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Zirconocene catalysts supported on modified and nonmodified silica***)

Summary — The temperature-programmed desorption (TPD) technique was used to study, by mass spectrometry (MS), the desorbates released from SiO_2-supported MAO (I) and SiO_2-supported Cp_2ZrCl_2 (II) surfaces. With II, Cp groups were found to be copiously released at temperatures exceeding 200°C. Hence, decomposition of Cp_2ZrCl_2 while the compound is being heterogenized, cannot explain the low activity of the catalyst II in which Cp_2ZrCl_2 is chemically bonded to the carrier surface through OH groups. The MS (intensity *vs.* temperature) curves recorded for the I desorbates exhibit maxima (Fig. 2) for m/z = 15—16 at about 200°C and 400°C. They represent the methyl groups liberated on thermal destruction of =Al-C- bonds in respectively $AlO(Me)_2$ and AlO_2Me. At about 400°C, the MAO oligomer molecules were fragmented to produce AlOMe (m/z = 58), AlOAl (m/z = 70), $AlOMe_2$ (m/z = 73), AlO_2Me (m/z = 74), Al_3O_3 rings (m/z = 131), and (Al_3O_3)-O- rings (m/z = 147). Alternating adsorption (up to 8 times) of $AlMe_3$ vapor followed by H_2O vapor on SiO_2 surface was tried to synthesize SiO_2-supported MAO with no "free" $AlMe_3$. As a result, surface structures of the type ≡Si-O-$(AlMeO)_n$ (n = 8) were produced. The MAO thus synthesized was showed by TPD studies to have a linear or a planar net structure.

Key words: supported metallocene, methylaluminoxane (MAO), heterogenization, temperature-programmed desorption (TPD).

Heterogenization of metallocene-MAO catalysts is an important goal in recent catalysis of polymerization of olefins. Pretreatment of a SiO_2 support with MAO and a subsequent reaction with metallocene [1—4] is the way most generally employed.

Attempts have also been undertaken to synthesize MAO directly on the surface of the support by the reaction of trimethylaluminum (TMA) with hydrated SiO_2 [5—7].

This paper sets out to describe a study on silica-supported MAO and Cp_2ZrCl_2 carried out by the method of temperature-programmed desorption (TPD). Results of the synthesis on silica that involved alternating adsorption of first $AlMe_3$ vapor and then H_2O vapor with multiple repetition of this operation are also reported.

EXPERIMENTAL

Materials

Cp_2ZrCl_2 and MAO (10 wt. % MAO in toluene) were purchased from Aldrich. Aldrich's toluene was stored over molecular sieves and distilled from sodium in an argon atmosphere. SiO_2-aerosil (USSR's trade mark 14922-77) had a specific area of 300 m^2/g, which corresponds to an average particle size of 15 nm. $AlMe_3$ and TIBA were taken from GNIHTEOS, Moscow. Ethylene was polymerization grade purity.

Temperature-programmed desorption (TPD)

The TPD desorbates liberated from silica-supported MAO (MAO/SiO_2), silica-supported Cp_2ZrCl_2(Cp_2ZrCl_2/SiO_2) and from the MAO synthesized on the silica surface (MAO^*/SiO_2) were studied by mass spectroscopy by using programmed linear heating of the samples [8, 9].

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Sample preparation for TPD study

Silica was pre-evacuated at 700°C. The supported zirconocene catalyst was obtained by treating 0.1 g silica with 2 mL of a 0.004 M zirconocene solution in toluene with stirring. The mixture was kept at 20°C for 1 hour and dried in vacuum at 20°C for 3 hours. The Zr content on the silica surface was equal to 0.3 $\mu mol/m^2$; this content corresponds to 30% of hydroxyl groups. The MAO/SiO_2 samples were obtained by the same way. Silica, 0.1 g, was treated with 2 mL of a 0.02 M MAO solution in toluene. The MAO content was equal to 1.2 $\mu mol/m^2$; that corresponds to 100% of hydroxyl groups. The pre-formed samples were distributed in vacuum into microflasks for the TPD study. The sample in each microflask was weighed, 0.001—0.003 g.

Modification of SiO_2

The silica support activated by alternatingly adsorbing first $AlMe_3$ vapor and then water vapor; the activation operation was repeated up to eight times. In each operation, the $Al:H_2O$ mole ratio was equal to about 1:1. The excess of $AlMe_3$ and then the excess of H_2O were pumped away from the surface after each operation. The Al/H_2O overall mole ratio in the final product formed on the surface was equal to 1.3. The synthesis of MAO^*/SiO_2 was carried out in a MacBain balance device with gravimetric control of the content of the components on the silica surface [10].

Polymerization procedures

Polymerization was carried out at 35°C and 50°C in a 400 mL glass reactor equipped with an electromagnetic stirrer. The synthesized-MAO-activated silica support (MAO^*/SiO_2), 0.1—0.15 g, was placed in the reactor in an Ar atmosphere. Then the reactor was evacuated and filled with 70 mL toluene and zirconocene previously dissolved in toluene. In some experiments, MAO or TIBA or $AlMe_3$ was added. Ethylene was introduced so as to have a concentration of $3.2 \cdot 10^{-2}$ mol/L; the zirconocene concentration was $5 \cdot 10^{-5}$ mol/L; and [Al]/[Zr] = 500. Polymerization was terminated by adding a 5 wt. % solution of hydrochloric acid in ethanol. The product was filtered, washed with ethanol and dried in vacuo at 40°C.

Table 1. Results of ethylene polymerization over Cp_2ZrCl_2 and MAO^*/SiO_2 and various cocatalysts

Run No.	Cocatalyst	Cocatalyst/Zr mol/mol	[Zr] mol/L	Activity kg PE/ (mol Zr · h · bar)	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$
1	none	—	$5 \cdot 10^{-5}$	—	—	—
2	TIBA	150	$5 \cdot 10^{-5}$	—	—	—
3	$AlMe_3$	130	$3 \cdot 10^{-3}$	10	100	4.5
4	MAO	500	$5 \cdot 10^{-5}$	1000	120	2.8

Polymerization conditions: temperature, 50°C; ethylene pressure, 1 bar; toluene as solvent; time, 1 h.

Polymer characterization

Molecular weight and MWD of the resulting polymers were measured with a Waters GPC in *o*-dichlorobenzene at 140°C (Table 1).

RESULTS AND DISCUSSION

Figure 1 shows a TPD spectrum of supported dicyclopentadienylzirconium dichloride; the main products of desorption had masses of 66 (curve 1) and 65 (curve 2), corresponding to cyclopentadienyl groups. A remarkable abstraction of these groups from the catalyst surface is seen to start only at temperatures higher than 200°C. The supported catalysts involving a zirconocene chemically bonded to the carrier surface through hydroxyl groups are slightly active in the polymerization [4]. This fact cannot be explained by the decomposition of dicyclopentadienylzirconium dichloride during its heterogenization.

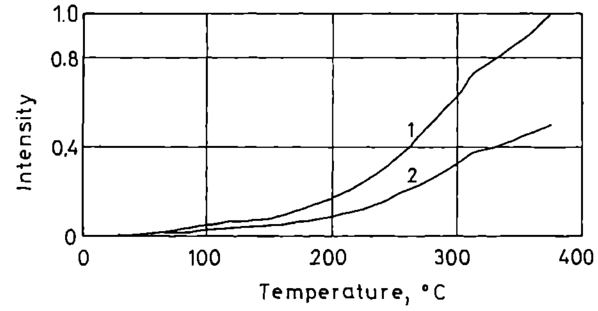
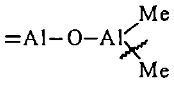
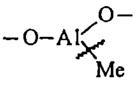


Fig. 1. The curves for TPD desorbates from Cp_2ZrCl_2 surface: (1) m/z = 66 and (2) m/z = 65

The products of desorption from the MAO/SiO_2 surface can be divided into several groups:



(I)



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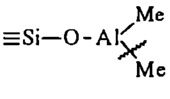

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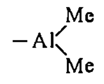

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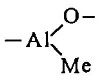

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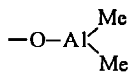

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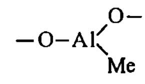

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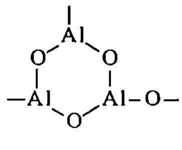

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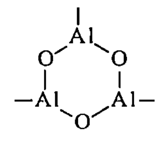


(IX)

In Fig. 2 (curve 1), the TPD spectrum of products endowed with a mass of 15 is presented. The curve shows maxima, one at about 200°C and another at about 400°C. The maxima appear to be associated with the methyl groups releasing upon thermal destruction of the Al-C bonds in structures (I) and (II), respectively. These structures differ in thermal stability of the Al-C bond.

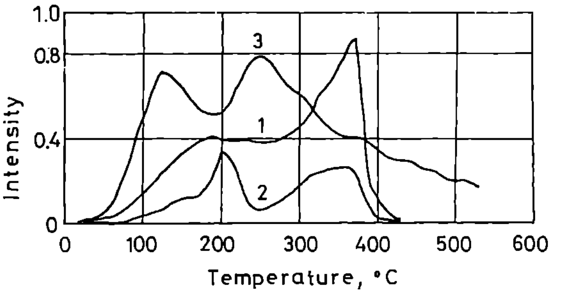
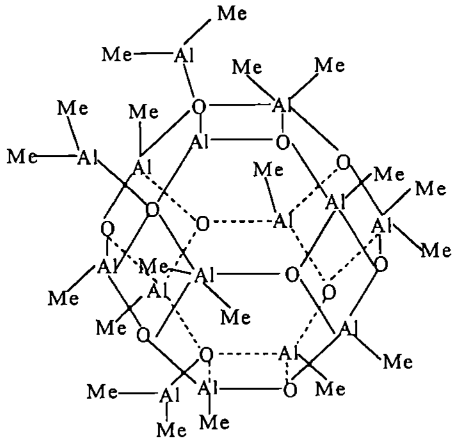


Fig. 2. The curve for TPD desorbates from MAO/SiO$_2$ surface: (1) m/z = 15, (2) m/z = 57; and from MAO synthesized on SiO$_2$ surface: (3) m/z = 15

The complex shape of the maximum at 200°C indicates that structures (III) may well have formed also by a reaction of OH groups in the silica with "free" trimethylaluminum in the MAO, the Al-Me bond in structure (I) being less stable than that in structure (III).

In the high temperature region, the MAO oligomer molecules undergo destruction and release other fragments, too.



(X)

The TPD spectrum for a mass of 57 corresponding to structure (IV) (Fig. 2, curve 2) also exhibits two maxima occurring within temperature ranges of 200°C and 350°C. This fragment appears to have been produced at two different places, as may be deduced from formula X which shows the presumed structure of MAO [4]. In Figure 3, the TPD spectra for masses of 58 (curve 1), 73 (curve 2), and 74 (curve 3) are shown. Based on the structure of MAO, these masses can be attributed to structures (V), (VI), and (VII), respectively.

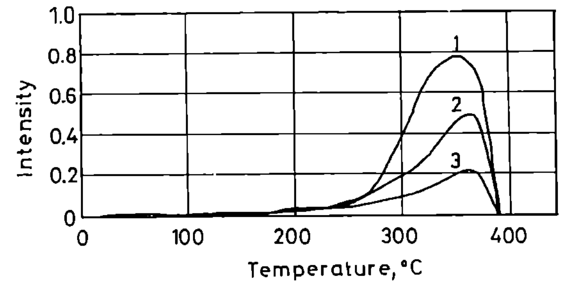


Fig. 3. The curve for TPD desorbates from MAO/SiO$_2$ surface: (1) m/z = 58, (2) m/z = 73 and (3) m/z = 74

Figure 4 shows the TPD spectra for m/z = 147 and 131. The occurrence of these masses makes us suggest the presence of cyclic fragments among the TPD products. The line for mass of 147 is more intense and can be attributed to the evolution of a ring (Al$_3$O$_3$)-O- structure (VIII). The line for mass 131 is less intense and can correspond to the ring Al$_3$O$_3$ structure (IX) (Fig. 4). Each TPD curve (Fig. 4) exhibits one maximum at 352°C. The release of such ring structures appears to reconfirm the structure advanced elsewhere [4].

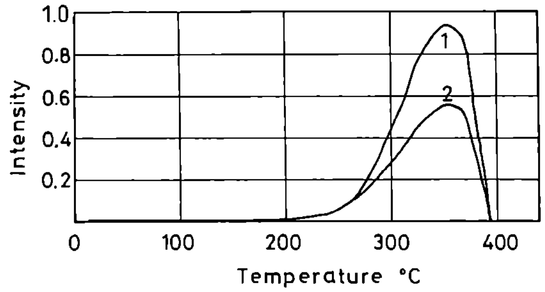
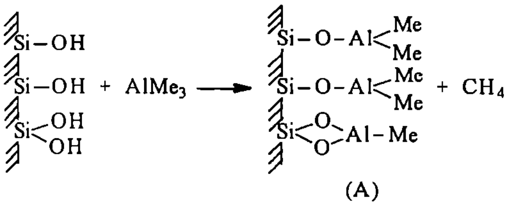


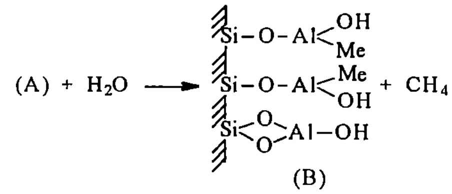
Fig. 4. The curve for TPD desorbates from MAO/SiO$_2$ surface: (1) m/z = 147 and (2) m/z = 131

It is interesting to note the absence of mass 72, which corresponds to AlMe$_3$. The AlMe$_3$, unreacted with OH groups, must have been entirely removed together with toluene on prior drying of the sample in vacuo.

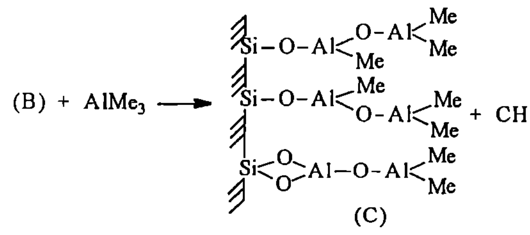
An attempt was made to synthesize MAO directly on the silica surface by alternatingly adsorbing first AlMe$_3$ vapor and then water vapor and repeating this operation up to eight times (eqns. 1—4).



(1)



(2)



(3)

$(C) + H_2O \longrightarrow$ etc. (4)

The TPD investigation of the final products released by MAO*/SiO_2 showed methyl groups to evolve from the silica surface in remarkable quantities. The TPD spectrum for m/z = 15 is presented in Fig. 2 (curve 3). There are two maxima on the TPD curves that occur around 100°C and 230°C. The peaks can be attributed to the methyl groups released upon thermal destruction of Al-C bonds in structures (I) and (II), respectively, similarly as in the case of MAO/SiO_2 (Fig. 2, curve 1). An intensive line is also observed for m/z = 18, attributable to the release of H_2O, which attains a maximum at 200°C. On hydrolysis, H_2O is thus believed not only to react with methyl groups, but also to form complex species with Al atoms. In Fig. 5 are given the TPD curves for m/z = 70 (-Al-O-Al-structure) evolving from MAO/SiO_2 (curve 1) and from MAO*/SiO_2 (curve 2). With MAO/SiO_2, such fragments are seen to have evolved at lower temperatures. The -Al-O-Al- fragments are likely to have appeared on account of the decomposition of the three-dimensional cyclic structure; in the case of MAO*, the linear structure is decomposed. It is worth noting that the masses 147 and 131 corresponding to cyclic structures of (Al_3O_3)-O- and (Al_3O_3), are absent among the TPD products in the case of MAO*/SiO_2.

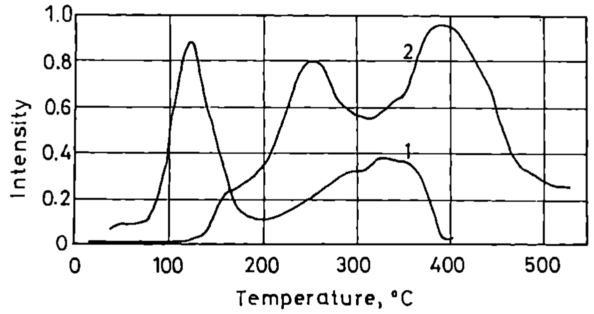


Fig. 5. The curve for TPD desorbates (1) from MAO/SiO_2 surface: m/z = 70; (2) from MAO/SiO_2 surface: m/z = 70*

The present data allow to conclude that the MAO synthesized on the SiO_2 surface (MAO*/SiO_2) has a linear or a planar net structure in contrast to the three-dimensional cyclic structure of the MAO/SiO_2.

Ethylene polymerization over Cp_2ZrCl_2 and MAO*/SiO_2 was also studied with addition of TIBA, $AlMe_3$ or MAO. Results are shown in Table 1.

The Cp_2ZrCl_2—MAO*/SiO_2 catalyst is seen to be practically inactive in the polymerization. TIBA as an additive gave no positive result, whereas $AlMe_3$ activated the catalyst but slightly. The introduction of MAO resulted in high activities up to 1000 kg PE/(mol Zr · h · bar). The resulting PE had M_w equal to 120,000 and its *MWD* was 2.8. The low molecular weight and the narrow *MWD* of the polymer are suggestive of a linear polymerization.

The MAO* synthesized on the SiO_2 surface, having the linear or the planar net structure, is obviously unfavorable to yielding a high-activity zirconocene catalyst.

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