Supported Zr- and Hf-cene Catalysts for Propylene Polymerization

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Summary: The supported metallocene catalysts were obtained on the layered silicate montmorillonite (MMT), using $AlMe_3$ and $AliBu_3$ for synthesis of alkylaluminoxane directly on a support surface, followed by metallocene supporting. It was shown that the MMT-H_2O/$AliBu_3$ forms with *ansa*-Zr-cenes of C_1 and C_2-symmetry the significantly more active supported metal-alkyl complexes in propene polymerization, than MMT-H_2O/$AlMe_3$. The MMT-H_2O/$AliBu_3$ is the effective activator of the *ansa*-Hf-cenes, in contrast to MAO and MMT-H_2O/$AlMe_3$, giving the high active supported catalysts for synthesis of isotactic and elastic polypropene. The character of influence of metallocene fixation on support on the isotactic pentad [mmmm] content in polymer, compared to homogeneous analogues, depends on the metallocene nature. The introduction of borate $Ph_3CB(C_6F_5)_4$ in the case of both Zr-cene and Hf-cene catalysts increases significantly the activity at the reduced ratio of Al/Zr, Hf (100–500 instead of 2000–3000) and stabilizes the catalytic complexes.

Keywords: metallocene catalyst; polymerization; polypropylene (PP)

Introduction

For an application of metallocene catalysts in modern industrial processes of polyolefin production, they have to be supported on solid carrier. One of the method of metallocene heterogenization is the synthesis of alkylaluminoxanes directly on a support surface by a reaction of partial hydrolysis of the aluminum alkyls with a mobile support water, followed by metallocene supporting.[1–3] The properties of alkylaluminoxane as an activator of metallocene, including the alkylating capacity and the possibility of ion pair stabilization, depend on the nature of the alkyl group bonded to aluminum, and the nature of metallocene in this problem is of importance.[4,5] In the paper the supported metallocene catalysts were obtained on the layered silicate montmorillonite (MMT), using $AlMe_3$ and $AliBu_3$ for synthesis of surface alkylaluminoxane, and the effect of alkyl group (CH_3-, iBu_3-) nature in MMT-H_2O/AlR_3, on the efficiency of supported *ansa*-metallocenes of different type in propene polymerization was investigated. It was considered the influence of fixation of *ansa*-metallocene precatalysts, differing by the symmetry type, nature of η-bonded ligands, the substitutes in the ligands, metal (Zr, Hf), on a support solid surface on the catalytic properties of formed supported catalysts in propene polymerization (activity, microstructure of obtained polypropene, molecular mass characteristics) in comparison with properties of analogous homogeneous systems,

Experimental Part

Materials

All procedures were carried out under an argon atmosphere. Toluene (Aldrich Co)

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was stored over 4 Å molecular sieves and distilled from sodium. Propene was of polymerization grade of purity. Montmorillonite (MMT) K-10 (Aldrich Co) was used as a support and contained 9.6 mas.% ($5.2 \cdot 10^{-3}$ mol/g_{MMT}) of mobile water.[6] MAO (10% solution in toluene), $AlMe_3$ (2M solution in toluene), $AliBu_3$ (1M solution in toluene) and $Ph_3CB(C_6F_5)_4$ were purchased from Aldrich Co. The *ansa*-zirconocenes *rac*-$Me_2Si(Ind)_2ZrCl_2$ **(1),** *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ (**2**), *rac*-[1-(9-η^5Flu)-2-(5,6-Cp-2-Me-1-η^5-Ind)Et]$ZrCl_2$ (**3**) and *ansa*-hafnocenes *rac*-$Me_2Si(Ind)_2HfCl_2$ **(1a),** *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2HfCl_2$ (**2a**), *rac*-[1-(9-η^5Flu)-2-(5,6-Cp-2-Me-1-η^5-Ind)-Et]$HfCl_2$ (**3a**) were used as precatalysts (Figure 1). Zirconocene (**1**) was purchased from Aldrich Co, compounds **1a**, **2** and **2a** were performed according to the procedures reported in,[7–9] compounds **3** and **3a** were synthesized and donated by B.Rieger.[10,11]

Preparation of Supported Metallocene Catalysts

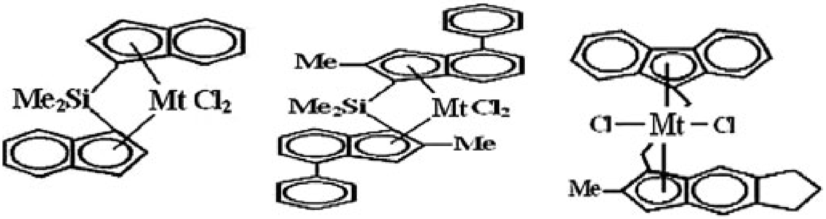
Methylaluminoxane and isobutylaluminoxane fixed on the support surface were synthesized by the reaction of partial hydrolysis of AlR_3 with MMT mobile water. The procedures were carried out in a 0.2 L glass reactor in vacuum, under vigorous stirring at 22 °C. Typically 0.2–1.0 g of MMT, containing $5.2 \cdot 10^{-3}$ mole of mobile H_2O in 1 g, was added gradually, over 20 min, to 30 ml of toluene containing calculated amount of $AlMe_3$ or $AliBu_3$ to give a molar ratio of $H_2O/AlR_3 = 1$. A mixture was stirred over 20 min, then gaseous products of the reaction were removed and the reactor was filled by Ar. A solution of metallocene in toluene was added to suspension of MMT with fixed aluminoxanes to form the supported catalysts MMT-H_2O/$AliBu_3$/Mt-cene for propene polymerization. Molar ratio Al/Mt was varied from 100 to 3700. The solution of $Ph_3CB(C_6F_5)_4$ in toluene was introduced into the system to obtain supported catalysts MMT-H_2O/$AliBu_3$/Mt-cene/B.

Propene Polymerization in Slurry and in Bulk

The experiments were performed in a 0.4 glass jacketed reactor with 70 ml of toluene as a solvent (polymerization in slurry) and in 0.4 L still reactor (polymerization in bulk), as described in [2]. The both reactors were equipped with stirrers. In the course of the experiments, the monomer concentration and temperature were kept constant and were varied from 0.1 to 9.6 mol/l and from 30 to 65 °C, respectively. A 5% HCl solution in ethanol was added to the reactor to stop polymerization.

Characteriation of PP

The molecular-weight characteristics were measured by viscosimetry in decaline at 135 °C and by GPC (Waters, 150C) in ortho-dichlorbensene at 140 °C. The polymer microstructure was determined by ^{13}C NMR spectroscopy. $C_2D_2Cl_4$ was added to the PP solution in $C_2H_2Cl_4$. ^{13}C NMR spectra were registered with spectrometer Bruker AC 200 at 360 K. Macrotacticity



Mt = Zr (**1**), Hf (**1a**) Mt = Zr (**2**), Hf (**2a**) Mt = Zr (**3**), Hf (**3a**)

Figure 1.
Structures of used zirconocenes and hafnocenes.

index was measured using the ratio D_{999}/D_{973} (Bruker TENSOR-27).

Results and Discussion

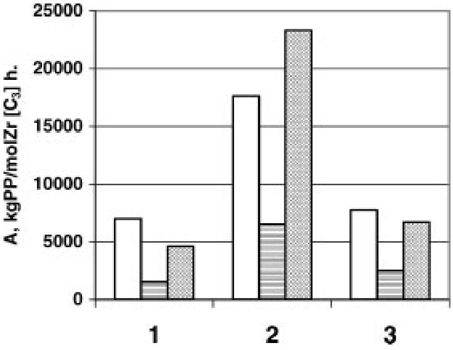


Figure 2.
Activity of MMT-H_2O/AlR_3/Zr-cene and Zr-cene/MAO catalysts in propene polymerization. 50 °C, Al/Zr = 2500, [C_3H_6], mol/l: 1,2–0.1, 3–0.2. Activators: - □ - MAO, ▤- MMT-H_2O/$AlMe_3$, ▨ - MMT-H_2O/Al(*i*-Bu)$_3$

The influence of alkyl group (CH_3-, iBu_3-) nature in alkylaluminoxane, synthesized on the support surface MMT-H_2O/AlR_3, on the efficiency of immobilized *ansa*-metallo (Zr, Hf)-cenes of different type in propene polymerization was investigated. The results obtained for the zirconocene supported catalysts are presented in Table 1 and Figure 2. As it is seen, the support-activator MMT-H_2O/$AliBu_3$ forms the significantly more active metal-alkyl complexes with all used ansa-zirconocenes **1, 2** and **3**, than MMT-H_2O/$AlMe_3$, on the propene polymerization in toluene as well as in liquid monomer. The most effect is reached for *ansa*-zirconocene **2** with substitutes in the indenyl ligands. The activity of the catalyst MMT-H_2O/$AliBu_3$/**2** comprises 23280 kg PP/mol Zr × h × [C_3H_6] at 50 °C (Table 1, Run 7), that corresponds by the order of value to the activity of the homogeneous **2**/MAO catalyst under the same conditions (17550 kg PP/mol Zr × h × [C_3H_6]) (Table 1, Run 4). Figure 3 (curve 1) shows the dependence of logarithm of the initial rate (polymerization time is 2 min) versus 1/T in the range of 40–60 °C for propene polymerization with MMT-H_2O/

Table 1.
Results of propene polymerization with the supported catalysts MMT-H_2O/AlR_3/Mt-cene and homogeneous catalysts Mt-cene/MAO.

Run.	Mt-cene	Activator	Al/Mt	t_{pol}, °C	[C_3], mol/l	A[a]	R_p[b]	Mη, g/cm³	II, % D_{999}/D_{973}	[mmmm], %
1	**1**	MAO	2500	50	0.13	7000	7800	12134	–	68.0
2	**1**	MMT-H_2O/$AlMe_3$	2200	50	0.13	1500	2500	–	–	85.6
3	**1**	MMT-H_2O/$AliBu_3$	2300	50	0.13	4550	12000	–	–	79,2
4	**2**	MAO	2200	50	0.1	17550	58500	17500	97.0	97.0
5	**2**	MMT-H_2O/$AlMe_3$	2240	50	0.1	6470	15000	32000	96.0	92.0
6	**2**	MMT-H_2O/$AliBu_3$	2600	40	0.1	10800	35600	141250	90.6	–
7	**2**	MMT-H_2O/$AliBu_3$	2130	50	0.1	23280	75700	62000	90.2	89.4
8	**2**	MMT-H_2O/$AliBu_3$	2400	60	0.1	31500	108200	–	–	85.8
9	**3**	MAO	2500	50	0.2	7440	7490	19000	77.8	75.8
10	**3**	MMT-H_2O/$AlMe_3$	3000	50	0.2	2500	3040	39300	–	48.0
11	**3**	MMT-H_2O/$AlMe_3$	4000	50	9.6	3000	–	85500	52.4	38.5
12	**3**	MMT-H_2O/$AlMe_3$	2500	70	0.2	5950	9360	waxes	–	–
13	**3**	MMT-H_2O/$AliBu_3$	1800	50	0.2	6700	9400	41000	76.6	51.7
14	**3**	MMT-H_2O/$AliBu_3$	2700	50	9.6	6800	–	120000	70.5	50.3
15	**1a**	MMT-H_2O/$AliBu_3$	3000	50	0.1	1700	7500	–	–	64.3
16	**2a**	MMT-H_2O/$AliBu_3$	2300	50	0,1	35800	75900	13800	85.0	–
17	**3a**	MMT-H_2O/$AliBu_3$	2800	30	0.2	2250	4900	–	47.0	–
18	**3a**	MMT-H_2O/$AliBu_3$	2100	40	0.2	5625	7380	–	55.7	–
19	**3a**	MMT-H_2O/$AliBu_3$	3700	50	0.2	7600	12060	–	–	44.9
20	**3a**	MMT-H_2O/$AliBu_3$	2000	50	9.6	6000	–	140000	50.4	50.5
21	**3a**	MMT-H_2O/Al(iBu)$_3$	2450	65	0.2	26200	83600	wax	–	–

[a] A – activity, kg PP/mol Zr × h × [C_3H_6];
[b] Rp – the initial polymerization rate, kg PP/mol Zr × h × [C_3H_6] (polymerization time is 2 min).

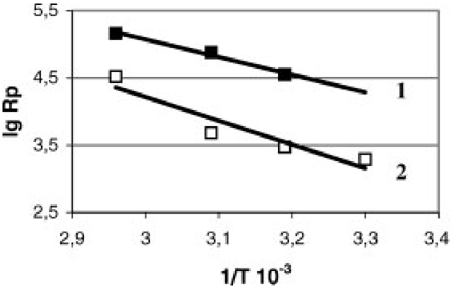


Figure 3.
Arrhenius plot for propene polymerization on supported Mt-cene catalysts. 1- MMT-H_2O/Al(*i*-Bu)$_3$/**2**, 2-MMT-H_2O/Al(*i*-Bu)$_3$/**3a**.

$AliBu_3$/**2.** The dependence is linear, and the activation energy is equal to 47,5 kJ/mol.

In the case of the asymmetric *ansa*-substituted zirconocene **3**, the activity of the supported catalyst MMT-H_2O/$AliBu_3$/**3** at 50 °C is practically equal to the activity of homogeneous catalyst **3**/MAO under similar conditions. At that, on polymerization in toluene and in liquid propene the supported catalyst shows the identical activity, related to the monomer concentration (Table 1, Runs 9–14). The immobilization of the metallocene complexes on the support-activator surface affects the stereospecific properties of a catalyst, and a character of influence depends on a metallocene structure. A homogeneous zirconocene catalyst **1** (C_2-symmetry) gives with MAO an isotactic polypropene. An isotactic pentad [mmmm] content in polymer depends on a monomer concentration,[12] and it is 90% for polymer, obtained at 50 °C in liquid monomer polymerization,[13] whereas according to our data it is only 68% (Table 1, Run 1) for polymer, obtained in toluene polymerization at propene concentration equal to 0,13 mol/l. The immobilization of this catalyst on MMT-H_2O/AlR_3 results to a high degree of polymer isotacticity ([mmmm] = 86–79,2%) already at a low propylene concentration 0.13 mol/l (Table 1, Runs 2,3). A high isospecific homogeneous catalyst, which includes precatalyst **2** with 2-Me- and 4-Ph- substitutes in the indenyl ligands, gives a polymer with [mmmm] = 97% already at low monomer concentration (Table 1, Run 4). After immobilization of this catalyst, the synthesized PP is characterized by close content of isotactic pentads [mmmm] = 92–89.4% (Table 1, Runs 5,7) at the same monomer concentration.

It should be noted that support-activator MMT-H_2O/$AliBu_3$ with both zirconocenes **1** and **2** (Table 1, Runs 3, 7) gives PP having slightly lower isotacticity than MMT-H_2O/$AlMe_3$ (Table 1, Runs 2,5).

The homogeneous catalyst, based on the asymmetric *ansa*-zirconocene **3** and MAO, allows one to introduce single stereoerrors into an isotactic polypropylene chain and to produce elastic polypropylene, according to "dual-side" mechanism.[10] An increase of a monomer concentration leads to an decrease of isotactic pentad content in polymer for this homogeneous catalyst.[10] For the immobilized catalysts MMT-H_2O/AlR_3/**3** we observed the same dependence Table 1. However, an isotactic pentad content in polymer, obtained at low monomer concentration with the immobilized catalyst is significantly lower (48 and 51.7%, Table 1, Runs 10,13) than in polymer, prepared under the same conditions with homogeneous **3/**MAO (75.8%) (Table 1, Run 9). It can be assumed that the support surface, at which a precatalyst is fixed, is an supplementary steric factor responsible for the increase of probability of stereoerrors formation by "dual-side" mechanism.

The heterogenization of zirconocenes is accompanied by the increase of molecular weight of the obtained polymer in comparison with one, prepared with homogeneous analogues (Table 1). Increasing the monomer concentration and decreasing the polymerization temperature lead to the rise of molecular weight of polypropene synthesized with supported catalysts.

It is known, that Hf-cenes are very poorly activated by MAO. The activity of Hf-cene/MAO complexes is negligible compared to the Zr analogues after MAO activation.[11,14] The same we observed, when used MMT-H_2O/$AlMe_3$ as the support-activator for the Hf-cene complexes. At the same time, the immobilization of

Hf-cenes **1a, 2a, 3a** on MMT-H_2O/AliBu$_3$ leads to the formation of high active in propene polymerization catalysts, and the level of their activity depends on the ansa-Hf-cene structure (Table 1, Runs 14,15,18). Activity of supported catalysts MMT-H_2O/AliBu$_3$/Hf-cene is close to the activity of MMT-H_2O/AliBu$_3$/Zr-cene (**1,2,3**) catalysts (Table 1, Figure 4).

So, Hf-cene **2a** gives with MMT-H_2O/AliBu$_3$ even the more active catalyst, than Zr-cene **2**.

The asymmetric Hf-cene **3a** (the structural analogue of zirconocene **3**), heterogenized at MMT-H_2O/AliBu$_3$, on polymerization at 50 °C both in liquid propene and in toluene shows the high activity 6000–7600 kg PP/mol Hf $\times$ h $\times$ [C_3H_6] (Table 1, Runs 20,19), that is the same as was obtained for suitable Zr complex (6800–7700 kg PP/mol Zr $\times$ h $\times$ [C_3H_6]), (Table 1, Runs 14,13). The propene polymerization catalyzed by the supported Hf-cene **3a** occurs with positive coefficient with activation energy is equal to 52.4 kJ/mol (Figure 3, curve 2). The molecular weights of polymers, obtained in liquid propylene with both catalysts, based on **3** and **3a**, are similar and equal to 120000–140000 at 50°C (Table 1, Runs 15,21). The isotacticity of the elastic PP, prepared with the supported Hf-cene **3a** ([mmmm] = 44.9–50.5) and Zr-cene **3** ([mmmm] = 50.3–51.7) are very closely (Table 1, Runs 19,20 and13,14).

As it is well known, the active in polymerization cationic metallocene complexes are formed on the interaction of metallocene dimethyl with the strong Lewis acids such as borates. For an activation of homogeneous systems based on metallocene dichlorides, the borates are used together with AlR_3 (usually AliBu$_3$) for alkylation. For obtaining the high active supported metallocene catalysts, we used also the alkylaluminoxanes, prepared *in situ* on a support surface (MMT-H_2O/AlR_3), in combination with borate $Ph_3CB(C_6F_5)_4$ (Table 2, Figure 5,6). Such combination allows one to obtain the high activity in polymerization and to reduce the amount of Al-organic compound on the stage of supported catalyst formation.

The kinetic curves of propene polymerization with the catalysts of C_2-symmetry Zr-cene **2** and Hf-cene **1a**, activated by MMT-H_2O/AliBu$_3$ and MMT-H_2O/AliBu$_3$ + $Ph_3CB(C_6F_5)_4$ are presented in Figure 5. The introduction of borate in the case of both catalysts gives significant increasing the polymerization rate at the reduced ratio of Al/Zr, Hf (100–500 instead of 2000–3000). The action of borate shows itself also as stabilization of catalytic

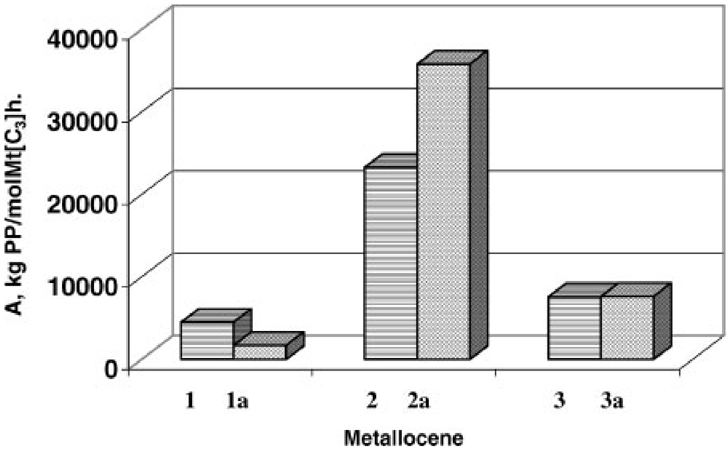


Figure 4.
Activity of supported catalysts MMT-H_2O/Al(*i*-Bu)$_3$/Zr-cene (**1,2,3**) and MMT-H_2O/Al(*i*-Bu)$_3$/Hf-cene (**1a,2a,3a**) in propene polymerization. 50 °C.

Table 2.
Influence of borate $Ph_3CB(C_6F_5)_4$ on propene polymerization with $MMT-H_2O/AliBu_3$/Mt-cene.

Run	Mt-cene	Al/Mt	B/Mt	T, °C	$[C_3]$, mol/l	$A^{a)}$	M_η	*II*, % D_{999}/D_{973}	[mmmm], %
1	**2**	2600	–	40	0.1	10800	141250	90.6	–
2	**2**	552	–	40	0.1	2070	–	86.0	–
3	**2**	450	4	40	0.13	24400	–	94.0	90.6
4	**2**	552	4	40	0.25	17300	300000	95.0	–
5	**2**	500	4	40	0.325	20500	316000	96.0	–
6	**2**	170	4	40	0.13	10770	–	98.0	–
7	**1a**	3000	–	50	0.13	1700	–	–	64.3
8	**1a**	500	4	50	0.13	3000	131000	84.0	70.0
9	**3a**	3700	–	50	0.2	7630	–	–	44.9
10	**3a**	500	–	50	0.2	2760	–	–	–
11	**3a**	500	4,3	50	0.2	5200	–	63.3	20.7
12	**3a**	500	4,6	50	0.97	10400	–	37.5	24.7
13	**3a**	523	4,6	50	9.6	12000	–	41.6	30.3
14	**3a**	108	4,9	50	0.13	8350	–	36.0	–

a) A – activity, kg PP/mol Zr × h × $[C_3H_6]$.

complexes. The propene polymerization on the supported Zr- and Hf-cenes, modified by borate, occurs with constant rate. The activating action of borate on the supported asymmetric Hf-cene **3a** at low Al/Hf ratio is shown in Figure 6, but the stabilization of polymerization rate takes place in this case not from the outset of process.

As evident from Table 2 (Runs 1–6) for the isospecific supported Zr-cene catalyst **2,** the introduction of $Ph_3CB(C_6F_5)_4$ leads to the rise of PP molecular weight and the isotacticity index (*II*). The increase of isotactic pentad [mmmm] content in polymer with the borate introduction from 64.3% (without borate) to 70% is observed also for the supported Hf-cene catalyst **1a** (Tab.II, Runs 7,8). In contrast to this, for the Hf-cene catalyst **3a,** producing the elastic PP, a borate decreases the isotactic pentad [mmmm] content in polymer from 44.9% (without borate) to 20.7% under similar other conditions (Table 2, Runs 9–11). When borate is presence, increasing the monomer concentration (0.2–9.6 mol/l) is accompanied by a rise of [mmmm] in PP from 20.7 to 30.3% for Hf-cene catalyst **3a** (Table 2, Runs 11–13).

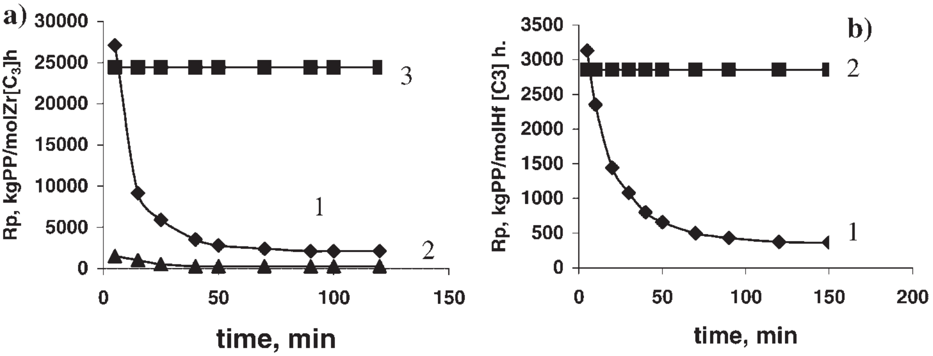


Figure 5.
The influence of $Ph_3CB(C_6F_5)_4$ on the activity of supported catalysts $MMT-H_2O/AliBu_3$/**2** (a) and $MMT-H_2O/AliBu_3$/**1a** (b) in propene polymerization. $[C_3H_6] = 0.1$ mol/l. (a) 40 °C, catalysts: 1 - $MMT-H_2O/AliBu_3$/**2,** Al/Zr = 2600; 2 - $MMT-H_2O/AliBu_3$/**2,** Al/Zr = 550; 3 - $MMT-H_2O/AliBu_3$/**2**/B, Al/Zr = 450, B/Zr = 4. (b) 50 °C, catalysts: 1 - $MMT-H_2O/AliBu_3$/**1a,** Al/Zr = 3000; 2 - $MMT-H_2O/AliBu_3$/**1a**/B, Al/Zr = 500, B/Zr = 4.

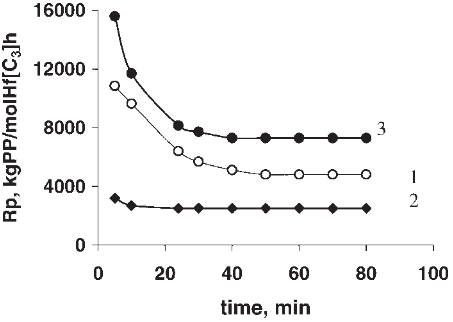


Figure 6.
The influence of $Ph_3CB(C_6F_5)_4$ on the activity of supported catalyst MMT-H_2O/AliBu$_3$/**3a** in propene polymerization. 50 °C, $[C_3H_6] = 0.2$ mol/l. Catalysts: 1 - MMT-H_2O/AliBu$_3$/**3a**, Al/Zr = 3700; 2 - MMT-H_2O/AliBu$_3$/**3a**, Al/Zr = 500; 3 - MMT-H_2O/AliBu$_3$/**3a**/B, Al/Zr = 500, B/Zr = 4.3.

Conclusion

In the supported on montmorillonite metallocene catalysts, using $AlMe_3$ and $AliBu_3$ for synthesis of alkylaluminoxane directly on a support surface, followed by metallocene supporting, the support-activator MMT-H_2O/AliBu$_3$ forms with *ansa*-Zr-cenes of C_1 and C_2-symmetry the significantly more active in propene polymerization supported metal-alkyl complexes, than MMT-H_2O/AlMe$_3$. It was shown that MMT-H_2O/AliBu$_3$ is the effective activator of the *ansa*-Hf-cenes in contrast to MAO and MMT-H_2O/AlMe$_3$. giving the high active supported catalysts for synthesis of isotactic and elastic polypropene. The character of influence of metallocene fixation on support on the isotactic pentad [mmmm] content in polymer, compared to homogeneous analogues, depends on the metallocene nature. The introduction of borate $Ph_3CB(C_6F_5)_4$ in the case of both Zr- and Hf-cene catalysts increases significantly the activity at the reduced ratio of Al/Zr, Hf (100–500 instead 2000–3000) and stabilizes the catalytic complexes. The monomer concentration affects the stereoselectivity of supported metallocene catalysts, and the character of effect is up to metallocene nature.

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