

# Structure and performance of the solid methylalumoxane at temperatures 20–250°C Experimental and DFT calculation study

V.N. Panchenko, V.A. Zakharov\*, I.G. Danilova, E.A. Paukshtis,  
I.I. Zakharov, V.G. Goncharov, A.P. Suknev

*Borshkov Institute of Catalysis, Prospect Akademika Lavrentieva, 5, Novosibirsk 630090, Russia*

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## Abstract

The structure of solid methylalumoxane (MAO) and its behavior in the temperature interval from 20 to 250°C have been studied using IR spectroscopy in diffusion reflection mode (DRIFT) and mass-spectrometric (MS) methods. It has been shown that three-dimensional MAO molecule may entrap water molecule in its volume (absorption bands (a.b.) 3550 cm<sup>-1</sup> in the IR-spectrum). Using a density functional theory (DFT) quantum-chemical method, the three-dimensional molecular model of MAO with composition (–Al(CH<sub>3</sub>)O–)<sub>12</sub>, comprising water molecule in its structure, has been calculated. The release of the water molecule from the structure of MAO molecule is accompanied by the protolysis of Al–CH<sub>3</sub> bonds and methane evolving. This reaction seems to be responsible for the observed evolving of methane on the MAO aging. As the temperature of MAO heating increases from 20 to 150°C, the process of methane evolving intensifies.

The heating of the solid MAO samples is also accompanied by the release of trimethylaluminum (TMA) in significant amount (0.18 mole AlMe<sub>3</sub>/mole Al<sub>MAO</sub> at 100°C). Obviously, the released TMA was strongly associated with the MAO in the initial sample.

The data on the activity in the ethylene polymerization of catalyst Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO prepared with the use of the MAO samples dried at temperatures 20–250°C are presented as well. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Methylalumoxane structure; Metallocene catalyst

## 1. Introduction

Methylalumoxane (MAO) is a highly efficient activator of homogeneous metallocene catalysts for olefine polymerization. MAO is the product of partial hydrolysis of trimethylaluminum (TMA) and usually appears as a complex compound consisting of proper MAO [–Al(CH<sub>3</sub>)O–]<sub>n</sub> (*n* = 6–20) and TMA associated with MAO [1]. The structure of MAO in solution

has been studied in numerous works [2–7], but owing to the product complexity, the questions on the MAO structure, the nature of its reaction centers and unique ability to activate metallocene catalysts still remain unclear.

According to the latest data obtained by multinuclear NMR spectroscopic method [7], in the temperature interval 40–120°C, the dissolved MAO forms oligomers with three-dimensional “cage” structure, in which aluminum atoms are tetra-coordinated and oxygen atoms are tri-coordinated; this means every CH<sub>3</sub>–Al-groups has three oxygen atoms as next

\* Corresponding author.

*E-mail address:* v.a.zakharov@catalysis.nsk.su (V.A. Zakharov).

neighbors and every O-atom has three CH<sub>3</sub>-Al-groups as neighbors. Such structure shows ratio Al:CH<sub>3</sub>:O = 1:1:1 and is referred to as a “classic” MAO. The “cage” structure of this type has been identified earlier for *tert*-butyalumoxane [2]. However, numerous experimental data prove [1,6,8–10] that at room temperature, the MAO composition corresponds to Al:CH<sub>3</sub>:O = 1:1.5:0.75 (“true” MAO by Sinn’s definition [1]). Similar ratio Al:CH<sub>3</sub> = 1:1.5 has been found in [11] for the sample of solid MAO prepared by vacuum drying of the MAO solution at room temperature. The composition of “true” MAO corresponding to these data has been suggested in [1] as [Al<sub>12</sub>O<sub>12</sub>(CH<sub>3</sub>)<sub>12</sub>]·[Al(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>. Molecular models of “true” MAO with composition Me<sub>18</sub>Al<sub>12</sub>O<sub>9</sub>, based on IRS study and density functional theory (DFT) quantum-chemical calculations, have been presented recently in [12].

The supported metallocene catalysts for olefin polymerization are studied extensively in recent years. The most widely used approach to the synthesis of these catalysts implies the use as the support of silica with the MAO introduced in its pores. The content of aluminum in such a support usually equals 10–20 wt.%. The MAO likely exists in the support as an individual phase [13]. In this regard, it is important to obtain experimental data on the composition, structure and reactivity of the solid MAO. However, only few works devoted to these questions can be found in literature. In particular, the results of the <sup>27</sup>Al NMR MAS studies of solid MAO in [14] and of solid MAO synthesized in the pores of mesoporous silica gel MCM-41 [15] are available.

In the present work, we used the DRIFT and mass-spectrometric (MS) methods to study the solid MAO samples in the temperature interval from 20 to 250°C. Some conclusions suggested by the obtained experimental data were simulated with the help of the DFT quantum-chemical method. The data on the activity in the ethylene polymerization of catalyst Cp<sub>2</sub>Zr-Cl<sub>2</sub>/MAO prepared with the use of the MAO samples dried at temperatures 20–250°C were obtained.

## 2. Experimental

The solid MAO samples were obtained by vacuum drying of commercial sample purchased from Witco

(38 wt.% MAO in toluene) at 20°C followed by a heating in vacuum at 50, 100 and 250°C for 1 h. The final MAO samples are looked as dry powders.

### 2.1. The IR spectroscopy in diffusion reflection mode (DRIFT) measurements

The dried MAO sample (0.3–0.5 g) were placed into a cell under argon to perform the DRIFT measurements. The DRIFT-spectra were recorded on a Bruker IFS-113v spectrometer (256 scans, resolution 4 cm<sup>-1</sup>) in the 1000–7000 cm<sup>-1</sup> range (in some cases in the 800–3000 cm<sup>-1</sup> range) using the home made accessory of diffusion reflection. The figures below show the obtained spectra in a form of the Kubelka–Munk function  $F(R)$  calculated using Eq. (1) according to [16]:

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

where  $R$  is a reflection coefficient.

### 2.2. Chemical analysis

The content of aluminum in the samples was measured by HCP-IES technique.

The total amount of CH<sub>3</sub>-groups in solid MAO sample was determined after dissolving of MAO sample in water/HCl (1:1) solution. The amount of methane, formed after dissolving MAO, was measured by comparing the intensity of peaks with  $m/e = 15$  and 13 in the studied and calibration mixture (methane and argon). Mass-spectra were recorded on quadruple mass-spectrometer VG Sensorlab V6.

### 2.3. Analysis of the gas phase by mass-spectrometric method

Two types of experiments have been performed with the use of quadruple mass-spectrometer VG Sensorlab V6 to analyze the gas phase.

The first type experiments were carried out in the flow regime. The sample of the dried MAO (0.3–0.5 g) was charged into a cell under argon flow, and the cell was placed into the mass-spectrometer. The heating rate of MAO sample in the mode of temperature-programmed desorption (TPD) was 11°C/min, helium flow rate — 2 ml/s. The desorption

methane and toluene was estimated by the intensities of peaks  $m/e = 16$  and 91, respectively. Analysis of fragments  $\text{Al}(\text{CH}_3)_x$  is based on peaks with  $m/e = 42$  ( $x = 1$ ), 57 ( $x = 2$ ) and 72 ( $x = 3$ ). Analysis of methyl radicals is based on peak with  $m/e = 15$  (with the subtraction of the methane contribution). The methane quantity was determined by comparing the intensity of peak with  $m/e = 16$  in the studied and calibration mixtures.

The second type experiments were performed to determine the methane content in the gas phase over the MAO samples heated at 50 or 150°C for 30 h. The gas phase pulse was fed into the mass-spectrometer and the analysis was performed in a static mode at room temperature. The integral of peak  $m/e = 16$  in coordinates (ionic current)/(time) corresponded to the content of methane in the gas phase. The methane quantity was determined by comparing the intensity of peak with  $m/e = 16$  in the studied and calibration mixtures.

#### 2.4. Analysis of the liquid products by NMR spectroscopic method

The samples of solid MAO (0.2–0.3 g), prepared by drying in vacuum at 20°C, have been heated at 50 or 100°C for 30 h in vacuum. The released gaseous products were condensed by liquid nitrogen and then

dissolved in toluene d-8 at room temperature. The composition and quantity of the products, TMA in particular, were determined by  $^1\text{H}$  NMR spectroscopic method.

#### 2.5. Ethylene polymerization

Polymerization of ethylene has been performed in a 0.21 steel autoclave under constant pressure and temperature. The polymerization conditions are given in Table 3.

### 3. Results and discussion

#### 3.1. The DRIFT data

The DRIFT-spectrum of the solid MAO samples prepared by heating at 50°C in vacuum is presented in Fig. 1. The low-frequency region of the spectrum (Fig. 1A) contains absorption bands (a.b.) with maximums at 870, 900, 950 and 985  $\text{cm}^{-1}$ . According to [12], these a.b. are characteristic for the stretching vibrations of Al–O bonds. Absorption bands with maximums at 1220 and 1250  $\text{cm}^{-1}$  (Fig. 1A) correspond to an umbrellas vibrations of  $\text{CH}_3$ -groups [11,12]. Absorption bands in the range

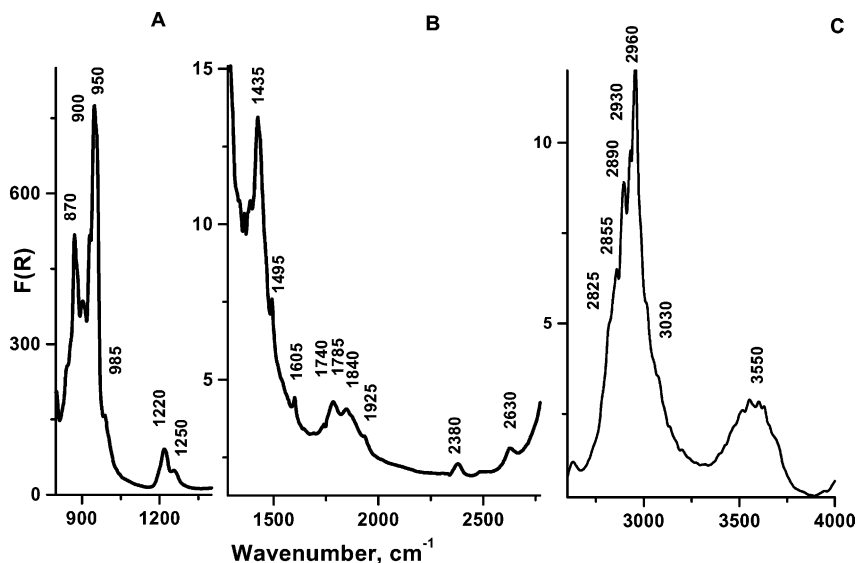


Fig. 1. DRIFT-spectrum of solid MAO sample heated in vacuum at 50°C.

of 1435–1450  $\text{cm}^{-1}$  (Fig. 1B) characterize bending vibrations of  $\text{CH}_3$ -groups.

At frequencies 2700–3000  $\text{cm}^{-1}$  (Fig. 1C), the spectrum exhibits a.b. 2855, 2890, 2930 and 2960  $\text{cm}^{-1}$  characteristic for the stretching vibrations of the C–H bonds ( $\nu_S$  and  $\nu_{AS}$ ). Since only two stretching vibration bands are expected for fragment Al– $\text{CH}_3$ , the presence of four bands in the spectrum suggests the existence of  $\text{CH}_3$ -groups of two types. Earlier Sinn [9] proposed MAO contains  $\text{CH}_3$ -groups of two types: one type as a “single”  $\text{CH}_3$ -groups in fragment Al– $\text{CH}_3$  and another type as a “double”  $\text{CH}_3$ -groups in fragment  $\text{H}_3\text{C}$ –Al– $\text{CH}_3$ . Later, IRS data have been shown that the two types of  $\text{CH}_3$ -groups: terminal and bridging  $\text{CH}_3$ -groups exist in MAO [11,12]. Bridging  $\text{CH}_3$ -groups are more reactive than terminal  $\text{CH}_3$ -groups. They easily are exchanged with chlorine atom when  $\text{Me}_2\text{AlCl}$  have been added to MAO [12].

Besides, the IR-spectrum of the MAO sample dried at 50°C exhibits a series of a.b. suggesting the presence of toluene: two stretching vibration bands of toluene aromatic ring, 1495 and 1605  $\text{cm}^{-1}$  (Fig. 1B), and stretching vibration bands of toluene’s C–H bonds at frequencies 3020–3080  $\text{cm}^{-1}$  (Fig. 1C). The sample drying at temperature above 50°C results in the disappearance of a.b. characteristic for toluene (Fig. 3).

Relative to the IR spectroscopy in transmission mode, the DRIFT provides higher intensities of a.b. characteristic for composed vibrations and overtones. Therefore, the DRIFT method allows recording of a.b. 1740, 1785, 1840 and 1925  $\text{cm}^{-1}$  that are the overtones of Al–O stretching vibrations ( $\nu_{\text{Al-O}}$  870, 890, 900, 950 and 985  $\text{cm}^{-1}$ ). The a.b. 2380  $\text{cm}^{-1}$  corresponds to the overtone of umbrella vibrations of  $\text{CH}_3$ -groups (1220  $\text{cm}^{-1}$ ); a.b. 2630  $\text{cm}^{-1}$  likely corresponds to composed vibration ( $\nu_{\text{Al-O}} + \delta_{\text{CH}_3} = 1220 + 1450 \text{ cm}^{-1}$ ); 2825  $\text{cm}^{-1}$  is the overtone of the bending vibrations of  $\text{CH}_3$ -group ( $\delta_{\text{CH}_3} = 1435\text{--}1450 \text{ cm}^{-1}$ ).

The most unexpected and intriguing feature of the IR-spectrum is the presence of an intensive and broad a.b. at 3550  $\text{cm}^{-1}$  (Fig. 1C). It is known [18] that both stretching vibrations of OH-groups and composed vibrations of Al–O- and  $\text{CH}_3$ -groups may be observed in this region. There is one possibility to distinguish these vibrations according to their half-width [17]. Typical values of the half-width of stretching vibration bands of OH-groups account to 200–800  $\text{cm}^{-1}$  at

formation of hydrogen bonds. While the half-width of composed vibration bands of  $\text{CH}_3$ -groups approximately equals to half-width of the stretching vibrations. The latter equals to less than 60  $\text{cm}^{-1}$ . The experimental IRS data of solutions of TMA and MAO are shown in Fig. 2. We observe three weak a.b. at 3443, 3548, 3640  $\text{cm}^{-1}$  for TMA solution (Fig. 2, curve 2). Half-width of this bands is less than 60  $\text{cm}^{-1}$ . While we observe the broad a.b. 3535  $\text{cm}^{-1}$  for MAO solution. Half-width of this band accounts to ca. 200  $\text{cm}^{-1}$ . We can compare too the relative intensity of a.b. at 3443, 3535–3548 and 3640  $\text{cm}^{-1}$  for the samples of TMA and MAO (Fig. 2). We see the relative intensity of the broad a.b. at 3535  $\text{cm}^{-1}$  for MAO sample is much higher than relative intensity of a.b. at 3548  $\text{cm}^{-1}$  for TMA sample. Based on these data, we believe that a.b. at 3443, 3548, 3640  $\text{cm}^{-1}$  in IR-spectra of TMA characterize the composed vibrations of  $\text{CH}_3$ -groups, but a.b. at 3535  $\text{cm}^{-1}$  in IR-spectra of MAO solution characterizes the sum of stretching vibrations of hydrogen-bonded OH-groups and composed vibrations of  $\text{CH}_3$ -groups.

So we propose that the broad a.b. at 3550  $\text{cm}^{-1}$  in IR-spectra of solid MAO (Fig. 1) may be attributed to the stretching vibrations of hydrogen-bonded OH-groups.

For example, Pasynekiewicz et al. [18] devoted to the IR spectroscopic studies of reaction mixture  $\text{Al}(\text{CH}_3)_3/\text{H}_2\text{O}$  in diethyl ether (D) at  $\text{Al}(\text{CH}_3)_3/\text{H}_2\text{O}$  molar ratio 2:1 observed a.b. 3180  $\text{cm}^{-1}$  and ascribed it to the Al–OH-groups in fragments  $(\text{CH}_3)_2\text{Al-OH}\cdot\text{D}$ . As an additional amount of water was introduced in the mixture, broad a.b. 3510  $\text{cm}^{-1}$  appeared in the spectrum that was attributed to the hydroxyl groups of water molecules dissolved in diethyl ether [18]. However, at first sight the presence of water molecules or Al–OH-groups in the MAO always containing significant amount of free TMA seems to be unlikely. This contradiction may be overcome in the assumption that water molecule is entrapped inside of the three-dimensional “cage” structure of MAO molecule that impedes the reaction of water with free TMA existing in the system (see Fig. 5). To some extent this situation corresponds to familiar data on the low reactivity of OH-groups of intra-globular (structural) water contained in silica. In particular, it is known [13,19,20] that TMA reacts stoichiometrically (quantitatively) with the silica surface OH-groups and does

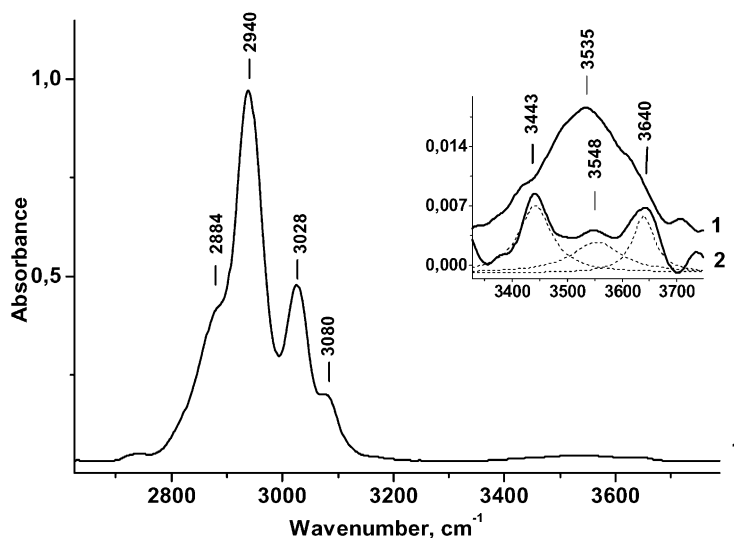


Fig. 2. IR-spectrum of toluene solutions: (1) TMA (0.23 M); (2) MAO (1.42 M).

not react with the intra-globular OH-groups, which are characterized by broad a.b.  $3680\text{ cm}^{-1}$  in the IR-spectrum. With this in mind, we treated the solid MAO samples with additional amount of TMA, but the intensity of a.b.  $3550\text{ cm}^{-1}$  did not change. So, the OH-groups in MAO (if any) are inaccessible for TMA molecules, similarly to the intra-globular OH-groups in silica gel.

Fig. 3 shows the DRIFT-spectra of the MAO samples prepared by drying in vacuum at temperatures

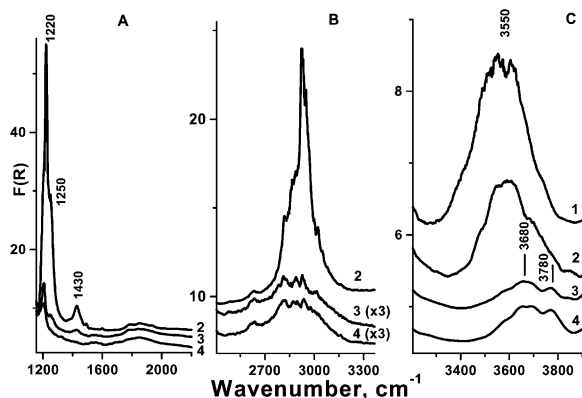
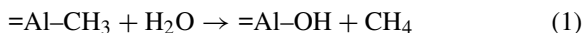


Fig. 3. DRIFT-spectra of solid MAO samples heated in vacuum at different temperatures: (1)  $20^\circ\text{C}$ ; (2)  $50^\circ\text{C}$ ; (3)  $100^\circ\text{C}$ ; (4)  $250^\circ\text{C}$ .

from  $20$  to  $250^\circ\text{C}$ . The sample dried at  $20^\circ\text{C}$  contains considerable amount of toluene that hampered the registering of the sample spectrum at frequencies below  $3100\text{ cm}^{-1}$  (the absorbance region of toluene molecule). The spectrum of this sample contains a broad asymmetric band with the maximum at  $3550\text{ cm}^{-1}$  (Fig. 3C) that was ascribed to OH-groups of “structural” water entrapped inside of MAO molecule.

The spectrum of the MAO sample prepared by the following heating at  $50^\circ\text{C}$  exhibited intensive a.b.  $1220$  and  $1250\text{ cm}^{-1}$  characteristic for the umbrellas bending vibrations of  $\text{CH}_3$ -groups (Fig. 3A, curve 2), and stretching vibrations bands of  $\text{CH}_3$ -groups in the region of  $2800$ – $3100\text{ cm}^{-1}$  (Fig. 3B, curve 2). As the heating temperature of the MAO samples increased from  $20$  to  $50^\circ\text{C}$ , the intensity of a.b.  $3550\text{ cm}^{-1}$  of structural water decreased (Fig. 3C, curves 1 and 2). When the heating temperature exceeded  $50^\circ\text{C}$ , further loss of intensities of a.b.  $3550\text{ cm}^{-1}$  and of a.b. in the regions of  $1200$ – $1300$  and  $2800$ – $3000\text{ cm}^{-1}$  was observed (Fig. 3C, curves 3, 4). That is, the heating of MAO samples at temperatures  $50$ – $100^\circ\text{C}$  causes synchronous decrease of intensities of broad a.b. at  $3550\text{ cm}^{-1}$  hypothetically ascribed to hydroxyl groups, and of absorption bands characteristic for  $\text{CH}_3$ -groups in fragments  $\text{Al-CH}_3$ . These data allow

suggesting that the structural water entrapped inside of MAO molecule with three-dimensional cage structure could diffuse from the MAO cages and react with free TMA molecules or Al-CH<sub>3</sub> fragments, existing in MAO, by the protolysis reaction:



Obviously, the diffusion of water from the MAO cages intensifies with increasing of temperature. The spectra of the MAO samples heated at 100°C and higher temperatures contain a broad a.b. 3680 and 3780 cm<sup>-1</sup> (Fig. 3C) that may be attributed to the formation of the Al-OH-groups by reaction (1).

### 3.2. Quantum-chemical modeling of the structure of MAO molecule with entrapped water molecule

Earlier [21,22], we used the non-empirical DFT method to model electronic structure of polymethylalumoxanes [-Al(CH<sub>3</sub>)O-]<sub>n</sub> differing by molecular masses. The calculations showed the three-dimensional “cage” structure to be the most stable for the MAO with oligomerization degree  $n \geq 6$ . The aluminum atoms in such a structure are tetra-coordinated and form fragments MeAlO<sub>3</sub>, while the oxygen atoms are tri-coordinated. Optimization of the MAO model performed in work [23] on the basis of comprehensive experimental data on MAO composition and structure allowed formulating the concept of two MAO forms differing by structure and composition and existing in equilibrium (see reaction 2). In “true” MAO of composition [Al(CH<sub>3</sub>)O]<sub>n</sub>·[Al(CH<sub>3</sub>)<sub>3</sub>]<sub>n/3</sub>, the TMA molecules are integral part of the MAO structure [1,22]. According to results, presented in [22] “true” MAO is in equilibrium with “classic” MAO of composition [-Al(CH<sub>3</sub>)O-]<sub>n</sub>.

#### 3.2.1. The DFT calculation details

All the calculations were carried out with use of the Gaussian92/DFT package [24]. The fully optimized geometries of various forms of the MAO-oligomers have been calculated using DFT, the LANL1 effective core potential for inner shells of Al [25] and basis set single-ξ (minimal basis) for valence shells of Al and for the carbon, oxygen and hydrogen atoms in MAO and in H<sub>2</sub>O molecules. The Vosko–Wilk–Nusair [26]

(VWN) local correlation parameters with  $X_\alpha$  — exchange functional ( $\alpha = 0.7$ ) were applied to evaluate the density functional (local density approximation — LDA). Comparison between calculated and experimental geometry of the [-Al(CH<sub>3</sub>)O-]<sub>6</sub> oligomer, and dissociated enthalpy of dimeric TMA have been presented in [21]. From these data we can see that the basis sets single-ξ introduce the same errors into the DFT/ $X_\alpha$ -VWN calculations as the double-ξ bases sets and we have preferred to use the minimal basis sets. The total charge densities of the MAO-oligomers were calculated using the Mulliken population analysis.

#### 3.2.2. Results of the DFT calculations

Fig. 4 illustrates the calculated model of MAO molecule with C<sub>4h</sub>-symmetry of composition [-Al(Me)O-]<sub>12</sub>, in which all Al-atoms are tetra-coordinated, and O-atoms are tri-coordinated. In order to estimate the probability of incorporation of water molecule in the structure of MAO molecule, we performed the DFT calculations for MAO with  $n = 9$  and 12. The calculation results are presented in Fig. 5 and Table 1. It is seen that the introduction of water molecule into three-dimensional structure of MAO molecule with  $n = 12$  is energetically profitable ( $\Delta H = -15.6$  kcal/mole). It may be compared with adsorption enthalpies for the molecular form of water in large cavity of zeolites: 15–20 kcal/mole [27]. In the case of MAO molecule with a lower oligomerization degree ( $n = 9$ ), the process is energetically inefficient. Fig. 5b illustrates the detailed structure of the inner layer of MAO molecule with water

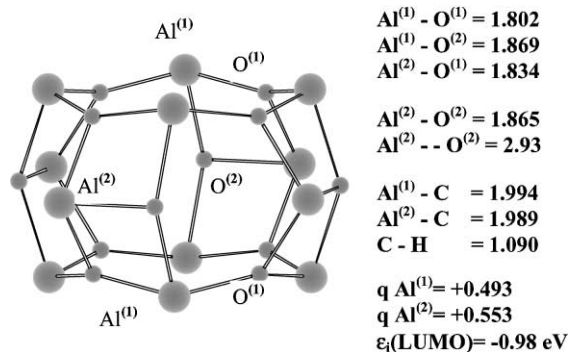


Fig. 4. Side view of a triple-layer cage structure [-Al(Me)O-]<sub>12</sub> with the C<sub>4h</sub>-symmetry, calculated at the DFT/LANL1MB level. CH<sub>3</sub>-group of MAO are omitted for clarity.

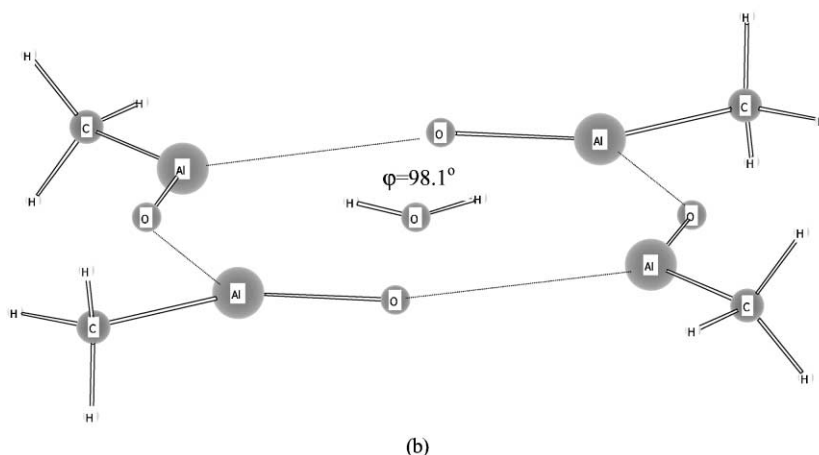
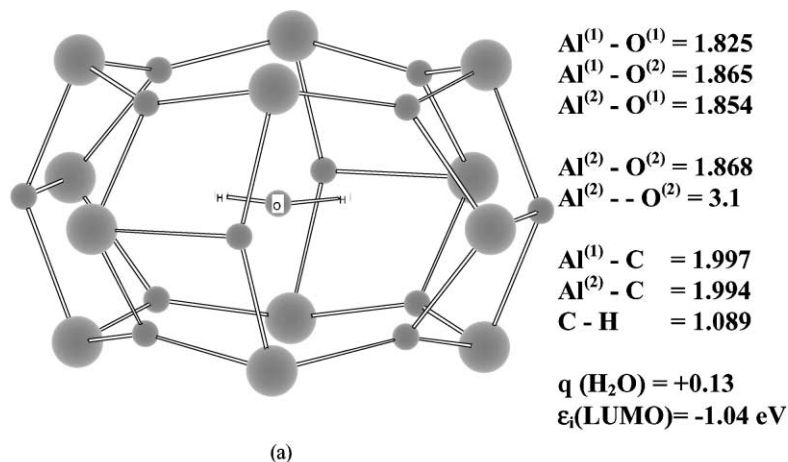


Fig. 5. A triple-layer cage structure  $[-\text{Al}(\text{Me})\text{O}-]_{12}$  with the occluded  $\text{H}_2\text{O}$  molecule calculated at the DFT/LANL1MB level (CH<sub>3</sub>-groups of MAO are omitted for clarity): (a) side view of cage structure  $[-\text{Al}(\text{Me})\text{O}-]_{12}$  with the occluded  $\text{H}_2\text{O}$  molecule; (b) the inner layer of the triple-layer cage structure  $[-\text{Al}(\text{Me})\text{O}-]_{12}$  with the occluded  $\text{H}_2\text{O}$  molecule.

Table 1

Calculated geometric and electronic characteristics of triple-cage structure of the  $[-\text{Al}(\text{Me})\text{O}-]_{12}$  with the  $\text{C}_{4h}$ -symmetry, the free  $\text{H}_2\text{O}$  molecule and occluded  $\text{H}_2\text{O}$  in the volume of MAO

Molecular system	Calculated geometry (Å)	Calculated net charges	DFT total energy (a.u.)
$\text{H}_2\text{O} + [-\text{Al}(\text{CH}_3)\text{O}-]_{12}$ $\Rightarrow (\text{H}_2\text{O})\cdot(\text{MAO})_{12}$	$r(\text{OH}) = 1.02$	$q(\text{O}) = -0.350$	-75.34702
	$\varphi(\text{HOH}) = 97.3^\circ$	$q(\text{H}) = +0.175$	
	$\text{Al}^1 - \text{O}^1 = 1.80$	$q(\text{Al}^1) = +0.49$	-1390.48053
	$\text{Al}^1 - \text{O}^2 = 1.87$	$q(\text{Al}^2) = +0.55$	
	$\text{Al}^2 - \text{O}^1 = 1.83$		
	$\text{Al}^2 - \text{O}^2 = 1.86$		
	$r(\text{OH}) = 1.02$	$q(\text{H}_2\text{O}) = +0.13$	-1465.85240 (-15.6 kcal/mole) <sup>a</sup>
	$\varphi(\text{HOH}) = 98.1^\circ$		

<sup>a</sup> Calculated stabilization energy of the  $\text{H}_2\text{O}$  molecule in volume of MAO.

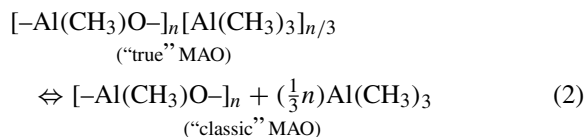
molecule located in the layer plane. According to the calculations with gradient corrections, the oxygen atom of water molecule locates almost in the spatial (“volume”) center of the MAO molecule, while the hydrogen atoms are at the distances of 2.3–2.5 Å from Al- and O-atoms of the MAO inner layer.

Thus, the DFT calculations prove that MAO molecule may contain water molecule inside. Encapsulation of water molecule most likely occurs at the initial stage of the formation of three-dimensional MAO structure. The entrapped water molecule becomes unavailable for TMA and thus, retains in the final MAO structure.

### 3.3. The data on the composition of products released at heating of MAO

Taking into account the DRIFT and DFT data, we studied by mass-spectrometric (MS) method the composition of gaseous products released at heating of MAO for 30 h at 50°C (MAO-50) or 150°C (MAO-150) (Table 2). The gas phase over both samples contained considerable amounts of methane. That is, the MS data proved the possibility of reaction (1) at temperatures 50–150°C. It was observed also that besides methane, the heating of the MAO sample released other products that condensed on the cell walls at room temperature. The released liquid products were collected and studied by <sup>1</sup>H NMR method. It was found that they contained toluene and TMA. Data on the amounts of TMA released from MAO-50 and MAO-100 are presented in Table 2. Considerable amount of TMA released at MAO heating at 100°C confirms the concept of two equilibrium MAO

structures, formulated in reaction (2).



Increasing temperature facilitates transformation of “true” MAO in “classic” MAO with the release of TMA.

The heating of MAO at high temperature may destroy it. In order to distinguish the protolysis reaction (1) and reversible transformation of two structures of MAO according to reaction (2) from the reaction of MAO destruction, we applied the method of TPD in helium flow and MS analysis to study the products released at the heating of MAO at temperatures from 20 to 450°C. Respective MS-spectrum is shown in Fig. 6. As it is seen in Fig. 6, two regions of MAO transformation under heating may be separated. In the first temperature interval ranging from 20 to 170°C, only methane is released from MAO. It should be noted that the fast heating of MAO in the interval of 20–100°C released insignificant amount of methane (Fig. 6A), while the sample keeping at 50°C for 30 h produced significant quantity of methane (0.38 mmole CH<sub>4</sub>/g MAO). As the sample was heated above 100°C, the amount of the released methane increased considerably. At temperatures 50–150°C toluene and TMA are released besides methane (Table 2).

According to data of chemical analysis (Table 2), the composition of MAO-50 (CH<sub>3</sub>/Al = 1.6) is close to composition of “true” MAO with binded TMA. The considerable amount of TMA is released after heating of MAO under vacuum at 100°C (Table 2).

Table 2

Data on the composition and amount of gaseous and liquid products, evolving at MAO heating<sup>a</sup>

Temperature of MAO heating <sup>b</sup> (°C)	Gaseous product <sup>c</sup>	Liquid product <sup>d</sup>	[CH <sub>3</sub> ]/[Al] <sup>e</sup> (mole/mole)
50	Methane, 0.38 mmole/g MAO	Toluene, AlMe <sub>3</sub> , 0.02 mole/mole Al(MAO)	1.6
100	–	Toluene, AlMe <sub>3</sub> , 0.18 mole/mole Al(MAO)	0.9
150	Methane, 1.9 mmole/g MAO	–	–

<sup>a</sup> Initial MAO sample (MAO-20) contains 13.6 mmole Al/g MAO.

<sup>b</sup> MAO-20 samples have been heated for 30 h.

<sup>c</sup> Data of mass spectrometry.

<sup>d</sup> Data of <sup>1</sup>H NMR spectroscopy.

<sup>e</sup> Data for samples of solid MAO were determined on the amount of methane, formed after dissolving of samples in H<sub>2</sub>O/HCl mixture.



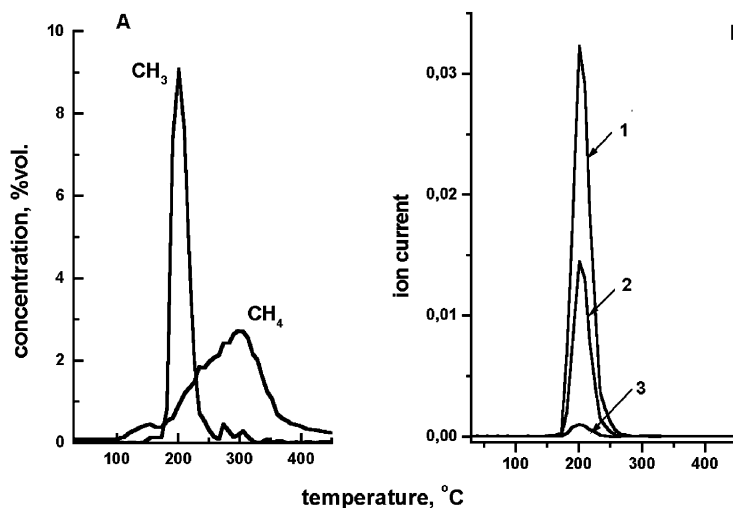


Fig. 6. Mass-spectra of products released at the heating of solid MAO within the temperature range 20–450°C: (A) methane and methyl radicals; (B) (1) AlMe<sub>2</sub>, (2) AlMe<sub>3</sub>, (3) AlMe.

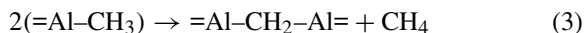
Accordingly the composition of MAO-100 sample (CH<sub>3</sub>/Al = 0.9) is more close to “classical” MAO.

The second region corresponds to the heating of MAO at temperatures above 170°C. Respective MS-spectrum exhibits, besides peaks of methane, the peaks corresponding to methyl radicals ( $m/e = 15$ ) (Fig. 6A), mono and dimethylaluminum fragments Al(CH<sub>3</sub>)<sub>x</sub> ( $x = 1, 2$ ;  $m/e = 42$  and  $m/e = 57$ , respectively, Fig. 6B and also peaks of TMA ( $m/e = 72$ ), and toluene ( $m/e = 91$ ). The maximum release of methyl radicals and Al(CH<sub>3</sub>)<sub>x</sub> fragments was observed at 200°C. The appearance of these species prove that the structure of MAO destroys under such conditions. Besides, at temperatures above 170°C, the amount of released methane increased sharply (Fig. 6A), most likely, owing to transformation of methyl radicals.

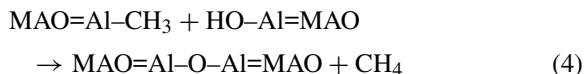
Thus, the above data suggest that in MAO samples heated at temperatures 20–170°C, the formation of methane occurs mainly by the protolysis of Al-CH<sub>3</sub>-groups (reaction 1). This reaction proceeds simultaneously with the transformation of “true” MAO into “classic” MAO, releasing TMA (reaction 2). At temperatures above 170°C, the processes leading to the MAO destruction begin.

Kaminski and co-workers first qualified the release of methane from MAO as a spontaneous reaction [28,29]. In particular, it was observed that the solution of MAO in toluene kept at 10°C for 20 h released

1.7 mmole CH<sub>4</sub>/mole Al<sub>MAO</sub>; the system SiO<sub>2</sub>/MAO kept at 30°C for 20 h released 8 mmole CH<sub>4</sub>/mole Al<sub>MAO</sub> [30]. It is suggested in works [29,30] that the formation of methane proceeds via reaction (3):



However, the results of our studies suggest another explanation for the methane formation (see reaction 1). Moreover, reaction (1) proceeding with the participation of “intra-globular” water may also explain the known effect of “MAO” aging in solution, which is accompanied by a precipitate formation. The precipitate most likely is a product of condensation of several MAO molecules (reaction 4) through the reaction of Al-CH<sub>3</sub>-groups in MAO with Al-OH-group formed in another MAO molecule via reaction (1).



Basing on the methane quantity released from MAO under long heating at 150°C (1.9 mmole CH<sub>4</sub>/g MAO, Table 2), one may estimate the content of “intra-globular” water in MAO. We used for this estimation the following data: (1) Al content in the initial MAO sample consists 13.6 mmole Al/g MAO; (2) one water molecule may facilitate the release of two methane molecules. According to this data, we cal-

Table 3

Effect of solid MAO heating on activity of catalyst Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO at ethylene polymerization

Experiment no.	Temperature of MAO heating <sup>a</sup> (°C)	Activity <sup>b</sup> (kg PE/mole Zr h)	MI <sup>c</sup> (g/10 min)
1 <sup>d</sup>	–	5100	>100
2	20	4670	0.19
3	50	5340	0.14
4	100 <sup>e</sup>	2550	0.15
5	250 <sup>e</sup>	200	–

<sup>a</sup> Heating under vacuum for 1 h.<sup>b</sup> Polymerization in toluene at temperature 50°C, ethylene pressure 6 bar, [Zr] = 1.4 × 10<sup>-5</sup> mole/l, [Al<sub>MAO</sub>]/[Zr] = 1000.<sup>c</sup> Melt index of PE is measured at load 21.6 kg.<sup>d</sup> Polymerization with initial solution of MAO.<sup>e</sup> Solid MAO is insoluble in toluene; so it was added into reactor as powder.

culated that MAO may contain 0.07 mole H<sub>2</sub>O/mole Al<sub>MAO</sub>.

### 3.4. The effect of MAO heating at different temperatures on the performance of zirconocene catalysts in the ethylene polymerization

The data on the ethylene polymerization with catalysts Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO prepared with the use of the MAO samples dried at different temperatures ranging between 20 and 250°C are shown in Table 3 (experiments 2–5). The activity of reference catalyst synthesized with the use initial MAO solution is also presented (Table 3, experiment 1). Note that samples MAO-20 and MAO-50 were easily soluble in toluene and therefore, were fed in the polymerization reactor in a form of toluene solutions. The catalysts prepared with the use of MAO-20 and MAO-50 exhibited similar activities, which were closed to the activity of reference catalyst. The higher melting index of polyethylene (smaller molecular mass) obtained with the reference catalyst may be attributed to significant amount of TMA contained in the initial MAO sample (30% of Al content). TMA is known as a highly efficient agent of the chain transfer reaction. Samples MAO-100 and MAO-250 were almost insoluble in toluene and were introduced in the polymerization reactor as dry powders. Nevertheless, the activity of the catalyst synthesized with the use of MAO-100 decreased insignificantly (nearly twice). Dramatic loss of activity (more than 20 times) was observed for the catalyst prepared with the use of MAO-250, the structure of which, as shown above, undergone thermal destruction.

Thus, the structural and compositional changes that occur in MAO under the heating at temperatures 20–100°C and relate to the proceeding of reactions (1) and (2) produce no essential effect on the MAO ability to activate metallocene catalysts for polymerization.

## References

- [1] H. Sinn, I. Schimmel, M. Ott, N. von Thienen, A. Harder, W. Hagendorf, B. Heitmann, E. Haupt, in: W. Kaminsky (Ed.), *Metalloorganic Catalysts for Synthesis and Polymerization*, Springer, Berlin, 1999, p. 105.
- [2] M.R. Mason, J.M. Smith, S.G. Bott, A.R. Barron, *J. Am. Chem. Soc.* 115 (1993) 4971.
- [3] T. Sugano, K. Matsubara, T. Fujita, T. Takahashi, *J. Mol. Catal. A: Chem.* 82 (1993) 93.
- [4] I. Tritto, M.C. Sacchi, P. Locatelli, S.X. Li, *Macromol. Chem. Phys.* 197 (1996) 1537.
- [5] I. Tritto, M.C. Sacchi, P. Locatelli, *Macromol. Chem. Phys.* 198 (1997) 3963.
- [6] D. Imhoff, L. Simeral, S. Sangokoya, L. Peel, *Organometallics* 17 (1998) 1941.
- [7] D.E. Babushkin, N.V. Semikolenova, V.N. Panchenko, A.P. Sobolev, V.A. Zakharov, E.P. Talsi, *Macromol. Chem. Phys.* 198 (1997) 3845.
- [8] E. Thorn-Csányi, J. Dehmel, O. Halle, W. Sciborski, *Macromol. Chem. Phys.* 195 (1994) 3017.
- [9] H. Sinn, *Macromol. Symp.* 97 (1995) 27.
- [10] W. Hagendorf, A. Harder, H. Sinn, *Macromol. Symp.* 97 (1995) 127.
- [11] J. Eilertsen, E. Rytter, M. Ystenes, in: W. Kaminsky (Ed.), *Metalloorganic Catalysts for Synthesis and Polymerization*, Springer, Berlin, 1999, p. 136.
- [12] M. Ystenes, J.L. Eilertsen, J. Liu, M. Ott, E. Rytter, J.A. Støvneng, *J. Polym. Sci. Part A: Polym. Chem.* 38 (2000) 3106–3127.

- [13] V.N. Panchenko, N.V. Semikolenova, I.G. Danilova, E.A. Paukshtis, V.A. Zakharov, *J. Mol. Catal. A: Chem.* 142 (1998) 27.
- [14] C. Janiak, B. Rieger, R. Voelkel, H.-G. Braun, *J. Polym. Sci. Part A: Polym. Chem.* 31 (1993) 2959.
- [15] L.K. Van Looveren, D.F. Geysen, K.A. Vercruyssen, B.H. Wouters, P.J. Grobet, P. Jacobs, *Angew. Chem. Int. Ed.* 37 (1998) 517.
- [16] L.M. Kustov, *Topics Catal.* 4 (1997) 131.
- [17] J.R. Scherer, in: R.J.H. Clack, R.E. Hester (Eds.), *Advances in Infrared and Raman Spectroscopy*, Vol. 5, Heyden, London, Reine, 1978, p. 149.
- [18] S. Pasynkiewicz, A. Sadownik, A. Kunicki, *J. Organomet. Chem.* 124 (1977) 265.
- [19] R.J. Peggler, F.H. Hambleton, J.H. Hockey, *J. Catal.* 20 (1971) 309.
- [20] D.J.C. Yates, G.W. Dembinski, W.R. Kroll, J.J. Elliott, *J. Phys. Chem.* 73 (1969) 911.
- [21] I.I. Zakharov, V.A. Zakharov, G.M. Zhidomirov, *Macromol. Theory Simul.* 8 (1999) 272.
- [22] I.I. Zakharov, V.A. Zakharov, G.M. Zhidomirov, in: W. Kaminsky (Eds.), *Metalloorganic Catalysts for Synthesis and Polymerization*, Springer, Berlin, 1999, p. 128.
- [23] I.I. Zakharov, V.A. Zakharov, *Macromol. Theory Simul.* 9 (2000), in press.
- [24] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.W. Wong, J.B. Foresman, M.A. Robb, M. Head-Gordon, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart, J.A. Pople, *Gaussian 92/DFT*, Revision G.2, Gaussian, Inc., Pittsburgh, PA, 1993.
- [25] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 270.
- [26] S.J. Vosco, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [27] R.M. Barrer, *Zeolites and Clays Mineral as Sorbents and Molecular Sieves*, Academic Press, London, 1978, p. 212.
- [28] W. Kaminsky, R. Steiger, *Polyhedron* 7 (1988) 2375.
- [29] W. Kaminsky, A. Bark, R. Steiger, *J. Mol. Catal. A: Chem.* 74 (1992) 109.
- [30] W. Kaminsky, C. Strübel, *J. Mol. Catal. A: Chem.* 128 (1998) 191.