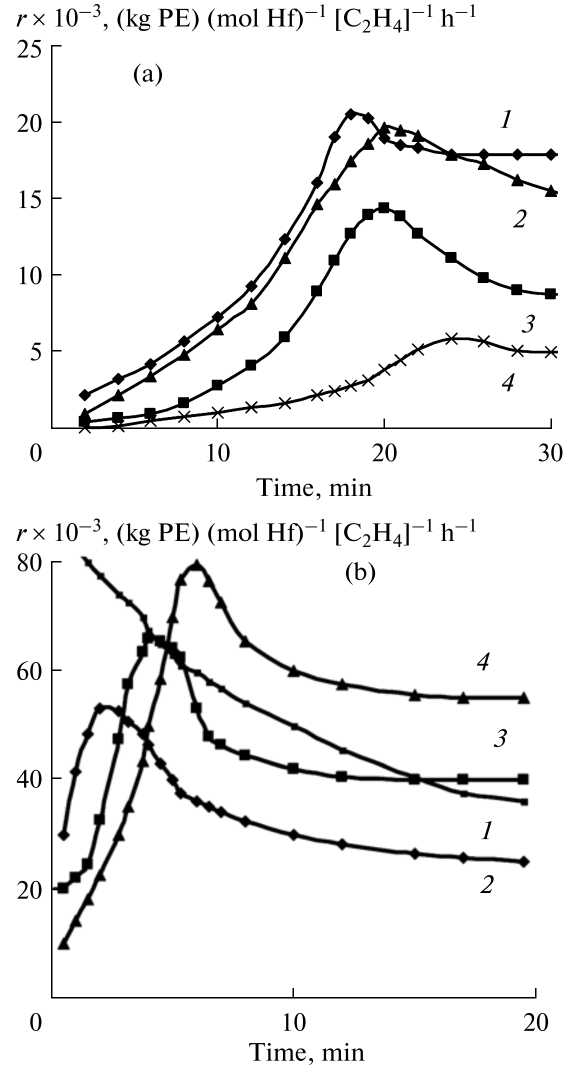

Fig. 3. Kinetics of ethylene–1-hexene copolymerization over the immobilized catalyst based on hafnocene **4**: (a) 30°C, [C_2H_4] = 4.65×10^{-2} mol/l, *f* = (*1*) 4.8, (*2*) 5.3, and (*3*) 6.2; (b) 50°C, [C_2H_4] = 4.65×10^{-2}mol/l, *f* = (*1*) 0, (*2*) 0.5, (*3*) 0.85, and (*4*) 2.6.

The comonomer concentration ratio in the reaction zone has an effect on the activity of the metal-

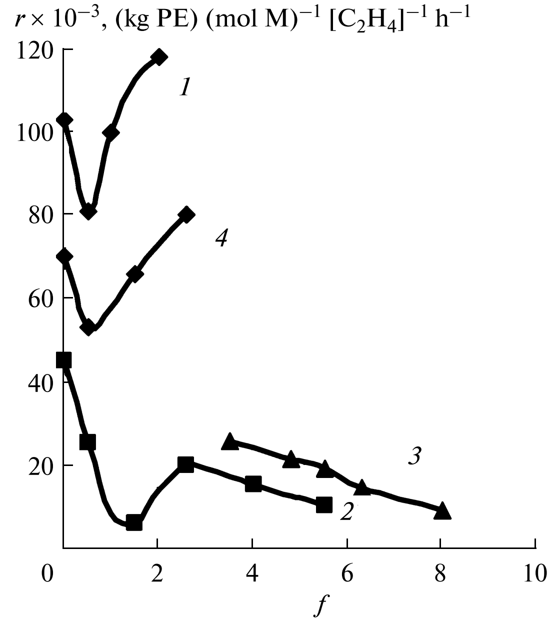

Fig. 4. r_{max} versus f for ethylene–1-hexene polymerization on the *ansa*-metallocene catalysts: (*1*) **3**/MAO, 30°C; (*2*) (MMT-H_2O)/Al*i*-Bu_3/**3**, 30°C; (*3*) (MMT-H_2O)/Al*i*-Bu_3/**4**, 30°C; (*4*) (MMT-H_2O)/Al*i*-Bu_3/**4**, 50°C.

locene catalysts. For the catalysts based on **3** and **4**, the maximum reduced copolymerization rate depends on f in a complicated way (Fig. 4). At small f values, the copolymerization rate is lower than the ethylene homopolymerization rate ($f = 0$), but it grows at larger f values. For **3**/MAO (30°C, Fig. 4, curve *1*) and MMT(H_2O)/Al*i*-Bu_3/**4** (50°C, cutve *4*) over a certain f range, r_{max} is higher than the initial ethylene homopolymerization rate. An increase in the ethylene or propylene uptake rate in the presence of a higher α-olefin (so-called monomer effect) and an extremum in the dependence of r_{max} on the monomer molar ratio are observed in copolymerization processes over a number of metallocene catalysts [6–9, 23, 25, 26]. There is no consensus as to the origin of the monomer effect. However, one of the most frequently named causes of this phenomenon is modification of active sites under the action of the comonomer, which accelerates polymer chain propagation or a change in their number [25–28]. It is interesting that we did not observe any monomer effect in the presence of (MMT-H_2O)/Al*i*-Bu_3/**3**. At $f = 1.6$, r_{max} reaches its maximum value of 20×10^3 (kg PE) (mol Zr)$^{-1}$ [C_2H_4]$^{-1}$ h^{-1}, which is not higher than the initial ethylene homopolymerization rate, 45×10^3 (kg PE) (mol Zr)$^{-1}$ [C_2H_4]$^{-1}$ h^{-1} (Fig. 4, curve *2*). As f is further increased, r_{max} decreases. It is also clear from Fig. 4 that rthe activated effect of isobutylaluminoxane synthesized on the support surface is stronger for **4** (Fig. 4, curve *3*) than for **3** (Fig. 4, curve *2*). This is in agreement with the above data concerning the difference between the activating effects of (MMT-H_2O)/Al*i*-Bu_3 on **4** and **3** in ethylene polymerization.

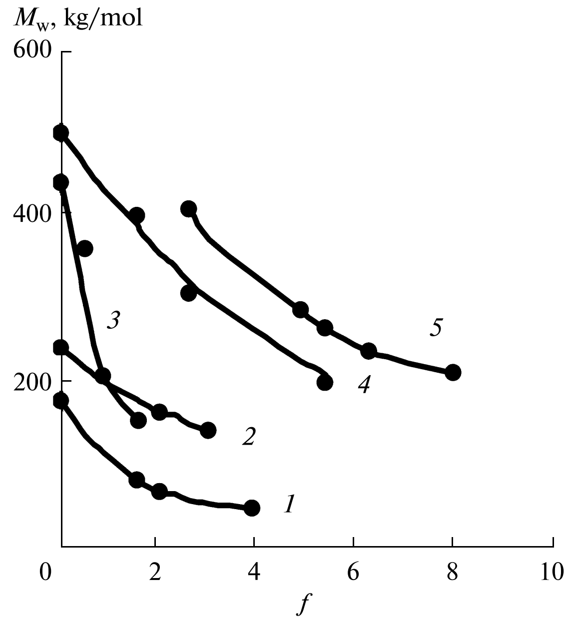

Fig. 5. Molar mass of the copolymer as a function of f: (*1*) **1**/MAO, 40°C, [C_2H_4] = 4.9×10^{-2} mol/l; (*2*) (MMT-H_2O)/ $AlMe_3$/**1**, 40°C, [C_2H_4] = 5.9×10^{-2} mol/l; (*3*) **3**/MAO, 30°C, [C_2H_4] = 7.0×10^{-2} mol/l; (*4*) (MMT-H_2O)/Al*i*-Bu_3/**3**, 30°C, [C_2H_4] = 7.0×10^{-2} mol/l; (*5*) (MMT-H_2O)/Al*i*-Bu_3/**4**, 30°C, [C_2H_4] = 4.65×10^{-2} mol/l.

The immobilization of **1**, **3**, and **4** leads to an increase in the molar mass of the polymers relative to those of the polymer products synthesized on the homogenous systems under the same conditions. Fig-

Table 2. Ethylene–1-hexene copolymerization on the metallocene catalysts

Entry	Metallocene	Activator	Temperature, °C	$[C_2H_4] \times 10^2$, mol/l	f	$r_{max} \times 10^{-3}$, (kg PE) × $(\text{mol M})^{-1} \times [C_2H_4]^{-1}h^{-1}$	C_{hex}, mol/l		M_w, kg/mol	MMD
							IR	^{13}C NMR		
1	**1**	MAO	40	4.9	0	40	–	–	180.0	3.0
2	**1**	MAO	40	4.9	2.0	19.2	4.4	–	66.8	2.5
3	**1**	MAO	40	4.9	3.9	39.8	5.7	–	46.8	3.0
4	**1**	$(MMT\text{-}H_2O)/AlMe_3$	40	5.9	0	17	–	–	452.0	3.2
5	**1**	$(MMT\text{-}H_2O)/AlMe_3$	40	5.9	2.3	12.8	2.0	–	160.0	5.0
6	**1**	$(MMT\text{-}H_2O)/AlMe_3$	40	5.9	3.0	26.8	2.7	–	140.0	3.9
7	**3**	MAO	30	7.0	0	103	–	–	612.4	2.7
8	**3**	MAO	30	7.0	0.5	83	2.5	1.88	530	2.85
9	**3**	MAO	30	7.0	0.85	118	2.7	5.5	482	2.6
10	**3**	MAO	30	7.0	1.6	108	6.25	7.35	462.1	2.5
11	**3**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	30	7.0	0	48	–	–	462.1	4.0
12	**3**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	30	7.0	1.55	5	4.7	5.8	–	–
13	**3**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	30	7.0	2.6	19.6	8.5	9.4	306.45	3.5
14	**3**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	30	7.0	4.9	15.5	–	–	–	–
15	**3**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	30	7.0	5.38	11	15.7	20.3	200.0	3.5
16	**4**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	30	4.65	4.88	20.6	–	15. 2	286	4.8
17	**4**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	30	4.65	5.13	19.7	–	16.0	270	3.9
18	**4**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	30	4.65	6.26	14.4	–	18.4	238	4.6
19	**4**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	30	4.65	8	5.9	–	23	210	4.3
20	**4**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	50	4.65	0	67	–	–	520	3.1
21	**4**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	50	4.65	0.5	53	–	–	416	6.5
22	**4**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	50	4.65	1.49	66	–	–	211	6.2
23	**4**	$(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$	50	4.65	2.6	76.9	–	–	223.3	8.0

Note: Zr or Hf content of the support, 0.015–0.03 wt %; Al content, 14 wt %. Dash – parameter not determined.

ure 5 plots the molar mass of the copolymer as a function of *f*. Clearly, in the reaction conducted in the presence of the homogeneous catalysts, M_w decreases more rapidly with an increasing *f* (Fig. 5, curves *1*, *3*) than it does in the reaction over the immobilized systems (curves *2*, *4*), Copolymerization over $(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$/**4** yields products with a larger M_w than copolymerization over $(MMT\text{-}H_2O)/Al\textit{i}\text{-}Bu_3$/**3**. The copolymers synthesized over the immobilized catalysts have a wider MMD (3.8–8) that the copolymers obtained using the corresponding homogeneous catalysts (2.5–2.7). This is apparently due to the active site nonuniformity caused by metallocene immobilization on the activator/support surface.

The composition of polymers synthesized under identical conditions depends on the nature of the metallocene precatalyst. The catalysts based on *ansa*-metallocenes **3** and **4** are more selective in comonomer

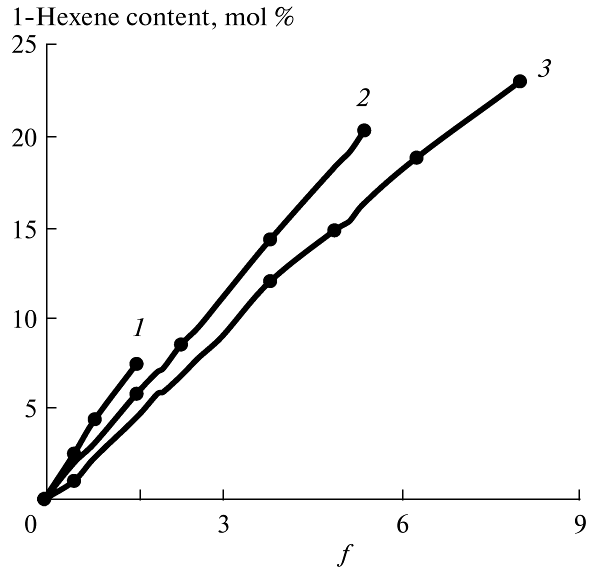

Fig. 6. 1-Hexene content of the copolymer as a function of *f*: (*1*) **3**/MAO, (*2*) MMT(H_2O)/Al*i*-Bu_3/**3**, and (*3*) MMT(H_2O)/Al*i*-Bu_3/**4**.

insertion (Table 2, entries 10, 13) than the catalysts containing non-bridged zirconocene **1** (Table 2, ebtried 2, 5). The immobilization of the metallocene complexes on the support somewhat hampers 1-hexene insertion into the polymer chain (Table 2, Fig. 6). However, copolymerization in the presence of the MMT(H_2O)/Al*i*-Bu_3/**3** and MMT(H_2O)/Al*i*-Bu_3/**4** catalysts under the conditions examined yields products with high 1-hexene contents of 20 mol % ($f = 5.38$) and 23 mol % ($f = 8.0$), respectively. From the Fineman–Ross plot of $F = H/E$, where H and E are the 1-hexene unit and ethylene unit contents of the copolymer, versus f, we determined the relative reactivity constants for ethylene (k_{eth}) and 1-hexene (k_{hex}) in copolymerization catalyzed by the *ansa*-metallocenes (Table 3). Both for the homogeneous catalyst and for the heterogeneous catalysts, the product $k_{eth}k_{hex}$ is close to unity, indicating the formation of statistical ethylene–1-hexene copolymers.

Table 3. Relative reactivity constants of ethylene and 1-hexane in copolymerization on the *ansa*-metallocene catalysts based on **3** and **4**

Metallocene	Activator	k_{eth}	k_{hex}	$k_{eth}k_{hex}$
3	MAO	15.2	0.048	0.73
3	(MMT-H_2O)/Al*i*-Bu_3	24.4	0.040	0.98
4	(MMT-H_2O)/Al*i*-Bu_3	27.6	0.038	1.05

CONCLUSIONS

The catalysts based on the zirconocene and hafnocene compounds immobilized on the support containing alkylaluminoxanes synthesized on its surface are very active in the polymerization processes considered here and do not need to be activated with oligomeric MAO or any other alkylaluminum. The effectiveness of the catalysts depends on the kind of metal (Zr, Hf), precatalyst composition and structure, and on the nature of the activator/support material. The higher effectiveness of the hafnocene catalyst immobilized on (MMT-H_2O)/Al*i*-Bu_3 as compared to the effectiveness of the homogeneous system Hf/MAO is apparently due to the changes in the properties of the polymerization-active Hf–C bond caused by the replacement of the methyl groups with isobutyl groups in the counterion making the intimate ion pair with the hafnocene cation in the catalytic complex. It is likely that the larger molar mass of the PE and ethylene–1-hexene copolymers synthesized on the immobilized MMT(H_2O)/Al*i*-R_3/M-cene catalysts as compared to the molar mass of the products obtained using the corresponding homogeneous systems is due to the steric hindrance caused by the support surface containing fixed alkylaluminoxane anions to β-hydride elimination. The formation of 1-hexene-rich copolymers in the presence of the immobilized metallocene catalysts is evidence that these catalysts inherit, from their homogeneous precursors, the important property of being highly selective toward the insertion of a higher α-olefin into the polymer macromolecule.

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