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Olefin Polymerization on Immobilized Zirconocene Catalysts Containing Alkylaluminoxanes Synthesized on the Support Surface

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Abstract—Ethylene and propylene polymerization on immobilized catalysts of composition MMT-H_2O/AlR_3/Zr-cene (MMT = montmorillonite) and on the corresponding homogeneous catalysts of composition Zr-cene–MAO (Zr-cene = *rac*-Et(Ind)$_2$ZrCl$_2$, *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$, *rac*-Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$, *rac*-1-(9-η^5-Flu)2-(5,6-Cp2-Me-1-η^5-Ind)Et]ZrCl$_2$) is considered. Here, the activating support for the zirconocenes is montmorillonite containing methylaluminoxane or isobutylaluminoxane synthesized directly on the monmorillonite surface by the partial hydrolysis of an alkylaluminum ($AlMe_3$, Al(*i*-Bu)$_3$, Al(*i*-Bu)$_2$H) with the mobile water of the support (MMT-H_2O/AlR_3). The MMT-H_2O/AlR_3 supports are demonstrated to be effective activators for *ansa*-zirconocenes. The catalytic properties of the immobilized systems (process kinetics and efficiency, the molar mass of the resulting polymer, and the structure of the macromolecules) depend on the activating support and the zirconocene precatalyst. The complexes of the MMT-H_2O/Al(*i*-Bu)$_3$ support with all zirconocene precatalysts are more active in propylene polymerization than the same complexes of MMT-$H_2O/AlMe_3$. The zirconocenes immobilized on MMT-H_2O/AlR_3 afford polyethylene and polypropylene with a higher molar mass than the corresponding homogeneous systems. Furthermore, immobilization causes active-site heterogeneity. As compared to the homogeneous single-site catalysts of composition Zr-cene–MAO, the corresponding catalysts immobilized on MMT-H_2O/AlR_3/Zr-cene are more stereospecific in the case of *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ (C_2 symmetry) and are less stereospecific in the case of *rac*-[1-(9-η^5-Flu)2-(5,6-Cp-2-Me-1-η^5-Ind)Et]ZrCl$_2$ (C_s symmetry).

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Various methods of preparing immobilized catalysts for olefin polymerization have been developed to date [1–3]. These methods are necessary to adapt the new generation of high-efficiency homogeneous metallocene catalysts to the existing gas-phase and slurry polymerization processes and to take advantage of the high activity and the stereoregulating and regioregulating properties of these catalysts in α-olefin homopolymerization and copolymerization. Another challenging problem is to find new metallocene precatalyst activators in order to replace methylaluminoxane (MAO), an expensive commercial activator.

Any known method of metallocene immobilization on a support surface has advantages and drawbacks that reveal themselves in olefin polymerization in the presence of the resulting catalysts [1–3]. The most common immobilization method is the adsorption of a zirconocene compound on the surface of a support (usually dehydrated SiO_2) pretreated with MAO [1, 3–9]. However, the SiO_2/MAO/metallocene catalysts require large amounts of MAO, an expensive commercial chemical, which is necessary for modifying the support surface and for raising the polymerization efficiency of the catalyst (SiO_2/MAO/metallocene–MAO system).

We have developed an immobilization method in which zirconocene compounds are activated by alkylaluminoxanes synthesized on the surface of highly hydrated aluminosilicates, such as montmorillonite (MMT-H_2O) and zeolites, by the partial hydrolysis of an alkylaluminum with the mobile water of the support to obtain a support–H_2O/AlR_3 system [9–13]. Unlike commercial MAO, which is tightly bound to dehydrated SiO_2, the aluminoxanes thus obtained are mainly bound by coordination bonds with surface –0-Al(R)$_2$ groups that have resulted from the reaction between AlR_3 and –OH groups of the support. This reaction takes place along with the partial hydrolysis of the alkylaluminum in the support–H_2O + AlR_3 system [9]. As a result, the aluminoxanes synthesized on the surface retain their most reactive alkyl groups and their structure is identical to the structure of the molecules of commercial MAO [9, 14]. The support–H_2O/AlR_3 system serves both as the support immobilizing the zirconium compound and as an effective activator of the cat-

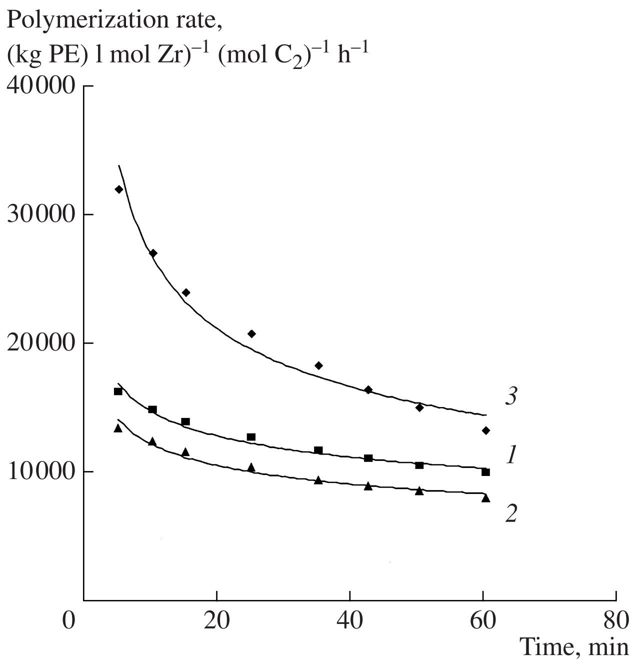

Fig. 1. Time dependence of the rate of ethylene polymerization on the immobilized catalysts (*1*) MMT-$H_2O/AlMe_3$/*rac*-Et(Ind)$_2$ZrCl$_2$ and (*2*) MMT-H_2O/Al(*i*-Bu)$_2$H/*rac*-Et(Ind)$_2$ZrCl$_2$ and (*3*) on the homogeneous catalyst *rac*-Et(Ind)$_2$ZrCl$_2$-MAO at $[C_2H_4] = 3.4 \times 10^{-2}$ mol/l and $T = 40$°C.

alytic system. Support–H_2O/AlR_3/Zr-cene catalysts (Zr-cene = Cp_2ZrCl_2, *rac*-Et(Ind)$_2$ZrCl$_2$, *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$) are as active as their homogeneous counterparts in olefin polymerization in the absence of external MAO or any other organoaluminum cocatalyst [9–14].

Here, we report ethylene and propylene polymerization on various immobilized MMT-H_2O/AlR_3/Zr-cene catalysts and in the presence of the corresponding homogeneous Zr-cene–MAO systems. This study was carried out to see how the catalytic properties of the immobilized systems depend on the nature of the activating support and the zirconocene precatalyst. We used *ansa*-substituted zirconocenes with different bridges, different η-ligands, and different substituents in the ligands (*rac*-Et(Ind)$_2$ZrCl$_2$, *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$, *rac*-Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$, and *rac*-[1-(9-η^5-Flu)-2-(5,6-Cp-2-Me-1-η^5-Ind)Et]ZrCl$_2$). The zirconocene-activating supports were montmorillonite containing MAO or isobutylaluminoxanes synthesized directly on its surface by the partial hydrolysis of alkylaluminums ($AlMe_3$, Al(*i*-Bu)$_3$, and Al(*i*-Bu)$_2$H) with the mobile water, namely, MMT-$H_2O/AlMe_3$, MMT-H_2O/Al(*i*-Bu)$_3$, and MMT-H_2O/Al(*i*-Bu)$_2$H.

EXPERIMENTAL

The zirconium compounds Et(Ind)$_2$ZrCl$_2$ (**1**) and Me$_2$Si(Ind)$_2$ZrCl$_2$ (**2**) (Aldrich) were used as received. Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$ (**3**) and *rac*-[1-(9-η^5-Flu)-2-(5,6-Cp-2-Me-1-η^5-Ind)Et]ZrCl$_2$ (**4**) were synthesized according to earlier reported procedures [15, 16]. Poly(methylaluminoxane) was used as a 10% solution in toluene; $AlMe_3$, as a 2 M solution in toluene; Al(*i*-Bu)$_3$ and Al(*i*-Bu)$_2$H, as 1 M solutions in toluene (all from Aldrich). The solvent was toluene (spectroscopic-purity grade) held over the molecular sieve 5A and distilled from $LiAlH_4$ in an argon atmosphere. Ethylene and propylene were polymerization-purity grade. All manipulations involved in catalyst preparation were made in vacuo or in argon purified in columns packed with a Ni–Cr catalyst and the molecular sieve 5A. The support was montmorillonite (Cloisite^{R}Na$^+$) with an internal 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 of MMT. The synthesis of alkylaluminoxanes on the MMT surface is described elsewhere [9, 14].

Ethylene and propylene polymerization in toluene below atmospheric pressure and propylene polymerization in the liquid monomer medium were carried out in temperature-controlled glass and steel reactors, respectively, under vigorous stirring. The monomer pressure and the polymerization temperature during the reaction were maintained constant. The experimental procedure is detailed elsewhere [10]. Polymerization was terminated by introducing a 5% solution of HCl in ethanol into the reactor. The resulting polymers were isolated by filtration, washed with ethanol, and dried in vacuo at 60°C. In order to remove the support, the polymers were treated with HF, filtered, washed with water and ethanol, and dried in vacuo at 60°C.

The molar mass characteristics (M_w, M_n, and M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) on a Waters 150C chromatograph at 140°C using *o*-dichlorobenzene as the mobile phase. M_n was also determined by the ozonation of terminal double bonds [17]. The viscosity-average molar mass (M_η) of the polymers was determined viscometrically in decalin at 135°C. Isotactic pentads in polypropylene samples were quantified by ^{13}C NMR spectroscopy. $C_2H_2Cl_4$ was added to polypropylene solutions in $C_2D_2Cl_4$ for stabilization of the magnetic field. ^{13}C NMR spectra were recorded at 87°C on a Bruker AC 200 spectrometer.

RESULTS AND DISCUSSION

Figure 1 compares the ethylene polymerization rate curves for the supported catalysts based on *rac*-Et(Ind)$_2$ZrCl$_2$ (**1**) and methylaluminoxane or isobutylaluminoxane synthesized on the MMT surface (MMT-$H_2O/AlMe_3$, MMT-H_2O/Al(*i*-Bu)$_2$H) and for the homogeneous catalytic system **1**/MAO (curves *1–3*, respec-

Table 1. Ethylene polymerization on MMT-$H_2O/AlR_3/Et(Ind)_2ZrCl_2$ supported catalysts

Entry	Activator	$Q_{Zr} \times 10^6$, mol/(g MMT)	$\frac{[Al]}{[Zr]}, \frac{mol}{mol}$	T_{pol}, °C	W	A_{PE}	$\bar{M}_w \times 10^{-3}$, g/mol	$\frac{\bar{M}_w}{\bar{M}_n}$
1	MAO	4.0×10^{-5} mol/l	1100	40	45000	26000	180	3.0
2	MMT-$H_2O/AlMe_3$	2.4	2000	40	21230	14700	220	3.3
3	MMT-$H_2O/AlMe_3$	2.4	2270	55	37890	21450	85	4.2
4	MMT-$H_2O/AlMe_3$	2.4	2000	65	90120	54850	–	–
5	MMT-$H_2O/Al(i\text{-}Bu)_2H$	2.3	1700	40	17500	10050	260*	–
6	MMT-$H_2O/Al(i\text{-}Bu)_2H$	3.4	1500	65	31000	17760	102*	–

Note: $[C_2H_4] = 3.4 \times 10^{-2}$ mol/l.
Q_{Zr} is the zirconium content of the heterogeneous catalyst; W is the initial polymerization rate (at a polymerization time of 2 min), (kg PE) l (mol Zr)$^{-1}$ (mol C_2)$^{-1}$ h^{-1}; A_{PE} is the polyethylene yield after 1-h-long polymerization, (kg PE) l (mol Zr)$^{-1}$ (mol C_2)$^{-1}$.
* Viscosity-average molar mass.

tively). Clearly, the immobilization of **1** causes some decrease in the activity of the system. The catalyst immobilized on MMT-$H_2O/AlMe_3$ is more active than the catalyst containing MMT-$H_2O/Al(i\text{-}Bu)_2H$. At the same time, the time stability of the active metal–alkyl complexes in MMT-H_2O/AlR_3/**1** is higher than that of the similar homogeneous system **1**/MAO.

Ethylene polymerization between 40 and 65°C on MMT-$H_2O/AlMe_3$/**1** proceeds with a positive temperature coefficient. The polymer yield after 1-h-long polymerization at 40 and 65°C is, respectively, 14700 and 54850 kg PE l (mol Zr)$^{-1}$ (mol C_2)$^{-1}$ (Table 1). The activation energy of ethylene polymerization derived from the Arrhenius plot of the initial polymerization rate (Table 1, entries 2–4; polymerization time of 2 min) is 13.3 kcal/mol. Furthermore, it is clear from the data presented in Table 1 (entries 1, 2, 5) that the reactions in the presence of the immobilized catalysts MMT-$H_2O/AlMe_3$/**1** and MMT-$H_2O/Al(i\text{-}Bu)_2H$/**1** yield polyethylene with a higher molar mass (M_w = 220000 g/mol and M_η = 260000 g/mol, respectively) than the reaction in the presence of the homogeneous system **1**/MAO (M_w = 180000 g/mol). Raising the polymerization temperature causes a decrease in the molar mass of the polymer (Table 1; compare entry 2 to entry 3 and entry 5 to entry 6).

Propylene polymerization was studied in the presence of immobilized catalysts and on the corresponding homogeneous *ansa*-zirconocene-based catalysts with different η- and σ-bonded ligands, namely, *rac*-$Me_2Si(Ind)_2ZrCl_2$ (**2**), *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ (**3**), and *rac*-[1-(9-η^5-Flu)-2-(5,6-Cp-2-Me-1-η^5-Ind)Et]$ZrCl_2$ (**4**). The activating supports were MMT-$H_2O/AlMe_3$ and MMT-$H_2O/Al(i\text{-}Bu)_3$. The polymerization conditions were identical for all catalytic systems containing the same precatalyst. The propylene polymerization efficiency of an MMT-H_2O/AlR_3/Zr-cene catalyst depends on the composition and structure of the zirconocene compound (Table 2), as in the case of the corresponding homogeneous system, and on the nature of the activating support. The highest polymer yield is observed for the catalysts involving precatalyst **3**. As compared to methylaluminoxane in MMT-$H_2O/AlMe_3$, isobutylaluminoxane synthesized on the montmorillonite surface forms more active metal-alkyl complexes with all of the zirconocenes examined. At 50°C and a low propylene concentration of 0.1 mol/l, MMT-$H_2O/Al(i\text{-}Bu)_3$/**3** is catalytically more active than the corresponding homogeneous system **3**/MAO. The polymer yield after 1-h-long polymerization is 23280 and 17550 kg PP l (mol Zr)$^{-1}$ (mol C_3)$^{-1}$, respectively.

The possibility of enhancing the activity of catalytic systems involving substituted zirconocenes (Me_5-$CpZrCl_2$ and *rac*-Et(4,7-Me_2-Ind)$_2ZrCl_2$) by using β-alkyl-substituted aluminoxanes (isobutylaluminoxane and isooctylaluminoxane) as activators in place of methylaluminoxane was reported for homogeneous zirconocene catalysts for ethylene polymerization [19, 20]. Tritto et al. [20], who studied the interaction of Cp_2ZrCl_2 and Me_5-Cp_2ZrCl_2 with the above alkylaluminoxanes by ^{13}C NMR spectroscopy, inferred that the difference between the catalytic properties of methyl- and β-alkyl-substituted aluminoxanes manifests itself at the active site formation stage and can be explained in terms of the alkylating properties of the aluminoxanes and their capacity to stabilize ion pairs. Tritto et al. [20] believe that, as compared to MAO, isooctylaluminoxane more readily forms alkylated zirconocene ion pairs with Me_5-Cp_2ZrCl_2 that can be responsible for polymerization activity. The substituents in the cyclopentadienyl ligands of Me_5-Cp_2ZrCl_2 stabilize the alkylated zirconium compounds by offering steric hindrance to β-hydride transfer, a reaction breaking these compounds.

At the same time, this study demonstrates that the time stability of the catalysts containing supported isobutylaluminoxane (e.g., MMT-$H_2O/Al(i\text{-}Bu_3)$/**2** (Fig. 2) and MMT-$H_2O/Al(i\text{-}Bu)_3$/**3** (Fig. 3)) in propy-

Table 2. Activity of MMT-H_2O/AlR_3/Zr-cene immobilized and Zr-cene–MAO homogeneous catalysts in propylene polymerization

Entry	Zirconium compound	Activator	Zr content of the surface, wt %	[Al]/[Zr], mol/mol	$[C_3]$, mol/l	A_{PP}^{*}
1	**2**	MAO	0.7×10^{-5} mol/l	2500	0.13	7000
2	**2**	MMT-H_2O/$AlMe_3$	0.020	2200	0.13	1500
3	**2**	MMT-H_2O/Al(*i*-Bu_3)	0.020	2300	0.13	4550
4	**3**	MAO	3.7×10^{-5} mol/l	2200	0.10	17550
5	**3**	MMT-H_2O/$AlMe_3$	0.022	2240	0.10	6470
6	**3**	MMT-H_2O/Al(*i*-Bu_3)	0.022	2130	0.10	23280
7	**4**	MAO	1×10^{-5} mol/l	2500	0.20	7800
8	**4**	MMT-H_2O/$AlMe_3$	0.020	2500	0.20	2600
9	**4**	MMT-H_2O/$AlMe_3$	0.020	2400	9.60	3000
10	**4**	MMT-H_2O/Al(*i*-Bu_3)	0.020	2000	0.20	7000
11	**4**	MMT-H_2O/Al(*i*-Bu_3)	0.020	2000	9.60	7700

Note: $T_{pol} = 50°C$.
* Polypropylene yield after 1-h-long polymerization, (kg PP) l (mol Zr)$^{-1}$ (mol C_3)$^{-1}$.

lene polymerization is lower than the time stability of the catalysts prepared by the immobilization of the same zirconocene compounds on the MMT-H_2O/$AlMe_3$ surface.

Propylene polymerization in the presence of an MMT-H_2O/AlR_3/Zr-cene catalyst yields polypropylene with a higher molar mass than propylene polymerization in the presence of a Zr-cene–MAO system (Table 3). With **3** immobilized on MMT-H_2O/$AlMe_3$ and MMT-H_2O/Al(*i*-Bu)$_3$, the resulting polypropylene has M_η = 22000 and 41700 g/mol, respectively (Table 3, entries 2, 3); with **4** immobilized on the same supports, M_η = 39300 and 41000 g/mol, respectively (Table 3, entries 5, 7). Because of the lack of GPC data for these polymers, their MMD width is illustrated here by the ratio of M_η to the number-average molar mass determined by the ozonation of terminal double bonds [17] for polypropylene obtained on the supported and homogeneous catalyst based on **4** (Table 3). In the case of single-site homogeneous zirconocene catalysts, the polydispersity index (M_w/M_n) of polypropylene and polyethylene derived from GPC data is close to 2 [1, 21]. For example, for polypropylene synthesized at T = 50°C and $[C_3H_6]$ = 0.4 mol/l in the presence of **4**/MAO, M_w/M_n = 2.6 [16]. Under our experimental conditions

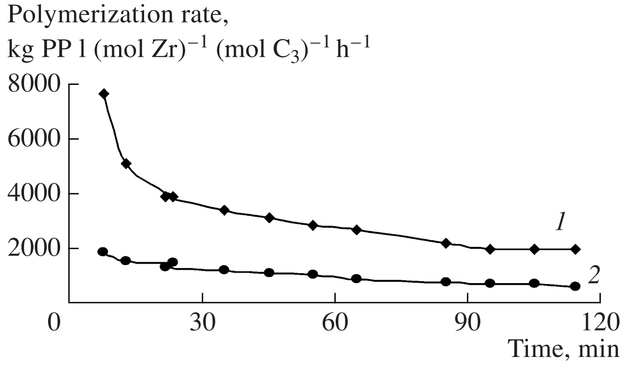

Fig. 2. Time dependence of the rate of propylene polymerization on (*1*) MMT-H_2O/Al(*i*-Bu)$_3$/*rac*-$Me_2Si(Ind)_2ZrCl_2$ and (*2*) MMT-H_2O/$AlMe_3$/*rac*-$Me_2Si(Ind)_2ZrCl_2$ at $[C_3H_6]$ = 0.13 mol/l and T = 50°C.

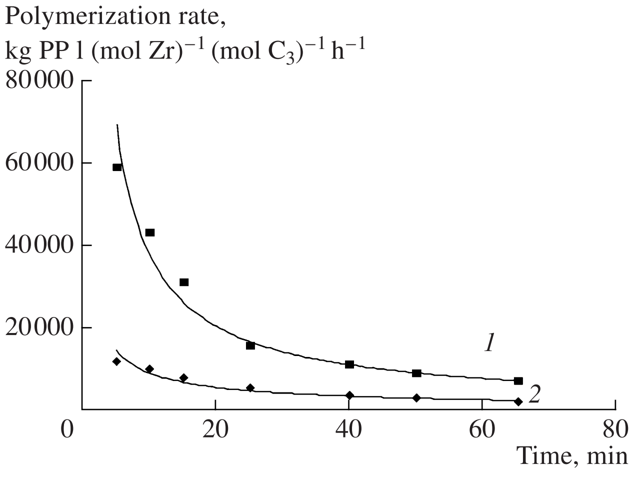

Fig. 3. Time dependence of the rate of propylene polymerization on (*1*) MMT-H_2O/Al(*i*-Bu)$_3$/*rac*-Me_2Si(2-Me-4-Ph-Ind)$_2ZrCl_2$ and (*2*) MMT-H_2O/$AlMe_3$/*rac*-Me_2Si(2-Me-4-Ph-Ind)$_2ZrCl_2$ at $[C_3]$ = 0.1 mol/l and T = 50°C.

Table 3. Molar mass characteristics of polypropylene synthesized on MMT-H_2O/AlR_3/Zr-cene immobilized and Zr-cene–MAO homogeneous catalysts*

Entry	Zirconium compound	Activator	$[C_3]$, mol/l	M_η, g/mol	M_n, g/mol	M_η/M_n
1	**3**	MAO	0.10	17300	–	–
2	**3**	MMT-H_2O/$AlMe_3$	0.10	22000	–	–
3	**3**	MMT-H_2O/Al(*i*-Bu)$_3$	0.10	41700	–	–
4	**4**	MAO	0.23	19000	8960	2.1
5	**4**	MMT-H_2O/$AlMe_3$	0.23	39300	10352	3.8
6	**4**	MMT-H_2O/$AlMe_3$	9.60	85500	23300	3.7
7	**4**	MMT-H_2O/Al(*i*-Bu)$_3$	0.23	41000	7558	5.4
8	**4**	MMT-H_2O/Al(*i*-Bu)$_3$	9.60	120000	22687	5.3

* For the polymerization condition, see Table 2.

Table 4. Stereoregularity of polypropylene obtained on MMT-H_2O/AR_3/Zr-cene immobilized catalysts

Entry	Zr-cene	Activator	$[C_3]$, mol/l	[*mmmm*], %	[*mmmr*], %	[*rmmr*], %	[*mmrr*], %	[*mmrm*] + [*rmrr*], %	[*mrmr*], %	[*rrrr*], %	[*mrrr*], %	[*mrrm*], %
1	**2**	MAO	0.13	67.8	18.3	–	8.5	–	–	–	–	5.4
2	**2**	MMT-H_2O/$AlMe_3$	0.13	85.6	5.5	–	4.9	–	–	–	–	4.0
3	**2**	MMT-H_2O/Al(*i*-Bu)$_3$	0.13	79.3	11.3	–	5.0	–	–	–	–	2.4
4	**3**	MAO	0.10	97.0	1.3	–	1.7	–	–	–	–	–
5	**3**	MMT-H_2O/$AlMe_3$	0.10	92.5	4.2	–	3.3	–	–	–	–	–
6	**3**	MMT-H_2O/Al(*i*-Bu)$_3$	0.10	89.4	4.4	–	4.1	2.1	–	–	–	–
7	**4**	MAO	0.20	75.8	10.3	–	8.5	1.8	–	–	–	3.6
8	**4**	MMT-H_2O/$AlMe_3$	0.20	48.0	18.7	–	14.0	6.4	2.4	2.0	2.8	5.7
9	**4**	MMT-H_2O/$AlMe_3$	9.60	38.5	11.1	3.2	19.6	7.4	2.2	4.0	4.0	10.0
10	**4**	MMT-H_2O/Al(*i*-Bu)$_3$	0.20	51.7	15.7	–	13.6	6.3	2.4	2.1	2.9	5.5

(T = 50°C and $[C_3H_6]$ = 0.23 mol/l), homogeneous **4**/MAO and the same precatalyst immobilized on MMT-H_2O/$AlMe_3$ and MMT-H_2O/Al(*i*-Bu)$_3$ afford polypropylene with M_η/M_n = 2.1, 3.8, and 5.4, respectively (Table 3, entries 4, 5, 7). Since $M_w > M_\eta$, the MMD width for polypropylene obtained with these catalysts is at least 3.8–5.4, indicating the heterogeneity of the active sites in the immobilized systems. Furthermore, raising the monomer concentration results in an increase in the molar mass of the polymer (Table 3; compare entry 5 to entry 6 and entry 7 to entry 8).

Table 4 lists data characterizing the stereoregularity of the resulting polypropylene. The isotactic pentad content of polypropylene synthesized on the immobilized catalysts depends on the composition and symmetry of the zirconocene compound, as in the case of the homogeneous systems. The activating support has only a weak effect on the stereospecificity of the catalysts. However, precatalysts **2** and **3** immobilized on MMT-H_2O/Al(*i*-Bu)$_3$ afford polypropylene with a lower isotacticity than the MMT-H_2O/$AlMe_3$/Zr-cene catalysts.

A comparison between the polypropylene stereoregularity data for the immobilized and the corresponding homogeneous catalysts shows that the immobilization of a catalytic complex on an activating support affects the stereospecificity of the system. This effect depends on the metallocene structure. For example, polypropylene obtained in the presence of the homogeneous catalyst based on **2**, a compound with C_2 symmetry, at T = 50°C and a low monomer concentration (Table 4, entry 1) has a comparatively low proportion (67.8%) of *mmmm* isotactic pentads, although it was found by other researchers [18, 22] that propylene polymerization on this catalyst in a liquid monomer medium affords highly isotactic polypropylene with *mmmm* > 80% even at 70°C. The immobilization of **2** on the MMT-H_2O/$AlMe_3$ or MMT-H_2O/Al(*i*-Bu)$_3$ surface enhances the stereospecificity of the catalyst. The isotactic pentad concentration in polypropylene obtained at a low propylene concentration of 0.13 mol/l increases from 67.8 to 85.6 or 79.2%, depending on the nature of the activating support (Table 4, entries 2, 3). As this takes place, the *mmmr*, *mmrr*, and *mrrm* stereoerror concentrations decrease.

At the same time, according to the data presented in Table 4 (entries 4–6), the stereoregularity of polypropylene obtained in the presence of the immobilized catalysts based on compound **3** (which has C_2 symmetry and 2,4-substituted indenyl ligands) is somewhat lower (*mmmm* = 92.5 and 89.4%) than the stereoregularity of propylene synthesized with the highly stereospecific homogeneous system **3**/MAO (*mmmm* = 97.0%).

The catalytic complexes that contain precatalyst **4** (C_s symmetry) and are formed on the activating supports MMT-H_2O/AlR_3 exhibit a lower stereospecificity than the homogeneous system **4**/MAO. The isotactic pentad content is 75.8% for the homogeneous system and takes smaller values of 48.0 and 51.7% for the catalysts immobilized on MMT-H_2O/$AlMe_3$ and MMT-H_2O/Al(*i*-Bu)$_3$, respectively. Furthermore, immobilization leads to an increase in the *mmmr, mmrr*, and *mrrm* stereoerror contents of the polymer (Table 4; compare entry 7 to entries 8 and 10). Based on the stereoerror formation mechanism suggested for propylene polymerization in the presence of the homogeneous system **4**/MAO [16], it can be assumed that the surface of the activating support in the immobilized catalysts based on **4** is another steric factor increasing the probability of the formation of these stereoerrors. As in the case of the homogeneous system **4**/MAO [16], raising the monomer concentration decreases the stereospecificity of the immobilized catalysts. For monomer concentrations of 0.20 and 9.60 mol/l, the isotactic pentad content of polypropylene synthesized on the MMT-H_2O/$AlMe_3$/**4** catalyst is 48.0 and 38.5%, respectively (Table 4, entries 8, 9).

CONCLUSIONS

Methylaluminoxane and isobutylaluminoxane synthesized on the montmorillonite surface are very effective activators for *absa*-zirconocenes with various η- and σ-bonded ligands. The metal–alkyl complexes formed by the activating support MMT-H_2O/Al(*i*-Bu)$_3$ with all *ansa*-zirconocenes are more active in propylene polymerization than the same complexes formed by MMT-H_2O/$AlMe_3$. The immobilization of the zirconocenes on the MMT-H_2O/AlR_3 surface affords polyethylene and polypropylene having a higher molar mass than the polymers synthesized in the presence of the corresponding homogeneous systems. Furthermore, immobilization causes active-site heterogeneity. The stereoregularity of polypropylene synthesized on the MMT-H_2O/AlR_3/Zr-cene catalysts is determined by the symmetry of the zirconocene and depends only slightly on the nature of the activating support. The changes in the polypropylene microstructure that result from replacing various homogeneous zirconocene catalysts with the respective immobilized catalyst can likely be explained in terms of the formation of complexes with different stereospecificities on the surface and the formation of multisite catalytic systems. Furthermore, the rather rigid fixation of the metallocene complexes on the surface of the activating support can affect the stereocontrol of the growth of polymer chains on catalytic sites.

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