

Interaction of zirconocenes with polymethylalumoxane. Kinetics of methane liberation

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Abstract

The kinetics of methane liberation during polymethylalumoxane (MAO) interaction with zirconocenes Cp_2ZrCl_2 , $\text{Ind}_2\text{ZrCl}_2$, $\text{Me}_2\text{SiCp}_2\text{ZrX}_2$, $\text{Me}_2\text{SiInd}_2\text{ZrX}_2$, and $\text{Me}_2\text{SiCp}^*\text{N}^i\text{BuZrX}_2$ ($\text{X} = \text{Cl}, \text{Me}$), were studied in a wide range of metallocene concentration (1×10^{-3} – 1×10^{-5} mol/l) and Al/Zr ratio (100–24 000) at the narrow range of MAO concentrations (0.1–0.3 mol/l). The reaction of methane liberation follows apparent first order on zirconium. The total methane yield is suggested to be determined by active aluminum species present in MAO, so that $[\text{CH}_4]_{\infty}$ being $\sim 0.01 [\text{Al}]$ both in reactions of MAO self-condensation and those catalyzed by dissolved zirconocenes. Comparison of the kinetic parameters of the reaction derived in the presence of zirconocenes shows considerable increase in both specific initial rates of methane liberation and the specific methane yield (per mole of zirconium) at metallocene concentration lower than 1×10^{-4} mol/l. Multiple regeneration of metal–carbon (M–C) bonds was revealed. According to the data of analysis of the effect in terms of dissociative equilibrium, the active species that catalyze the reaction of condensation of MAO are cationic particles. It has been demonstrated that the kinetic parameters of the reaction were also sensitive to the nature of zirconocene. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metallocenes; Methylalumoxane; Complexes; Metallocene cation; Methane; Methane evolution; Metallocene catalysts; Catalysts; Active center; Kinetics; Mechanism

1. Introduction

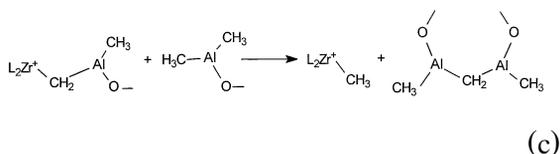
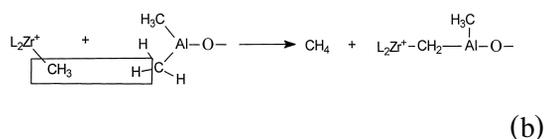
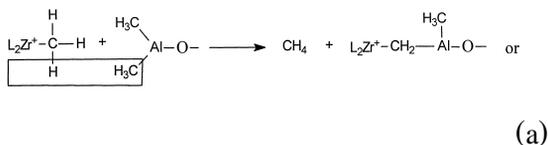
Homogeneous complexes derived from metallocenes of IVB group and polymethylalumoxane (MAO) have been the subject of a great number of publications as extremely effective catalysts of olefin poly and (co)polymerization. The role of MAO as an activator is widely known to be significant in several aspects: (i) alkylation of a catalyst precursor metallocene

dichloride, (ii) generation of cationic electron-deficient metallocene complex, and (iii) stabilization of cationic complexes. Insertion of an olefin into metal–carbon (M–C) bond leads to the polymer chain growth, while M–C bond cleavage takes place in chain transfer reactions or in the course of deactivation, multiple regeneration of active sites proceeds in the course of polymerization.

Formation of catalytically active cationic complex of the type $[\text{L}_2\text{M-Me}]^+ \dots \text{MAOX}^-$, providing the highest rate of the olefin incorporation, is the main route of metallocene interac-

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tion with MAO. At the same time, it is well known that in the absence of a monomer, such interaction leads to the formation of considerable amount of methane up to several dozens per mole of Zr [1–3] despite a considerably slower reaction rate than that of polymerization reaction. A formal scenario for the reaction proposed by Kaminsky et al. [1,2] may be generalized as follows:



Reactions (a) and (b) reflect the possible ways for methane formation and route, while reaction (c) is attributed to regeneration of active particles. There is no direct evidence in the participation of either the terminal methyl groups present in MAO or the other active species. Most importantly, there are no experimental evidences for cationic particles (rather than neutral methyl derivatives) which are involved in the reaction of methane formation. If the latter is true, then the reaction may be considered as the reaction taking active cationic species away, i.e., the deactivation reaction concurrent to the aimed reaction of polymerization [2]. The studies of the mechanisms of reactions are complicated by the fact that MAO itself is capable of yielding methane molecules thus, showing the presence of active species responsible for the reaction of self-condensation [4].

The experimental results on reaction kinetics, as well as on reaction sensitivity to the nature of metallocene, etc., in particular, were surpris-

ingly scarce [4,5]. At the same time, the kinetics of methane liberation may provide the information on transformations of complexes formed and intermediates which cannot be detected by other means. The study of the methane liberation kinetics reveals, to some extent, the main stages of metallocene/MAO interaction such as alkylation of dichloride derivatives, decomposition of M–C bond and following regeneration.

May and do the cationic species catalyze the reaction of methane formation? Driven with the question, we made the study of the kinetics of methane liberation under interaction of a series of different zirconocene [Cp₂ZrCl₂ (1), Ind₂ZrCl₂ (2), Me₂SiCp₂ZrCl₂ (3), Me₂SiInd₂ZrCl₂ (4), Me₂SiCp**N*'BuZrCl₂ (5) (Cp* = CpMe₄)] with MAO by varying the ranges of the zirconocene concentration. The effect of the pre-catalyst nature on the reaction of methane formation has been analyzed. Dimethylated complexes Me₂SiCp₂ZrMe₂ (6), Me₂SiInd₂ZrMe₂ (7), Me₂SiCp**N*'BuZrMe₂ (8) were used for comparative analysis.

2. Results and discussion

As demonstrated in our recent paper [3], the kinetics of methane liberation under interaction

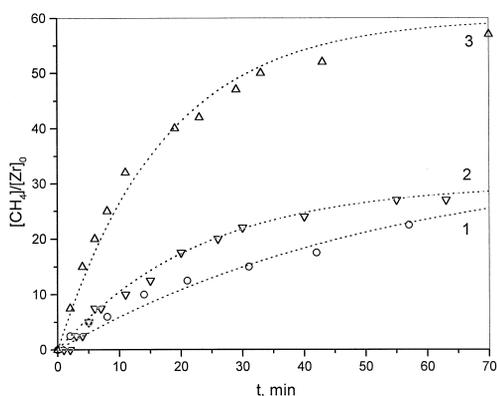


Fig. 1. Kinetics of specific methane yield under interaction of (1) Me₂SiCp₂ZrCl₂ (3), (2) Me₂SiCp**N*'BuZrCl₂ (5), and (3) Me₂SiInd₂ZrCl₂ (4), with MAO in toluene. Dotted lines correspond to the simulated reaction kinetics according to Eqs. (11) and (12). Reaction conditions: toluene, 15°C, [Zr] ≈ 1 × 10⁻⁴ mol/l, Al/Zr ≈ 3000.

of the series of zirconocenes with MAO followed the apparent second order on zirconium at high metallocene concentrations ($[\text{Zr}] \geq 1 \times 10^{-3}$ mol/l, toluene). The main route for methane formation was proposed to be the interaction of cationic particles with neutral dimethyl derivatives. The formation of binuclear metallocenium cations of Ti, Zr, and Hf, with μ -bound CH_3 or Cl ligands formed under the action of different cocatalysts in excess of dimethylated metallocenes, was reported by Lancaster et al. [6], Bochmann and Lancaster [7] and Haselwender et al. [8].

Lowering the metallocene concentration leads to considerable changes in kinetics of methane liberation for all examined complexes. Considerable enhance of both specific methane yield ($[\text{CH}_4]_{\infty}/\text{Zr}_0$) up to several tenths of moles per mole of zirconium, and initial reaction rates with simultaneous shortening of the reaction time were found. The kinetics of methane liberation may be exemplified by Fig. 1 for interactions of three Me_2Si -bridged zirconium complexes with MAO carried out under other similar conditions (reaction temperature, complex concentration, and Al/Zr ratio). The main

Table 1

Reaction conditions and some kinetical characteristics of interaction of the series of zirconocenes with MAO (reaction temperature 15°C, toluene, 60 min)

Run	Metallocene	$[\text{Zr}]_0 \times 10^4$ (mol/l)	$[\text{Al}]_0$ (mol/l)	Al/Zr	$W_0/[\text{Zr}]_0 \times 10^3$ (1/s)	$[\text{CH}_4]_{\infty}/\text{Zr}_0$	$[\text{CH}_4]_{\infty}/\text{Al}_0$
1	Cp_2ZrCl_2 (1)	13.0	0.12	90	0.3	2	0.03
2	Cp_2ZrCl_2 (1)	7.5	0.14	190	0.6	2	0.01
3	Cp_2ZrCl_2 (1)	3.0	0.24	800	4.7	13	0.02
4	Cp_2ZrCl_2 (1)	2.2	0.22	1000	18.0	20	0.02
5	Cp_2ZrCl_2 (1)	1.5	0.24	1600	21.0	23	0.01
6	Cp_2ZrCl_2 (1)	0.9	0.27	3000	40.6	40	0.01
7	Cp_2ZrCl_2 (1)	0.5	0.24	4800	73.3	60	0.01
8	$\text{Ind}_2\text{ZrCl}_2$ (2)	7.0	0.18	250	1.2	2	0.01
9	$\text{Ind}_2\text{ZrCl}_2$ (2)	4.5	0.13	290	1.5	3	0.01
10	$\text{Ind}_2\text{ZrCl}_2$ (2)	2.5	0.20	800	5.3	8	0.01
11	$\text{Ind}_2\text{ZrCl}_2$ (2)	1.6	0.16	1000	10.3	14	0.02
12	$\text{Ind}_2\text{ZrCl}_2$ (2)	0.8	0.16	2000	16.7	16	0.01
13	$\text{Me}_2\text{SiCp}_2\text{ZrCl}_2$ (3)	16.0	0.24	150	0.8	2	0.01
14	$\text{Me}_2\text{SiCp}_2\text{ZrCl}_2$ (3)	3.2	0.24	750	9.8	12	0.02
15	$\text{Me}_2\text{SiCp}_2\text{ZrMe}_2$ (6)	3.2	0.20	650	8.0	9	0.02
16	$\text{Me}_2\text{SiCp}_2\text{ZrCl}_2$ (3)	0.8	0.24	3000	10.8	35	0.01
17	$\text{Me}_2\text{SiCp}_2\text{ZrMe}_2$ (6)	0.9	0.20	2300	21.5	24	0.01
18	$\text{Me}_2\text{SiCp}_2\text{ZrCl}_2$ (3)	0.4	0.24	6000	100.0	90	0.02
19	$\text{Me}_2\text{SiInd}_2\text{ZrMe}_2$ (7)	3.2	0.20	600	22.1	11	0.02
20	$\text{Me}_2\text{SiInd}_2\text{ZrCl}_2$ (4)	0.8	0.24	3000	58.3	60	0.02
21	$\text{Me}_2\text{SiInd}_2\text{ZrMe}_2$ (7)	0.9	0.20	2300	88.2	45	0.02
22	$\text{Me}_2\text{SiInd}_2\text{ZrCl}_2$ (4)	0.4	0.24	6000	83.3	50	0.01
23	$\text{Me}_2\text{SiInd}_2\text{ZrCl}_2$ (4)	0.2	0.24	12000	100.0	70	0.01
24	$\text{Me}_2\text{SiInd}_2\text{ZrCl}_2$ (4)	0.1	0.24	24000	132.0	200	0.01
25	$\text{Me}_2\text{SiCp}^* \text{N}^i\text{BuZrCl}_2$ (5)	3.7	0.28	750	24.7	9	0.01
26	$\text{Me}_2\text{SiCp}^* \text{N}^i\text{BuZrMe}_2$ (8)	3.6	0.20	660	17.4	9	0.02
27	$\text{Me}_2\text{SiCp}^* \text{N}^i\text{BuZrCl}_2$ (5)	1.9	0.29	1500	26.7	15	0.01
28	$\text{Me}_2\text{SiCp}^* \text{N}^i\text{BuZrCl}_2$ (5)	0.9	0.27	3000	21.7	30	0.01
29	$\text{Me}_2\text{SiCp}^* \text{N}^i\text{BuZrMe}_2$ (8)	0.9	0.20	2300	49.1	27	0.01
30	$\text{Me}_2\text{SiCp}^* \text{N}^i\text{BuZrCl}_2$ (5)	0.5	0.30	6000	83.3	45	0.01
31	$\text{Me}_2\text{SiCp}^* \text{N}^i\text{BuZrCl}_2$ (5)	0.5	0.30	6000	79.1	50	0.01

characteristics of the reaction are summarized in Table 1, where it can be seen that both the specific initial rate of methane liberation,

$$W_0/Zr_0 = \left. \frac{d[CH_4]}{dt} \right|_{t \rightarrow 0} / Zr_0$$

(1/s), and the specific total methane yield, $[CH_4]_{\infty}/Zr_0$ (mol/mol), are very sensitive to the reaction conditions and nature of reactive complex. The latter characteristics show the changes from 2 (run 2) to 200 mol/mol (run 24). This fact indicates that multiple regeneration of active M–C bonds takes place in the course of the reaction.

As mentioned above, MAO itself is capable of eliminating methane in a self-condensation reaction via α -hydrogen transfer leading to the formation of Al–CH₂–Al links [4]. The study of methane liberation from MAO solution in toluene at concentration similar to those used in experiments with zirconocenes (~ 0.2 mol/l) showed that rate of methane formation was much slower than those in the presence of zirconocene. Total methane yield per aluminum atom tends to the value of 0.01 mol/mol after 200 h of aging (Fig. 2). The fact indicates that MAO contains some active Al-species involved in intermolecular association in proportion of about 1/100 of the total Al content. In this connection it is interesting to note that ESR

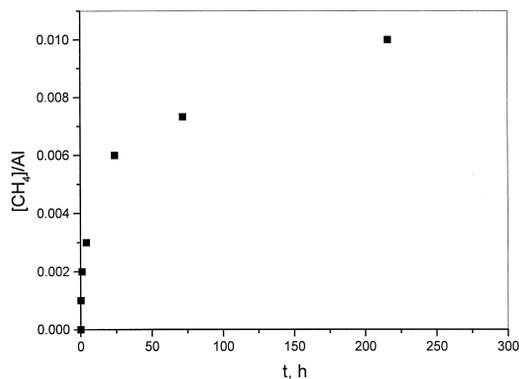


Fig. 2. The dependence of methane yield generated with individual MAO referred to total aluminum content on the time of MAO "aging". Experiment conditions: room temperature, $[Al] = 0.2$ mol/l, toluene.

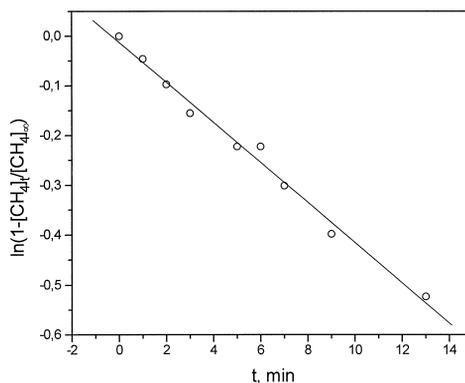


Fig. 3. Anamorphose of methane liberation kinetics in coordinates $\ln(1 - [CH_4]_t/[CH_4]_{\infty}) - t$ for the reaction of $Me_2SiInd_2ZrCl_2$ (4) with MAO. Reaction conditions: toluene, 15°C, $[Zr] = 4 \times 10^{-5}$ mol/l; $[Al] = 0.24$ mol/l.

studies of MAO trapped with the stable nitroxyl radical showed the presence of two different types of Lewis acidic centers in MAO of the same concentration at about $1/100 \pm 30$ atoms of aluminum [9]. These were unsaturated Al-species: $AlOMe_2$, and AlO_2Me . In Table 1, approximately the same amount of methane (10–20 mmol/mol of aluminum) is eliminated in the presence of zirconocenes, however within a very short time. So, it may be concluded that the reaction of methane formation is the condensation of MAO catalyzed by metallocene species.

Analysis of methane evolution in zirconocene/MAO systems at low concentration of the complex showed that specific methane yield–time profiles are of exponential type for all analyzed complexes, being rather sensitive to the nature of zirconocene (Fig. 1). Since exchange of CH_3 -groups is fast in these systems [3,10], M–C bond regeneration does not seem to be a rate-limiting stage of the process. Formally, the reaction order on zirconium is first (Fig. 3). A formal scheme of interaction may be taken for consideration:



where (1) is the stage of methane liberation under interaction of MAO with some active Zr–Me species (A) accompanied with formation of temporary inactive particles (X) that may be regenerated at stage (2). Particles X can also take part in the reactions leading to inactive products, stage (3). Reactions (1), (2) and probably (3) proceed with the participation of MAO. Since MAO is in great excess to zirconium, concentration of MAO (almost similar at all experiments, 0.1–0.3 mol/l) may be included into the effective values of reaction rate constants, k_1 , k_2 and k_3 . The reactions (1), (2) and (3) are described by the system of differential equations:

$$\frac{d[A]}{dt} = -k_1[A] + k_2[X], \quad (4)$$

$$\frac{d[X]}{dt} = k_1[A] - (k_2 + k_3)[X], \quad (5)$$

$$\frac{d[CH_4]}{dt} = k_1[A]. \quad (6)$$

General solution of the Eqs. (4) and (5) on [A] is

$$[A]_t = C_1 \exp\left[\left(-\frac{\alpha}{2} + \sqrt{\frac{\alpha^2}{4} - \beta}\right)t\right] + C_2 \exp\left[\left(-\frac{\alpha}{2} - \sqrt{\frac{\alpha^2}{4} - \beta}\right)t\right] \quad (7)$$

where $\alpha = k_1 + k_2 + k_3$, $\beta = k_1 \cdot k_3$. The constants C_1 and C_2 are determined from starting conditions:

$$[A]_{t=0} = [A]_0;$$

$$[X]_{t=0} = \frac{1}{k_2} \left\{ \frac{d[A]}{dt} + k_1[A] \right\} \Big|_{t=0} = 0.$$

The total solution on [A] looks as follows:

$$[A]_t = \frac{[A]_0}{2} \left\{ \left(1 - \frac{k_1 - \frac{\alpha}{2}}{\sqrt{\frac{\alpha^2}{4} - \beta}} \right) \times \exp\left[\left(-\frac{\alpha}{2} + \sqrt{\frac{\alpha^2}{4} - \beta}\right)t\right] + \left(1 + \frac{k_1 - \frac{\alpha}{2}}{\sqrt{\frac{\alpha^2}{4} - \beta}} \right) \times \exp\left[\left(-\frac{\alpha}{2} - \sqrt{\frac{\alpha^2}{4} - \beta}\right)t\right] \right\} \quad (8)$$

and according to Eq. (6), the rate of methane evaluation will follow

$$\frac{d[CH_4]}{dt} = k_1[A]_t. \quad (9)$$

Time-resolved rates of experimental specific methane liberation in logarithmic scale are well

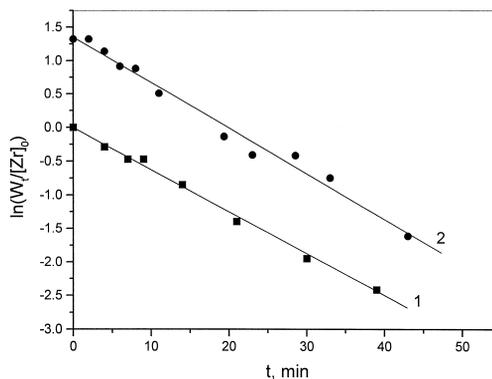


Fig. 4. Time resolved logarithmic dependencies of specific methane liberation rates under interaction of MAO with zirconocenes: (1) Cp_2ZrCl_2 (1), (2) $Me_2SiInd_2ZrCl_2$ (4). Reaction conditions: toluene, 15°C, $[Zr] = 9 \times 10^{-5}$ mol/l, Al/Zr \approx 3000.

represented by single exponential curve, as exemplified for two zirconocenes (Fig. 4). At the same time, Eq. (8) contains two exponential terms: the “slow” and “fast” decaying parts. Under the assumption that rate constant of the reaction of particles X deactivation (Eq. 3) is of the smallest value, we have three possibilities for k_1 and k_2 : (i) $k_1 \gg k_2$, (ii) $k_1 \sim k_2$, and $k_1 \ll k_2$. In order for expression (8) to be determined by the “slow” exponent, it’s amplitude must be much greater than the amplitude of “fast” exponent. As shown in the Appendix A, the condition holds for the case (iii), i.e., $k_1 \ll k_2$. In this case, the expression (8) is reduced to

$$[A]_t \approx [A]_0 \exp\left(-\frac{k_1 k_3}{k_2} t\right). \quad (10)$$

Then the expression (9) can be rewritten as:

$$\frac{1}{[Zr]_0} \frac{d[CH_4]}{dt} \approx k_1 \exp\left[-\frac{k_1 k_3}{k_2} t\right], \quad (11)$$

$$\frac{1}{[Zr]_0} [CH_4]_\infty = \frac{k_2}{k_3}. \quad (12)$$

According to (11), the rate constant k_1 can be found as the initial reaction rate divided by the

concentration of metallocene, while k_2/k_3 ratio (Eq. 12) can be determined from the experimentally deduced $[CH_4]_\infty$ value referred to the total concentration of zirconium. For example, these rate constant values for interaction of MAO with $Me_2SiInd_2ZrCl_2$ (curve 2, Fig. 4) are $k_1 = 6.5 \times 10^{-2} s^{-1}$ and $k_3 = 0.017k_2$.

A tendency exhibited by all examined complexes is to increase in both the specific methane yield and the specific initial rate of methane liberation with a decrease in the metallocene concentration (Fig. 5a,b). Both the characteristics are low-sensitive to the zirconium concentration within the range $1 \times 10^{-4} < [Zr] < 1 \times 10^{-3} mol/l$ and sharply enhance values at $[Zr] < 1 \times 10^{-4} mol/l$. Since a proposed scheme does not include the stage of active particles (A) formation, i.e., $[A] \neq [Zr]$, then k_1 value is the effective rate constant, and meanwhile, may include efficiency of active particles formation during the first stages of dichloride zirconocene interaction with MAO. As mentioned above, the interaction under conditions of polymerization (low concentration of metallocene combined with high Al/Zr ratios) includes step-wise alkylation of dichloride precursor [11], complexation

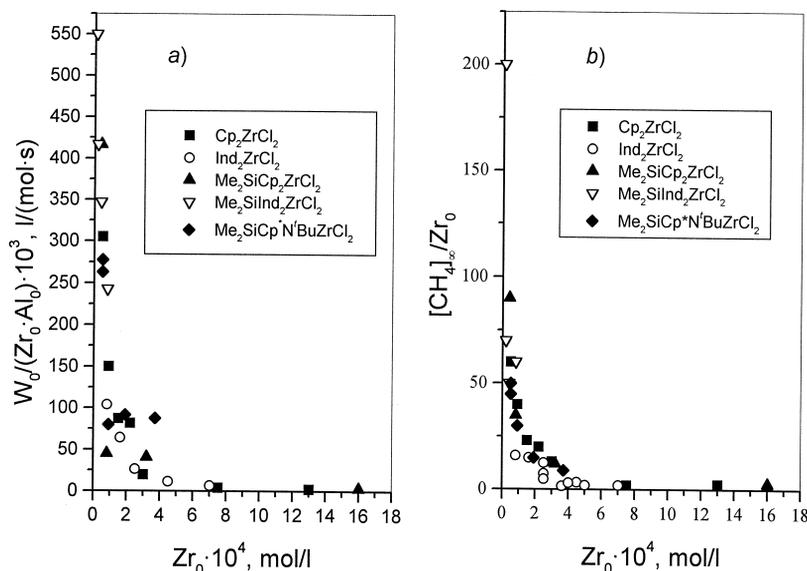


Fig. 5. Dependencies of (a) $W_0/(Zr_0 \cdot Al_0) - Zr_0$ and (b) $[CH_4]_\infty/Zr_0 - Zr_0$ for the reaction of the series of zirconocenes with MAO. Reaction conditions: toluene, 15°C, $[MAO] = 0.22-0.27 mol/l$.

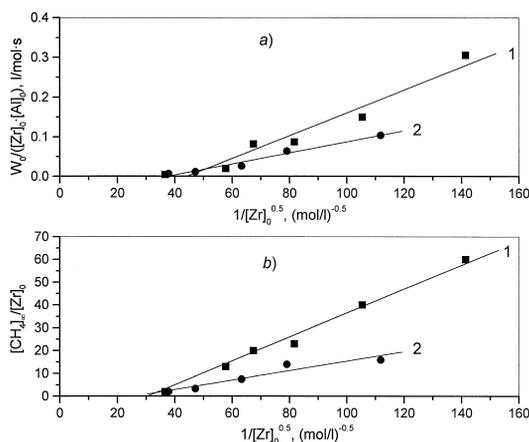


Fig. 6. Dependence of (a) $W_0/[Zr]_0 - 1/[Zr]_0^{0.5}$ and (b) $[CH_4]_{\infty}/Zr_0 - 1/[Zr]_0^{0.5}$ for the reaction of Cp_2ZrCl_2 (**1**) and Ind_2ZrCl_2 (**2**) with MAO. Reaction conditions: toluene, 17°C, $[MAO] = 0.22\text{--}0.27$ mol/l.

with MAO, and generation of cationic species in the form of ion pairs, $L_2Zr^+Me \dots MAO^-X$ ($X = Cl$ or Me) [12,13] or cationic complexes formed in the course of ionic pairs dissociation in the condensed phase due to solvation [14,15]. Since, decrease of metallocene concentration is accompanied by a sharp increase in specific initial reaction rates and specific methane yields, cationic species are thought to be the key intermediates in catalysis of the reaction of methane formation. If the most active methane-generated particles which also produce multiple regeneration for M–C bonds are cationic species formed under MAO action (the process is more favorable in diluted solutions) then, the analysis of the k_1 dependencies in terms of dissociative equilibrium may be useful:



where K is the dissociation equilibrium constant. Accordingly, the dependency of the cationic particle concentration on the initial concentration of zirconocene is given as follows:

$$Zr^+ = \sqrt{\frac{K^2}{4} + KZr_0} - \frac{K}{2} \quad (14)$$

$$\text{if } Zr_0 \ll K, \quad Zr^+ \approx Zr_0 \quad (15)$$

if $Zr_0 \gg K$,

$$Zr^+ \approx \sqrt{KZr_0} \quad \text{or} \quad \frac{Zr^+}{Zr_0} \approx \sqrt{\frac{K}{Zr_0}}. \quad (16)$$

If k_1 value is the effective parameter including the efficiency of the cationic particle formation, $k_1 = \gamma k_1^*$ where $\gamma = Zr^+/Zr_0$, then the linear dependence of $k_1 - 1/\sqrt{Zr_0}$ should be observed. In Fig. 6a specific rates ($W_0/(Zr_0 \cdot Al_0)$) of methane formation under interaction of MAO with both unbridged zirconocenes **1** and **2** are well-described in terms of dissociative equilibrium. The value of the segment which is cut off from the x -coordinate indicates that catalytic action of cationic zirconium species on MAO condensation reaction proceeds at zirconocene concentration below 5×10^{-4} mol/l. Degree of bimolecular interaction is high for these complexes at zirconocene concentration $> 5 \times 10^{-4}$ mol/l. Similar dependencies were found for complexes **4** (Fig. 7a) and **5** (Fig. 8a). Meanwhile, complex **5** shows ability to catalyze condensation of MAO according to the above mechanism at higher concentrations.

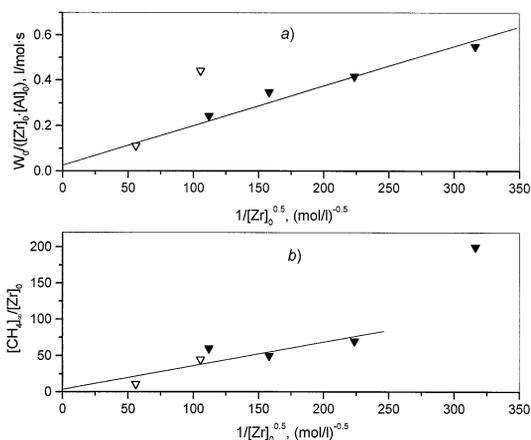


Fig. 7. Dependence of (a) $W_0/(Zr_0 \cdot Al_0) - 1/[Zr]_0^{0.5}$ and (b) $[CH_4]_{\infty}/Zr_0 - 1/[Zr]_0^{0.5}$ for the reaction of $Me_2SiInd_2ZrX_2$ (**4**)/MAO [$X = Cl$ (Δ), Me (\blacktriangle)]. Reaction conditions: toluene, 15°C, $[MAO] = 0.20\text{--}0.24$ mol/l.

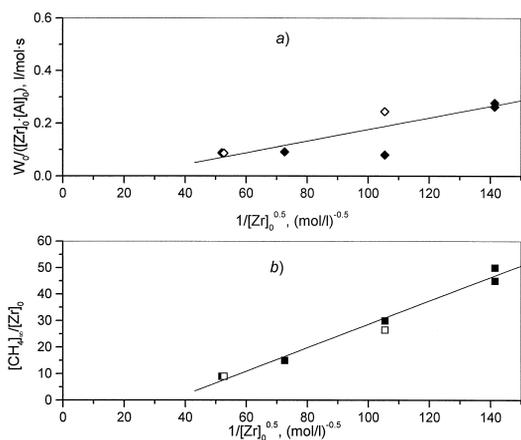


Fig. 8. Dependence of (a) $W_0/(Zr_0 \cdot Al_0) - 1/[Zr]_0^{0.5}$ and (b) $[CH_4]_{\infty}/Zr_0 - 1/[Zr]_0^{0.5}$ for the reaction of $Me_2SiCp^*N^tBuZrCl_2$ (**5**)/MAO [X = Cl (Δ), Me (\blacktriangle)]. Reaction conditions: toluene, 15°C, [MAO] = 0.20–0.24 mol/l.

The ratio k_2/k_3 ($[CH_4]_{\infty}/Zr_0$) indicates that the effective value of k_2 is about one to two order of magnitude greater than k_3 value and also, reveals the tendency to increase with the decrease in the metallocene concentration. The observed dependencies of $[CH_4]_{\infty}/Zr_0$ on $1/\sqrt{Zr_0}$ for complexes **1**, **2**, **4**, and **5** are presented in Figs. 6–8b. Such relation may be explained by a supposition that k_2 is an effective rate constant, also including the efficiency of the cationic particles formation, in a way similar to k_1 parameter. If so, the rate constant k_3 should be independent on concentration of cationic species.

We cannot separate the effects of K and k_1^* (or K and k_2^*) contributions from efficiency of the cationic species formation and their reactivity (or ability for regeneration) in the reaction of methane production. As an example, the increase in K value on one order of magnitude may be compensated by about three times lower than k_1^* value, leading to similar values of specific rates of methane formation. Thus, specific initial rates of methane formation decrease for zirconocenes at concentration of $\sim 1 \times 10^{-4}$ mol/l: **4** > **1** > **2** > **5** > **3**. At the same time, from the slope of $W_0/(Zr_0 \cdot Al_0) - 1/\sqrt{Zr_0}$ de-

pendency [the combined effect of dissociation equilibrium and reaction (1)] the complexes are arranged as follows: **1** > **5** > **4** > **2**. However, the K values can be determined by other means (electrochemical or NMR measurements) and after that the real values of k_1^* characterizing M–C bond activity can be obtained.

We compared the kinetics of methane formation under interaction of MAO with both dimethylated and dichloride complexes at two values of the metallocene concentration. Three dichloride complexes were converted to dimethyl derivatives. These were complexes **6**, **7** and **8**. The comparison showed that at a higher concentration of zirconocenes ($\sim 3 \times 10^{-4}$ mol/l) the initial rates of methane formation referred to (mole of Zr/mole of Al) are of close values for dichloride and dimethyl derivatives and are equal to $\sim 4.0 \times 10^{-2}$ l/mol·s for complexes **3** and **6** (runs 14–15), and $\sim 8.8 \times 10^{-2}$ l/mol·s for complexes **5** and **8** (runs 25–26). For complexes **4** and **7**, reactions were examined only at low concentration due to poor solubility of complex **4** in toluene. Dimethyl derivative **7** (run 19) showed the highest initial rate of methane formation, 11×10^{-2} l/mol·s, among all examined dimethylated zirconocenes. At lower metallocene concentrations, specific initial rates of methane liberation were two to three times higher for dimethyl zirconocene/MAO systems: 4.5, 10.8×10^{-2} l/mol·s (**3** and **6**; runs 16–17), 24.3, 44.0×10^{-2} l/mol·s (**4** and **7**; runs 20–21), and 8.0, 24.5×10^{-2} l/mol·s (**5** and **8**; runs 28–29), again with highest values for $Me_2SiInd_2ZrX_2$. The ratio of initial methane liberation rates with dimethyl and dichloride derivatives reached the lowest value of 1.8 for complexes **7** and **4**. The fact probably shows the highest ability of complex **4** for dimethylation. Thus, the rate of dimethylation of dichloride complex may also contribute to the efficiency of cationic particle formation. The values of Zr–Me cationic particles regeneration ($[CH_4]_{\infty}/Zr_0$) were similar within the experimental error for all compared pairs of the reactions (runs 14–15, 25–26, 16–17, 20–21,

28–29). Multiple regeneration of Zr–Me bonds during the observed reaction makes the differences between catalytic behavior of starting dichlorides and dimethylated derivatives.

3. Conclusions

Interaction of zirconocene complexes with MAO in the absence of olefin leads to methane formation. A few specific features of the reaction are considered. They are as follows [2,4]: (i) increase in the specific methane yield with the decrease of the metallocene concentration; (ii) formation of temporary inactive Zr–CH₂–Al species; (iii) multiple regeneration of the M–C bond in excess of MAO. At the same time, there was no experimental evidence for the participation of cationic species in the reaction. The reaction of MAO self-condensation yielding methane with low rate was reported as a factor complicating the kinetics study [2]. We demonstrate that (i) both in the presence and in the absence of metallocene, the reaction of methane formation is determined by the presence of some active particles Al* present in MAO in proportion at about 0.01 to the total aluminum content; (ii) under the action of MAO excess on metallocene dichloride, the cationic zirconium species Zr⁺–Me formed (the efficiency of their formation increases with decrease in zirconocene concentration as $1/\sqrt{Zr_0}$) and these particles are those that catalyze the reaction of MAO condensation accompanied by methane formation; (iii) comparison of the reaction kinetics at high ($[Zr] > 1 \times 10^{-3}$ mol/l) and low ($[Zr] < 1 \times 10^{-3}$ mol/l) zirconocene concentrations showed that decrease of apparent reaction order on zirconium from the second to the first is observed, therefore, in excess of zirconocene cationic species preferably react with neutral zirconium complexes forming methane; (iv) kinetic scheme of the reaction involving stages of methane formation (the apparent first order on zirco-

nium), temporary deactivation, reactivation (also the apparent first order on zirconium), and real deactivation was postulated; (v) the effect of the complex nature on effective rate constants of methane formation ($k_1 = k_1^* \sqrt{K/Zr_0}$, where K is the dissociation equilibrium rate constant) reflected a combined effect of dissociation and the M–C bond reactivity. Comparison of MAO interaction with dichloride zirconocenes and corresponding dimethylated derivatives showed higher specific rates of methane formation for the latter complexes within the lower concentration range, however, characterized with the similar regeneration ability of the compared complexes. Complete dimethylation of dichloride complex under action of MAO on dichloride derivatives with following generation of Zr⁺–Me species was thus concluded.

4. Experimental

Zirconocenes (1–5) were purchased from Boulder Scientific. Dimethyl derivatives were synthesized from the corresponding dichloride complexes according to standard procedure [16,17]. Elementary analysis showed (%) **6**: C = 54.07 (54.66), H = 6.92 (6.55), Zr = 29.03 (29.65); **7**: C = 64.44 (64.81), H = 6.50 (5.93), Zr = 21.12 (22.37); **8**: C = 55.42 (55.07), H = 8.82 (8.97), N = 3.52 (3.78), Zr = 24.36 (24.60). MAO 10% toluene solution containing 27% AlMe₃ was purchased from Witco and was used as it was. Toluene was dried over molecular sieves (3–4 Å) and distilled over LiAlH₄ prior to use. All procedures were carried out in an atmosphere of dry argon. Reagent solutions were prepared just before use. The reactions of zirconocene solutions with MAO were run under vacuum by mixing of zirconocene solutions of desired concentration with MAO. Composition of gaseous products was obtained from chromatographic measurements. The kinetics of methane liberation was measured by increasing

the pressure in a thermostated reactor. Accuracy of methane liberated measurements was within $\pm(2-3) \times 10^{-6}$ mol. So far as MAO itself is capable of generating methane in special experiments, the methane liberated from MAO in the absence of zirconocene was measured at MAO concentration of 0.2–0.3 mol/l. The highest value of methane liberated ranged within 10–20% of total methane yield in the reactions of metallocene solution with MAO. The kinetics of methane liberation in all examined systems was measured by subtraction of the “background” methane and toluene pressure.

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Appendix A

The expression (8) can be simplified significantly if we will assume that $k_3 \ll k_1$ and $k_3 \ll k_2$. Depending on the relationship between k_1 and k_2 , we will have three different approximations for $[A]_t$:

$$(i) \quad k_1 \gg k_2$$

$$[A]_t \approx \frac{[A]_0}{2} \left[\frac{2k_2}{k_1} \exp(-k_3 t) + 2 \exp(-k_1 t) \right] \quad (17)$$

$$(ii) \quad k_1 \sim k_2$$

$$[A]_t \approx \frac{[A]_0}{2} \left\{ \frac{2k_2}{k_1 + k_2} \exp\left(-\frac{k_1 k_3}{k_1 + k_2} t\right) + \frac{2k_1}{k_1 + k_2} \exp[-(k_1 + k_2)t] \right\} \quad (18)$$

$$(iii) \quad k_1 \ll k_2$$

$$[A]_t \approx \frac{[A]_0}{2} \left[2 \exp\left(-\frac{k_1 k_3}{k_2} t\right) + \frac{2k_1}{k_2} \exp(-k_2 t) \right] \quad (19)$$

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