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Study of propylene polymerization using zirconocenes $\text{Ph}_2\text{CCpFluZrCl}_2$ and $\text{rac-Me}_2\text{Si}(2\text{-Me},4\text{-PhInd})_2\text{ZrCl}_2$ activated by combined MAO/TIBA cocatalyst

Summary — Zirconocenes $\text{Ph}_2\text{CCpFluZrCl}_2$ (1) and $\text{rac-Me}_2\text{Si}(2\text{-Me},4\text{-PhInd})_2\text{ZrCl}_2$ (2) first preactivated with methylalumoxane (MAO) at rather low $\text{Al}_{\text{MAO}}/\text{Zr}$ molar ratio = 20–300 mol/mol and further activated either traditionally with MAO or non-traditionally with triisobutylaluminum (TIBA) have been studied and compared from the point of view of catalysts' activity in propylene polymerizations. The dependence of catalyst productivity on molar ratio of components has been analyzed. It has been shown by ^1H NMR that mainly tetraisobutyl alumoxane (TIBAO) was formed at about equimolar MAO/TIBA ratios thus assuming TIBAO participation in initiation of the catalysts in examined systems. It has been shown that TIBAO provides higher catalytic activity compared to MAO at lower cocatalyst (activator)/catalyst molar ratios and allows conducting of propylene polymerization in the medium of heptane.

Key words: propylene polymerization, metallocene catalyst, methylalumoxane, triisobutylaluminum, catalyst activity.

BADANIE POLIMERYZACJI PROPYLENU WOBEC CYRKONOCENÓW $\text{Ph}_2\text{CCpFluZrCl}_2$ i $\text{rac-Me}_2\text{Si}(2\text{-Me},4\text{-PhInd})_2\text{ZrCl}_2$ AKTYWOWANYCH UKŁADEM KOKATALIZATORÓW MAO/TIBA

Streszczenie — Cyrkonoceny $\text{Ph}_2\text{CCpFluZrCl}_2$ (1) i $\text{rac-Me}_2\text{Si}(2\text{-Me},4\text{-PhInd})_2\text{ZrCl}_2$ (2) wstępnie aktywowano metyloalumosanem (MAO) w warunkach względnie małej wartości stosunku molowego $\text{Al}_{\text{MAO}}/\text{Zr} = 20\text{--}300$, a następnie aktywowano je po raz drugi bądź w typowy sposób za pomocą MAO, bądź też triizobutyloglinem (TIBA). Zbadano zależność aktywności katalitycznej tak uzyskanych układów w procesie polimeryzacji propylenu — w tradycyjnym środowisku toluenu albo, korzystniejszym, heptanu — od stosunku molowego $\text{Al}_{\text{kokatal.}}/\text{Zr}$ (tabele 1 i 2, rys. 1 i 4). Metodą ^1H NMR udowodniono, że zastosowanie zbliżonego do równomolowego stosunku MAO/TIBA prowadzi do utworzenia przede wszystkim tetraizobutyloalumosanu (TIBAO) (rys. 2). Oznacza to, że TIBAO uczestniczy w inicjowaniu polimeryzacji wobec badanych układów katalitycznych. Stwierdzono również, że TIBAO przyczynia się do większej w porównaniu z MAO aktywności katalizatorów (z zachowaniem mniejszych stosunków molowych aktywatora do katalizatora) oraz umożliwia prowadzenie polimeryzacji propylenu w środowisku heptanu.

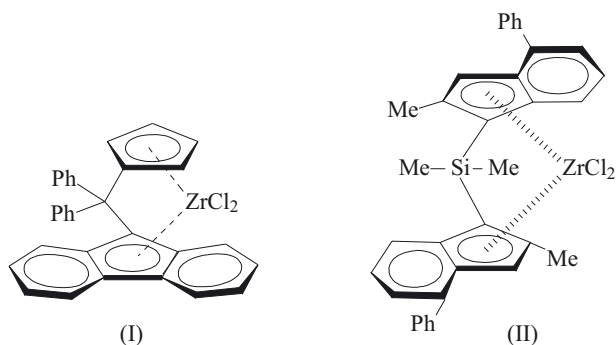
Słowa kluczowe: polimeryzacja propylenu, katalizator metalocenowy, metyloalumosan, triizobutyloglin, aktywność katalityczna.

Methylalumoxane (MAO), perfluorophenyl borane, borates, and aluminates are the most commonly used activators for IVB group metallocene derived catalysts for olefin polymerization [1–3]. MAO provides highly active catalytic systems however usually at very large molar excess to metallocene. High cost of MAO makes significant limitations for large scale polyolefin production with this activator. Higher alkylalumoxanes (HAO) and their modified versions [4–9] as well as tetraalkylalumoxanes (TAAO) [4–6, 10–12] have been reported in some cases as much more effective cocatalysts compared to MAO. However both commercial HAO and

TAAO are not cheaper than MAO; TAAO are besides inclined to association under storage which may cause reduction of Lewis acidity of the cocatalysts.

The possibility of effective activation of metallocene dichlorides in ethylene and propylene polymerizations by successive preactivation of metallocene with MAO at lower MAO/catalyst molar ratios inadequate for catalyst activation with following activation with triisobutylaluminum (TIBA) has been reported by several authors [13–15]. However there were no clear evidences about the role of TIBA in these combined catalytic systems with lower MAO content.

In this paper we report a detailed investigation of such an approach to activation of zirconocenes $\text{Ph}_2\text{CCpFluZrCl}_2$ (1) [formula (I)] and *rac*- $\text{Me}_2\text{Si}(2\text{-Me},4\text{-PhInd})_2\text{ZrCl}_2$ (2) [formula (II)] in propylene polymerization by successive preactivation of the catalyst with



(I) diphenylmethyl(1-cyclopentadienyl) (1-fluorenyl) zirconiumdichloride
 (II) *rac*-dimethylsilyl-bis(2-methyl-4-phenyl-1-indenyl) zirconiumdichloride

MAO at low $\text{Al}_{\text{MAO}}/\text{Zr}$ molar ratios and following activation with TIBA. The dependence of activity on the molar ratio of the components and sensitivity of examined catalytic systems to solvent used (toluene or heptane) have been analyzed and compared with those for catalysts activated only with MAO.

EXPERIMENTAL

Materials

Toluene and heptane (special purity grade, used as solvents) were distilled over LiAlH_4 and stored over 4A molecular sieves under atmosphere of dry argon.

Cocatalysts: MAO (Witco) was used as a 10 % solution in toluene, TIBA (Aldrich) was used as a 1 M solution in toluene.

The catalysts 1 and 2 (Boulder Scientific Co.) were purified by recrystallization in toluene/heptane before use.

Argon was dried by passing through a column with activated molecular sieves 5A. All the procedures on preparation of catalytic systems have been carried out under atmosphere of dry argon.

Reaction of MAO with TIBA

A solution of MAO was mixed with a TIBA solution (both in toluene) at a specified molar ratio of Al_{MAO} to Al_{TIBA} . The mixture was stored for 1 h at room temperature. After that the mixture has been placed into 5 mm NMR ampoule capped with special resin septa using gas-tight syringe. In this way tetraisobutylaluminum (TIBAO) was received and ^1H NMR spectra of the pro-

ducts were recorded using a "Bruker DPX_200" spectrometer (200.13 MHz).

Propylene polymerization

Polymerizations were conducted in a thermostatically controlled 80 ml Schlenk flask equipped with magnetic stirrer. Toluene (heptane), the cocatalysts (MAO, TIBA or TIBAO), propylene and zirconocene 1 or 2 preactivated with appropriate amount of MAO were introduced into the reactor in this order. The propylene pressure (including toluene vapor overpressure) was maintained as the constant value of 0.1 MPa (1 atm) during polymerization. The polymerization was terminated by pouring of acidified ethanol into the reactor. The precipitated polymer was washed by ethanol/water mixture and dried in vacuum at 60 °C to constant weight.

RESULTS AND DISCUSSION

Propylene polymerization with catalyst 1 activated with MAO or MAO/TIBA cocatalysts

To compare MAO and alternatively TIBA ability to activate the catalyst in propylene polymerization from the point of view of catalyst productivity we have chosen similar way of proceedings in the catalyst preactivation by preliminary dissolution of the catalyst moiety in MAO at fixed $\text{Al}_{\text{MAO}}/\text{Zr}$ molar ratio. All the polymerization experiments have been conducted at temp. 30 °C. The main results are reported in Table 1.

The productivity of the catalyst preactivated with MAO at $\text{Al}_{\text{MAO}}/\text{Zr} = 300$ mol/mol and further activated with additional amount of MAO exponentially decreases with increase in $\text{Al}_{\text{MAO}(\text{total})}/\text{Zr}$ from 500 to 3000 mol/mol (entries 1–5 in Table 1). The highest activity equal 1280 kg/(mol Zr · h · atm) was observed at $\text{Al}_{\text{MAO}(\text{total})}/\text{Zr} = 500$ mol/mol (entry 1). It should be mentioned that similar deactivating effect of MAO at increased $\text{Al}_{\text{MAO}}/\text{Zr}$ molar ratios has been reported for structurally related catalyst $\text{Me}_2\text{CCpFluZrCl}_2$ in propylene polymerization [16, 17]. The catalyst under activation with MAO shows rather stable propylene consumption rate-time resolved profiles at all examined molar ratios of MAO (Fig. 1a). The presence of induction periods has been observed at low $\text{Al}_{\text{MAO}}/\text{Zr}$ molar ratios (curves 1, 2) indicating that the process of active species formation is not very fast for the catalyst.

The catalyst showed no activity under activation with TIBA only (entry 6, Table 1) as well as under preactivation with MAO at lowest $\text{Al}_{\text{MAO}}/\text{Zr}$ molar ratio of only 20 mol/mol (entry 7). Increase in $\text{Al}_{\text{MAO}}/\text{Zr}$ molar ratio to 100 mol/mol with following activation with TIBA at $\text{Al}_{\text{TIBA}}/\text{Zr} = 100$ mol/mol provided rather active catalytic systems. Interestingly the catalyst shows nearly equal productivity in toluene and heptane (entries 8, 9, respectively). So far as aliphatic solvents are of higher

Table 1. Propylene polymerization^{a)} with catalyst 1 preactivated with MAO with following activation with different activators Y (Y = MAO, TIBA or TIBAO)

Entry	Cocatal. (Y)	Solvent	Al _{MAO} /Zr mol/mol (preactivation)	Al _Y /Zr mol/mol	t, min	Polym. yield, g	A ^{b)}
1	MAO	toluene	300	200	19	0.81	1280
2	MAO	toluene	300	500	16	0.46	860
3	MAO	toluene	300	700	37	0.56	570
4	MAO	toluene	300	1100	42	0.58	420
5	MAO	toluene	300	2700	60	0.42	260
6	TIBA	toluene	—	600	30	—	—
7	TIBA	toluene	20	600	30	—	—
8	TIBA	toluene	100	100	32	0.67	830
9	TIBA	heptane	100	100	20	0.72	850
10	TIBA	heptane	300	100	20	0.77	1450
11	TIBA	heptane	300	200	15	0.94	1880
12	TIBA	heptane	300	300	16	1.23	2310
13	TIBA	heptane	300	400	20	1.06	2000
14	TIBA	heptane	300	600	17	0.88	1960
15	TIBAO	toluene	300	300	20	0.93	1740

^{a)} Polymerization conditions: p = 0.1 MPa (1 atm), [Zr] = 1 · 10⁻⁴ mol/L, temp. 30 °C, volume of liquid phase 20 ml.

^{b)} A = activity in kg of PP/(mol Zr · h · atm).

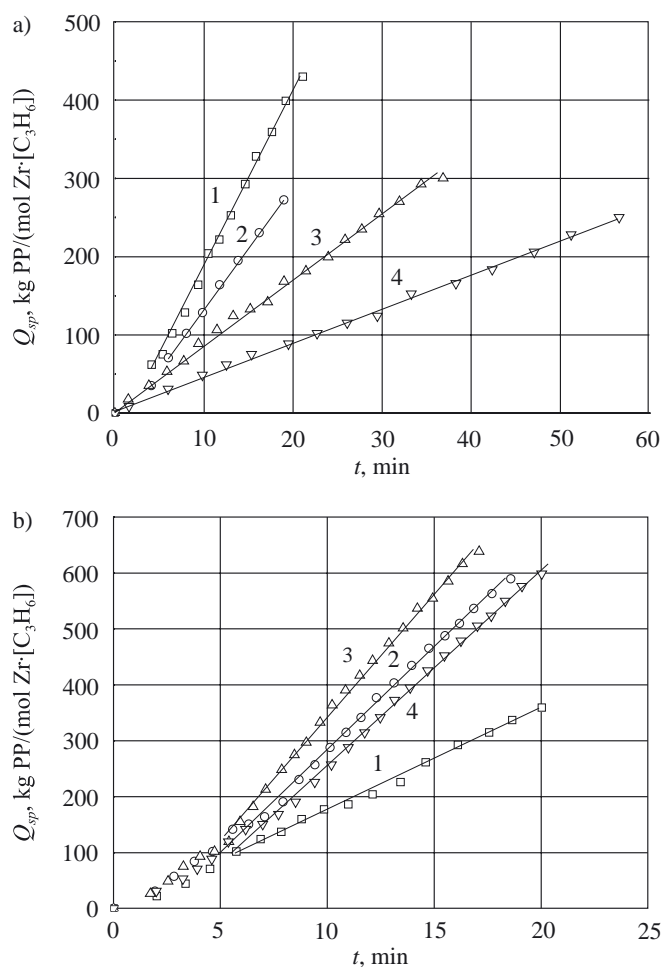


Fig. 1. Dependence of propylene consumption (Q_{sp}) by (1 + MAO)/X [X = MAO (a) or TIBA (b)] on reaction time (t); Al_{MAO}/Zr (preactivation) = 300 mol/mol: (a) solvent toluene, Al_{MAO}/Zr: 500 (1), 800 (2), 1000 (3), 3000 (4) mol/mol; (b) solvent heptane, Al_{TIBA}/Zr: 100 (1), 200 (2), 300 (3), 400 (4) mol/mol

practical value than toluene, the following set of propylene polymerization experiments, aimed to reveal the effect of Al_{TIBA}/Zr molar ratio on catalyst productivity, has been conducted in the medium of heptane (entries 10–14). Incremental increase in Al_{TIBA}/Zr molar ratio from 100 to 300 enlarged the catalyst productivity to the highest value of 2310 kg/(mol Zr · h · atm) with following lowering at higher Al_{TIBA}/Zr molar ratios. One can see that activity of the catalyst after preactivation with MAO at Al_{MAO}/Zr = 300 mol/mol with following activation with TIBA is considerably higher than with MAO and less sensitive to Al_{cocatalyst}/Zr molar ratio. Propylene consumption time resolved profiles (Fig. 1b) are very similar to those under activation with MAO however with somewhat higher values of induction periods.

To speculate about the role of TIBA in examined catalytic systems with combined MAO/TIBA activator we would like to make reference to our previous results on ¹H NMR analyses of MAO/TIBA reaction products formed at varying molar ratio of reagents [18]. It has been shown that at Al_{TIBA}/Al_{MAO} = 0.06 mol/mol ratio, the reaction between MAO and TIBA involves partial replacement of the methyl group of MAO by isobutyl groups of TIBA and yields mixed isobutylmethylalumoxane structures. When TIBA content in the system increases to 30 mol %, these structures are rearranged to form the products with a low degree of association with simultaneous formation of mentioned before tetraiso-butylalumoxane (TIBAO). In the case when molar ratio Al_{TIBA}/Al_{MAO} is 1.5, the main reaction product is TIBAO (Fig. 2a). However, these experiments have been conducted under conditions when reaction products were thoroughly dried prior to dilution in toluene-d₈. So, it was necessary to check out the contribution of AlMe₃/Al(iso-Bu)₃ realkylation compounds to the reac-

Table 2. Propylene polymerization^{a)} with catalyst 2 preactivated with MAO with following activation with different activators Y [Y = MAO or TIBAO formed during interaction of MAO with TIBA *in situ* or prior introduction of cocatalysts (MAO + TIBA)]

Entry	Cocatalyst (Y)	Solvent	Al _Y /Zr, mol/mol	t, min	Polym. yield, g	W ^{b)}	A ^{c)}
1	MAO	toluene	2700	15	0.36	82	1440
2	MAO	toluene	4200	15	2.12	233	8480
3	MAO	toluene	6000	13	2.54	382	11 720
4	MAO	toluene	8700	15	2.17	275	8680
5	TIBA	toluene	1000	8	0.96	105	10 910
6	TIBA	heptane	600	31	0.43	16	1260
7	TIBA	heptane	800	31	0.62	27	1820
8	TIBA	heptane	1000	10	0.80	100	7270
9	TIBA	heptane	1200	20	0.49	33	2230
10	TIBA	heptane	1500	31	0.41	18	1200
11	MAO + TIBA	toluene	500 + 300	10	0.86	62	7820
12	MAO + TIBA	toluene	500 + 500	7	0.77	101	10 000
13	MAO + TIBA	toluene	500 + 800	6	0.84	92	12 730
14	MAO + TIBA	toluene	500 + 1000	9	0.50	88	5050

^{a)} Polymerization conditions: Al_{MAO}/Zr (preactivation) = 300 mol/mol, [Zr] = 5 · 10⁻⁵ mol/L (entries 1–4), [Zr] = 3.3 · 10⁻⁵ mol/L (entries 5–14), p = 0.1 MPa (1 atm), polymerization temp. 20 °C, volume of liquid phase 20 ml.

^{b)} Propylene consumption rate at the initial stage of the reaction in kg PP/(mol Zr · min · [C₃H₆]).

^{c)} A = activity in kg of PP/(mol Zr · h · atm).

TIBA hydrolysis with water [18] and used it as cocatalyst for MAO preactivated catalyst 1 (Table 1, entry 15). One can see that activity of the system is at about similar level as that when TIBAO is formed in the course of interaction of MAO with TIBA (compare Table 1, entries 15, 12) and again higher than for MAO activated catalyst (entry 1). The comparison of productivity of the catalyst 1 preactivated with MAO at Al_{MAO}/Zr = 300 mol/mol ratio and further activated with MAO or TIBAO under other similar conditions is presented in Fig. 3.

Propylene polymerization with catalyst 2 activated with MAO or MAO/TIBA cocatalyst

It is well known that for effective activation of catalyst 2 a large excess of MAO is necessary (Al_{MAO}/Zr = 10³–10⁴ mol/mol) [1–3]. So, it was interesting to compare MAO and TIBAO activation of catalyst 2 preactivated with MAO with respect to lowering of MAO charges and possibility of carrying out the propylene polymerization in heptane. All the experiments have been conducted at 20 °C with the catalyst 2 preactivated with MAO at Al_{MAO}/Zr = 300 mol/mol ratio. The comparative results are presented in Table 2.

Similarly as for the catalyst 1, the first series of experiments was aimed to find out the dependence of catalyst productivity on Al_{MAO}/Zr molar ratio under activation with MAO. The catalyst 2 under activation with MAO unlike to catalysts 1 showed decay-like propylene consumption-time resolved profiles (Fig. 4a). So for comparison of catalyst productivity with different cocatalysts we have chosen both initial values of propylene consumption rate (column W in Table 2) and integral specific catalyst productivity (column A in Table 2). One can see that increase in Al_{MAO}/Zr molar ratio from 2700 to 6000 mol/mol leads to proportional increase in cata-

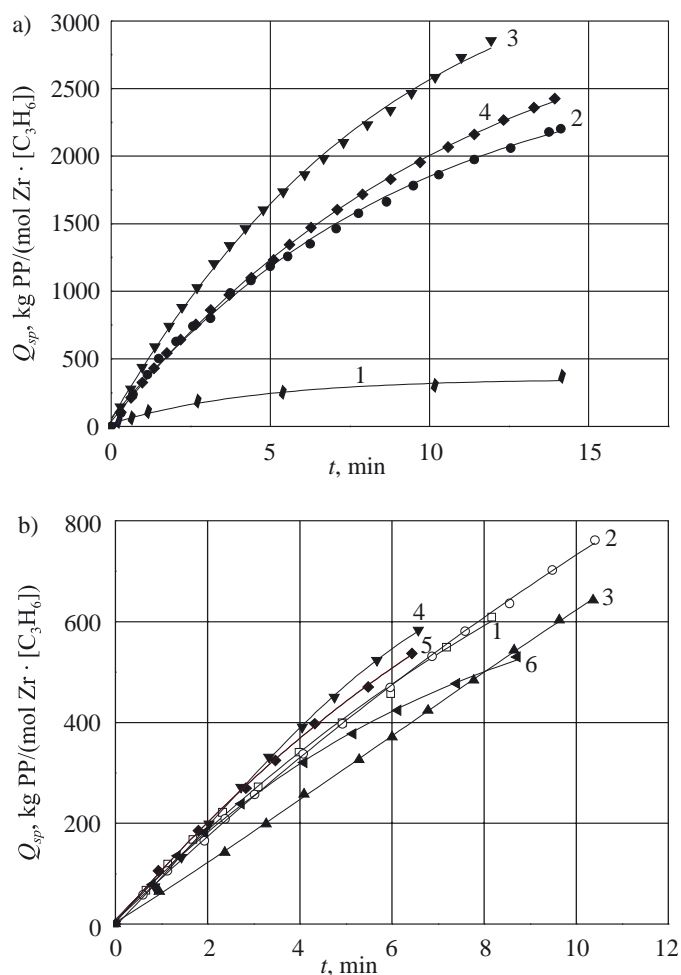


Fig. 4. Dependence of propylene consumption (Q_{sp}) by (2 + MAO)/Y [Y = MAO (a) or TIBA (b)] on polymerization time (t); Al_{MAO}/Zr (preactivation) = 300 mol/mol. (a) Solvent toluene, Al_{MAO}/Zr: 2700 (1), 4200 (2), 6000 (3), 8700 (4) mol/mol. (b) Solvent: 1, 3–6 toluene, 2 heptane; Al_{TIBA}/Zr: 600 (2), 800 (3), 1000 (1, 4), 1200 (5), 1500 (6) mol/mol

lyst productivity up to maximal value of 382 kg PP/(mol Zr · min · [C₃H₆]) with following decrease at Al_{MAO}/Zr = 8700 mol/mol to 275 kg PP/(mol Zr · min · [C₃H₆]). It should be mentioned that similar dependence of catalyst productivity in propylene polymerization on Al_{MAO}/Zr molar ratio has been observed for another C₂-symmetric catalyst *rac*-Me₂SiInd₂ZrCl₂ [16].

MAO preactivated and further TIBA activated (Al_{TIBA}/Zr = 1000 mol/mol) catalyst shows about 4 times lower value of initial propylene consumption rate than activated with MAO (compare Table 2, entries 5 *vs.* 3), however demonstrates considerably higher stability (compare curve 3 in Fig. 4a and curve 1 in Fig. 4b). In other words, one can obtain similar integral productivity of catalyst 2 [10 910 *vs.* 11 720 kg PP/(mol Zr · h · atm)] at about 20 times lower MAO charges. Similarly to catalyst 1, the catalyst 2 demonstrates equal catalytic behavior in the medium of toluene and heptane at similar conditions (compare entries 5, 8 in Table 2 and curves 1, 2 in Fig. 4b). However, the catalyst 2 preactivated with MAO in contrast to catalyst 1 shows very strong dependence of productivity on Al_{TIBA}/Zr molar ratio as was shown for polymerizations in the medium of heptane (entries 6–10). The maximum activity is reached at Al_{TIBA}/Zr molar ratio of 1000 mol/mol (entry 8) at molar TIBA amount about 3 times higher than MAO. Following increase in TIBA amount led to decrease in catalyst productivity (entries 9, 10). We assumed that the presence of zirconocene 2 in the system may suppress TIBAO formation so that maximum transformation of MAO to TIBAO is reached at higher excess of TIBA. To check the supposition we have carried out experiments with TIBAO preliminary formed inside the reactor in the medium of toluene with following introduction of MAO preactivated catalyst (entries 11–14). The productivities of thus prepared catalytic systems are higher than those for the previous series, reach their maximum values at about equimolar ratio of MAO and TIBA (entries 12, 13 *vs.* entry 5) and are at a level of MAO activated systems obtained at high Al_{MAO} molar ratios. It should be mentioned that stability of the system decrease with increase in TIBA concentration (curves 3–6 in Fig. 4b) similarly to the systems with TIBAO generated *in situ* in the presence of zirconocene 2.

CONCLUSION

Summarizing all the propylene polymerizations' results with the catalysts 1 and 2 with combined MAO/TIBA cocatalyst we may conclude that TIBAO which is formed in the reaction of MAO with TIBA at about equimolar ratio of the components is a better cocatalyst than MAO. It allows realization of propylene polymerization in the medium of aliphatic solvents due

to much better solubility of TIBAO compared to MAO and at much lower MAO charges. However, to provide capability of effective activation of catalysts 1 and 2 with TIBAO, the catalyst should be transferred into preactivated state under interaction with MAO. Low Al_{MAO}/Zr molar ratios at the stage of preactivation (*e.g.* Al_{MAO}/Zr = 20 mol/mol for catalyst 1) are not sufficient for the purpose and was optimized by us (especially for catalyst 2) towards the higher values for obtaining highly efficient catalytic systems.

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