Heterogenized Methylaluminoxane and Isobutylaluminoxane As Activators for Metallocene Catalysts

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Abstract—Heterogenized alkylaluminoxanes prepared in situ on the montmorillonite (MMT) surface by the partial hydrolysis of AlR_3 with water of the support are effective activators for metallocenes. The thermal destruction of isobutylaluminoxane molecules in the MMT-H_2O/Al(i-Bu)$_3$ system has been studied by the temperature-programmed desorption method coupled with mass spectrometry (TPD–MS). The process begins at a lower temperature and is more complicated than the destruction of methylaluminoxane (MAO) in MMT-H_2O/AlMe$_3$. Isobutyl-substituted aluminoxane and the *ansa*-metallocene Me$_2$Si(Ind)$_2$ZrCl$_2$ form metal–alkyl complexes that are more active in propylene polymerization than methyl-substituted aluminoxane. The TPD–MS study of the initial stages of gas-phase ethylene and propylene polymerization shows that the nature of the metallocene in the heterogenized metallocene catalysts is an essential factor in the distribution of active sites by the activation energy of the thermal destruction of active Zr–C bonds.

One of the methods developed recently for metallocene heterogenization is the synthesis of partial hydrolysis products, specifically, alkylaluminums (alkylaluminoxanes) directly on the support surface by the reaction between water of the support and AlR_3 followed by metallocene supporting [1–9]. MAO is an effective activator commonly used with metallocene systems. At the same time, alkylaluminoxanes $(RAlO)_n$ in which R is an alkyl substituent other than methyl (e.g., isobutyl) are also of practical interest as cocatalysts for metallocenes. In many presently known studies, Al(i-Bu)$_3$ is used as an activator of metallocene complexes heterogenized on a support pretreated with MAO. However, the activation mechanism in these systems remains unclear. The properties of aluminoxane as a cocatalyst, including alkylating capacity and the possibility of ion pair stabilization, depend on the nature of the alkyl group bonded to aluminum. The nature of metallocene is also of importance [10–14].

In the present work, support-H_2O/AlR_3 heterogenized activators were synthesized in situ by the partial hydrolysis of AlMe$_3$ and Al(i-Bu)$_3$ with water of the support followed by supporting the metallocene Me$_2$Si(Ind)$_2$ZrCl$_2$ or Cp$_2$ZrCl$_2$. Propylene polymerization on the catalysts prepared was studied. The layered silicate montmorillonite (MMT) was used as the support. To compare the structures of the methyl- and isobutyl-substituted aluminoxanes synthesized on the surface, we studied their thermal decomposition by

mass spectrometric analysis of the products of temperature-programmed desorption (TPD–MS). The initial stages of ethylene and propylene polymerization on the catalysts containing Cp$_2$ZrCl$_2$ and Me$_2$Si(Ind)$_2$ZrCl$_2$ were studied by TPD–MS to determine the energy characteristics and homogeneity of the active sites of these catalysts.

EXPERIMENTAL

Materials

We used the metallocenes Cp$_2$ZrCl$_2$ and Me$_2$Si(Ind)$_2$ZrCl$_2$, a 10% polymethylaluminoxane solution in toluene, 2 M AlMe$_3$ in toluene, and 1 M Al(i-Bu)$_3$ in toluene (all from Aldrich). Toluene (spectral purity grade) to be used as the solvent was held over the molecular sieve 5 Å and distilled from LiAlH$_4$ in argon. Ethylene and propylene were polymerization purity grade. All procedures involved in the preparation of the catalysts were carried out *in vacuo* or in argon passed through columns packed with the Ni–Cr catalyst and a molecular sieve of 5 Å. Montmorillonite (Cloisite[R]Na$^+$) used as the support had the following characteristics: constitutional water content 9.6 wt %, average particle size 8 μm, and cation-exchange capacity 92.6 mg-equiv per 100 g of MMT.

Preparation of Supported Alkylaluminoxane Followed by Supporting a Metallocene

The partial hydrolysis of AlMe₃ or Al(i-Bu)₃ was carried out with the constitutional water of the support to obtain surface-supported alkylaluminoxane. For this purpose, a vigorously stirred suspension of the support in toluene was treated with a toluene solution of AlR₃ at 22°C. The reaction was carried out using procedure 2 described in our earlier paper [15]. The resulting MMT-H₂O/AlR₃ systems were treated with solutions of Cp₂ZrCl₂ or Me₂Si(Ind)₂ZrCl₂ in toluene. The catalysts thus prepared were used in polymerization.

MMT-H₂O/AlMe₃, MMT-H₂O/Al(i-Bu)₃, and MMT-H₂O/AlR₃/metallocene samples to be characterized by TPD–MS were dried *in vacuo* at 22°C. Solid MAO prepared by pumping a toluene solution of commercial MAO at 22°C was also studied by TPD–MS.

TPD–MS

Solid MAO and MMT-H₂O/AlR₃ were analyzed by TPD–MS as follows [16, 17]. A sample, in a special cell connected directly to a mass spectrometer through a heated admission system, was first pumped and then heated from room temperature to 500°C at a constant rate of 10 K/min. The desorption products were continuously analyzed in the mass spectrometer, which could detect ions with $m/z = 10–300$. In order to study the initial stages of olefin polymerization by TPD–MS, a sample of the MMT-H₂O/AlR₃/metallocene catalyst was placed in the above-mentioned cell and pumped, and ethylene or propylene was added. Gas-phase olefin polymerization was carried out at 3–15 Torr and 20°C for several minutes. After pumping, temperature-programmed heating and an analysis of desorption products were carried out as described above. This procedure is detailed elsewhere [16].

Polymerization of Ethylene and Propylene

The olefins were polymerized in a glass reactor filled with toluene and fitted with an electromagnetic stirrer and a water jacket for temperature control. The pressure and temperature were maintained constant during experiment. This experimental procedure was described in detail in an earlier publication [5]. To terminate polymerization, a 5% solution of HCl in ethanol was added to the reactor. The polymers obtained were filtered out, washed with ethanol, and dried *in vacuo* at 60°C.
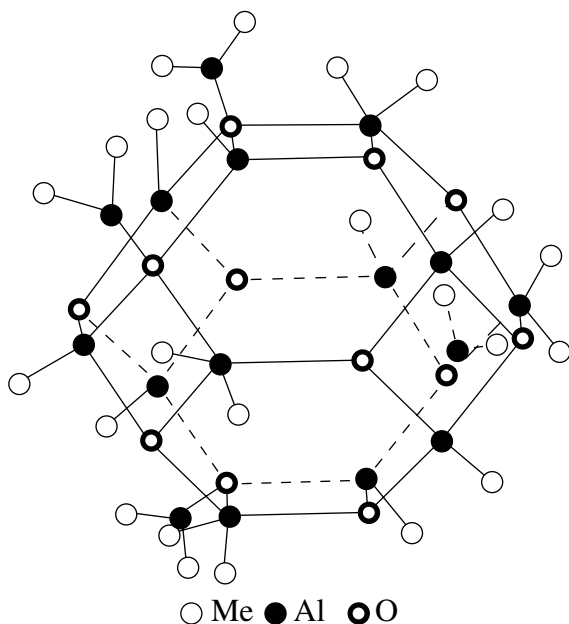
Characterization of Polymers

The polypropylene (PP) microstructure was studied by ¹³C NMR spectroscopy. The ¹³C NMR spectra of solutions of the polymer in o-dichlorobenzene (0.1–0.06 g/l) were recorded on a Bruker XR-400 instrument at 110°C. The magnetic field was stabilized by locking on the signal from internal hexadeuteriodimethyl sulfoxide.

RESULTS AND DISCUSSION

The support-H₂O/AlR₃ heterogenized activators for the metallocene catalysts were synthesized in situ on the support surface by the partial hydrolysis of alkylaluminums AlMe₃ and Al(i-Bu)₃ with the constitutional water of the support. We earlier found the optimum conditions for this reaction on the support surface [15]. The structures of the organoaluminum compounds synthesized on MMT using AlMe₃ were studied and compared with the structure of commercial MAO. For this purpose, the thermal destruction of the products liberated upon the thermal desorption of the organoaluminum compounds was studied by TPD–MS.

The organoaluminum component of MMT-H₂O/AlMe₃ and MAO release the same decomposition products, whose composition indicates the existence of fragments (AlMe₂, AlOAl, OAlMe, OAlMe₂, O₂AlMe, (AlO)₃, and O(AlO)₃) characteristic of the three-dimensional structure of the MAO molecule (Scheme 1) [18].

Furthermore, the same fragments in the organoaluminum component of MMT-H₂O/AlMe₃ and in MAO give rise to identical TPD spectra. By way of example, we show, in Fig. 1 (curves *1, 2*), the TPD spectra of the AlOAl and O(AlO)₃ fragments ($m/z = 70$ and 145, respectively) for both materials. Note that the treatment of MMT-H₂O with trimethylaluminum causes two reactions on the surface, specifically, the reaction between AlMe₃ and surface OH groups and the partial hydrolysis of AlMe₃ with the constitutional water of the

○ Me ● Al ◉ O

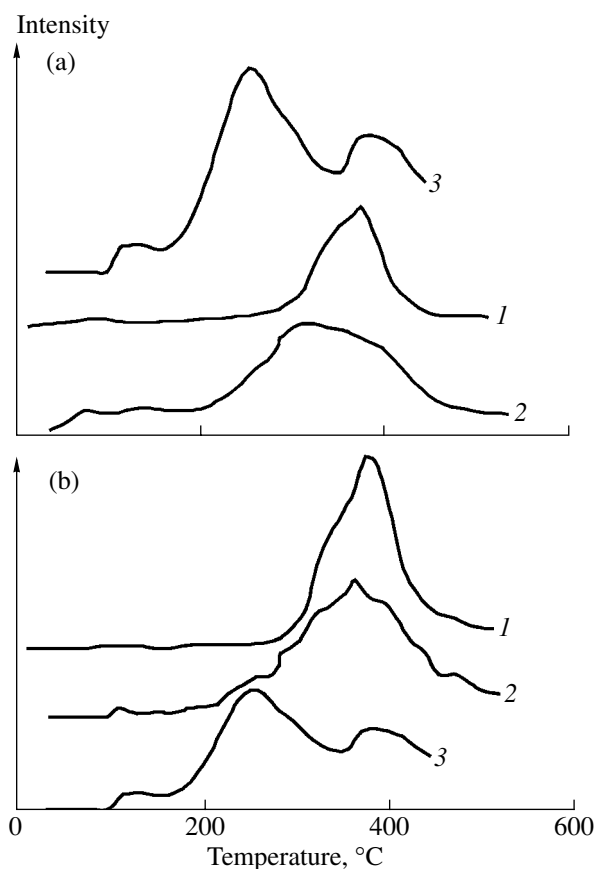**Scheme 1.** Structure of the MAO molecule [18].

Intensity

Fig. 1. TPD curves for the fragments resulting from the thermal decomposition of (*1*) solid MAO, (*2*) MMT-H$_2$O/AlMe$_3$, and (*3*) MMT-H$_2$O/Al(*i*-Bu)$_3$: (a) Al–O–Al (*m/z* = 70) and (b) O–(Al–O)$_3$ (*m/z* = 145).
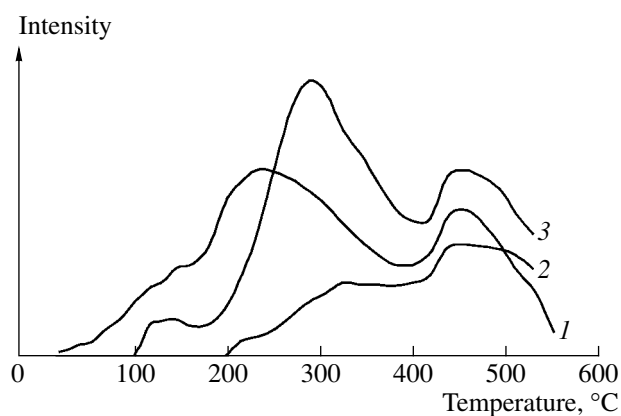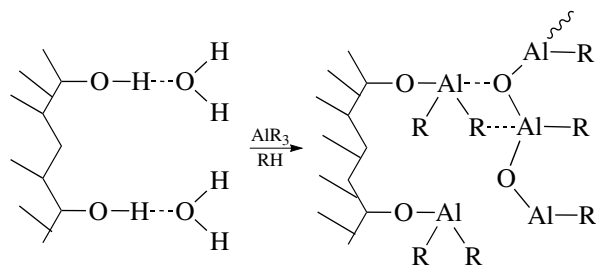
Intensity

Fig. 2. TPD curves for the fragments resulting from the thermal decomposition of MMT-H$_2$O/Al(*i*-Bu)$_3$: (*1*) Al–O–Al (*m/z* = 70), (*2*) O–Al–(*i*-Bu)$_2$ (*m/z* = 157), and (*3*) O–(Al–O)$_3$ (*m/z* = 145).

support, yielding alkylaluminoxane. The MAO formed in MMT-H$_2$O/AlMe$_3$ is bonded to the support surface, apparently through the donor–acceptor interaction with surface ≡Si–O–AlMe$_2$ groups (Scheme 2).

Scheme 2. General scheme of the formation of supported alkylaluminoxane by the reaction between alkylaluminum and water of the support.

The same structural fragments were found in the destruction products of MMT-H$_2$O/Al(*i*-Bu)$_3$ obtained from Al(*i*-Bu)$_3$ and in the destruction products of MMT-H$_2$O/AlMe$_3$. The TPD curves of the OAl(*i*-Bu)$_2$, AlOAl, and O(AlO)$_3$ fragments are shown in Fig. 2. However, a comparison between curves *2* and *3* in Fig. 1 shows that the spectra of the same structural fragments released by the methyl- and isobutyl-containing aluminoxanes are different. The spectrum of MMT-H$_2$O/Al(*i*-Bu)$_3$ shows not only a 350°C peak like that observed for MMT-H$_2$O/AlMe$_3$ but also a stronger peak at a lower temperature of ~250°C. Therefore, heterogenized isobutylaluminoxane decomposes more readily than MAO. This is apparently due to the fact that the alkylaluminoxane molecules containing isobutyl and methyl substituents differ in the steric and electron-donor properties. This difference is one of the factors determining the behavior of MAO and isobutylaluminoxane as activating cocatalysts in metallocene-catalyzed olefin polymerization.

The heterogenized alkylaluminoxanes prepared in situ are effective activators of metallocenes. The heterogenized metallocene catalysts thus obtained are very active in the polymerization of ethylene and propylene without commercial MAO. The metal–alkyl complexes formed by the heterogenized isobutyl-substituted aluminoxane MMT-H$_2$O/Al(*i*-Bu)$_3$ and some metallocenes, for example, Me$_2$Si(Ind)$_2$ZrCl$_2$ are more active in propylene polymerization than the complexes of methyl-substituted aluminoxane in MMT-H$_2$O/AlMe$_3$ (table).

At the same time, the active metal–alkyl complexes in MMT-H$_2$O/Al(*i*-Bu)$_3$/Me$_2$Si(Ind)$_2$ZrCl$_2$ are less stable in time in propylene polymerization than the complexes in MMT-H$_2$O/AlMe$_3$/Me$_2$Si(Ind)$_2$ZrCl$_2$. This is evident from the propylene polymerization rate curves for these catalysts (Fig. 3). The isotacticity of polypropylene forming in the presence of Me$_2$Si(Ind)$_2$ZrCl$_2$ is the same for both activators (table).

The heterogenization of the single-site metallocene catalysts usually causes a heterogeneity of active sites. In order to gain insight in the heterogeneity of active sites of the heterogenized metallocene catalysts, we
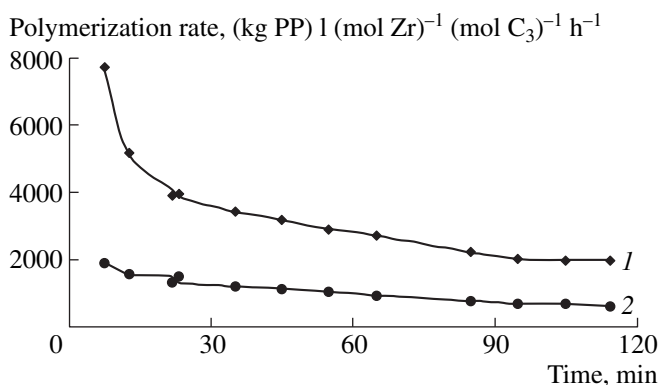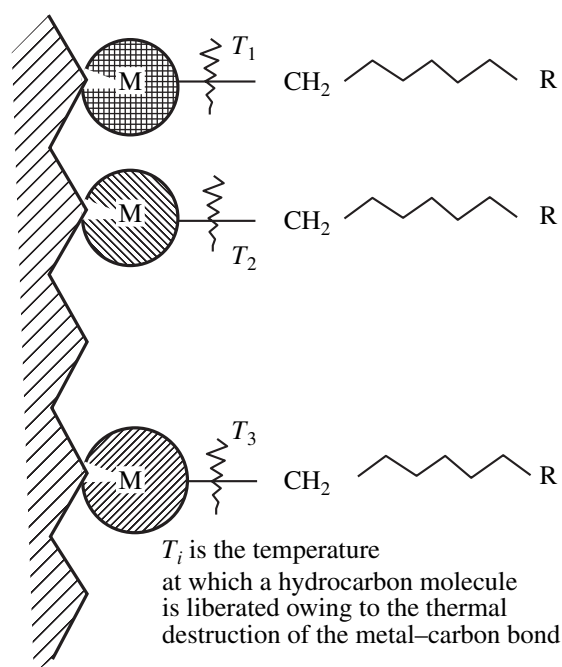
Polymerization rate, (kg PP) l (mol Zr)$^{-1}$ (mol C$_3$)$^{-1}$ h^{-1}

Fig. 3. Propylene polymerization rate curves for (*1*) MMT-H$_2$O/Al(*i*-Bu$_3$)/Me$_2$Si(Ind)$_2$ZrCl$_2$ and (*2*) MMT-H$_2$O/AlMe$_3$/Me$_2$Si(Ind)$_2$ZrCl$_2$ at [C$_3$H$_6$] = 0.13 mol/l and *T* = 40°C.

T_i is the temperature at which a hydrocarbon molecule is liberated owing to the thermal destruction of the metal–carbon bond

Scheme 3. Thermal destruction of the metal–carbon bond on different active sites of supported catalysts at the early stages of gas-phase olefin polymerization.

studied the initial stages of the gas-phase polymerization of ethylene and propylene using an earlier developed TPD–MS technique [16]. In this technique, the hydrocarbon (polyolefin) molecules that result from the thermal destruction of active (living) metal–carbon bonds when the polymer chains are still as short as several monomer units are determined mass-spectrometrically as a function of temperature of heating a catalyst sample *in vacuo* after polymerization. The metal–carbon (Zr–C) bonds in active surface metal–alkyl complexes with different compositions, structures, or other parameters dissociate at different temperatures (Scheme 3). As a consequence, the TPD spectra for the hydrocarbon molecules of a given length will contain a number of peaks. Therefore, heating a sample at a constant rate provides information on the energy distribution of active sites in this sample.

Figure 4a shows TPD curves for hydrocarbon molecules (1–4 ethylene units) that were inserted in Zr–CH$_3$ bonds and are released upon the thermal destruction of active Zr–C bonds on the MMT-H$_2$O/AlMe$_3$/Me$_2$Si(Ind)$_2$ZrCl$_2$ surface on which ethylene polymerization occurred. All these curves are similar and belong to the same family, and each contains two peaks between 200 and 400°C. The assumption that the TPD peaks in this temperature range are due to the liberation of hydrocarbon chains upon the destruction of "living," active metal–carbon bonds has been proved by us for supported Ziegler-type catalysts [19]. The results

presented in Fig. 4a suggest that, in ethylene polymerization on MMT-H$_2$O/AlMe$_3$/Me$_2$Si(Ind)$_2$ZrCl$_2$, the formation of polymer chains is initiated by surface metal–alkyl complexes of at least two types and most of the chains are formed on less stable sites.

The TPD curves for the same catalyst after propylene polymerization are identical in shape and peak positions to the spectra obtained after ethylene polymerization. The TPD spectra of the hydrocarbon molecules that contain one or two propylene units inserted in Zr–CH$_3$ bonds and are desorbed upon the thermal destruction of active Zr–CH$_3$ bonds are presented in Fig. 4b. Evidently, with this catalyst, the formation of polypropylene and polyethylene chains is catalyzed by metal–alkyl complexes of the same type.

It is of interest to compare catalysts containing different metallocenes. By way of example, Fig. 5 shows TPD curves for the hydrocarbon molecules (three ethylene units) that result from the thermal destruction of Zr–C bonds in Zr–CH$_2$–CH$_2$–(CH$_2$–CH$_2$)$_2$–CH$_3$ on the surface

Polymerization of propylene on the heterogenized catalysts MMT-H$_2$O/AlMe$_3$/Me$_2$Si(Ind)$_2$ZrCl$_2$ and MMT-H$_2$O/Al(*i*-Bu)$_3$/Me$_2$Si(Ind)$_2$ZrCl$_2$

Catalyst	Zr content, mol/(g MMT)	[Al]/[Zr]	Activity, (kg PP) l (mol Zr)$^{-1}$ (mol C$_3$)$^{-1}$ h^{-1}	*mmmm*, %
MMT-H$_2$O/AlMe$_3$/Me$_2$Si(Ind)$_2$ZrCl$_2$	2.3×10^{-6}	2200	1600	78
MMT-H$_2$O/Al(*i*-Bu)$_3$/Me$_2$Si(Ind)$_2$ZrCl$_2$	2.2×10^{-6}	2300	4600	77

Note: The polymerization temperature is 50°C; [C$_3$H$_6$] = 0.13 mol/l.

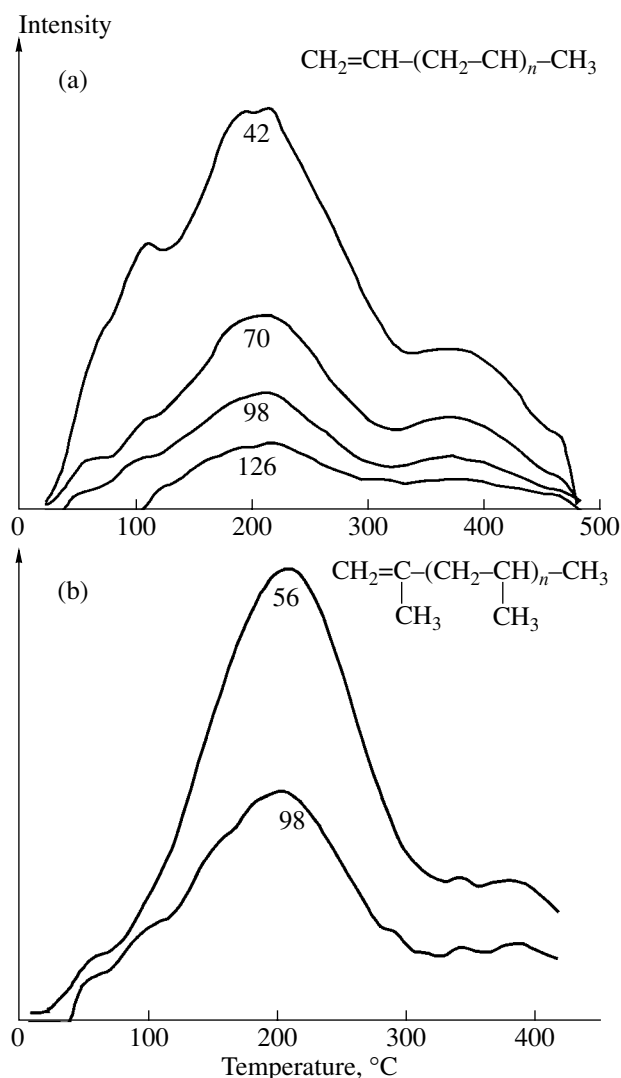**Fig. 4.** TPD curves for hydrocarbon molecules resulting from the destruction of Zr–C bonds on the MMT-$H_2O/AlMe_3/Me_2Si(Ind)_2ZrCl_2$ surface after the polymerization of (a) ethylene and (b) propylene: (a) molecules containing one to four monomer units (m/z = 42, 70, 98, and 126) and (b) molecules containing one or two monomer units (m/z = 56, 98).

Fig. 5. TPD curves for hydrocarbon molecules containing three monomer units (m/z = 98) that result from the destruction of Zr–C bonds on the (*1*) MMT-$H_2O/AlMe_3/Cp_2ZrCl_2$ and (*2*) MMT-$H_2O/AlMe_3/Me_2Si(Ind)_2ZrCl_2$ surfaces after ethylene polymerization.

Fig. 6. Probable active site distribution by the activation energy of the thermal destruction of active Zr–C bonds for the (*1*) MMT-$H_2O/AlMe_3/Cp_2ZrCl_2$ and (*2*) MMT-$H_2O/AlMe_3/Me_2Si(Ind)_2ZrCl_2$ catalyst surfaces during ethylene polymerization.

of the MMT-$H_2O/AlMe_3/Me_2Si(Ind)_2ZrCl_2$ and MMT-$H_2O/AlMe_3/Cp_2ZrCl_2$ catalysts after ethylene polymerization. The strongest TPD peak for the catalyst containing $Me_2Si(Ind)_2ZrCl_2$ occurs at a much lower temperature (~220°C) than the strongest peak for the Cp_2ZrCl_2-based catalyst (320°C). In our opinion, this finding correlates with the considerably higher polymerization activity of the catalyst containing $Me_2Si(Ind)_2ZrCl_2$.

The experimental data obtained make it possible to calculate the activation energies of the thermal destruction of active metal–carbon bonds in different active sites and to obtain energy spectra for the active sites of the catalysts [19]. These spectra are presented in Fig. 6 as the
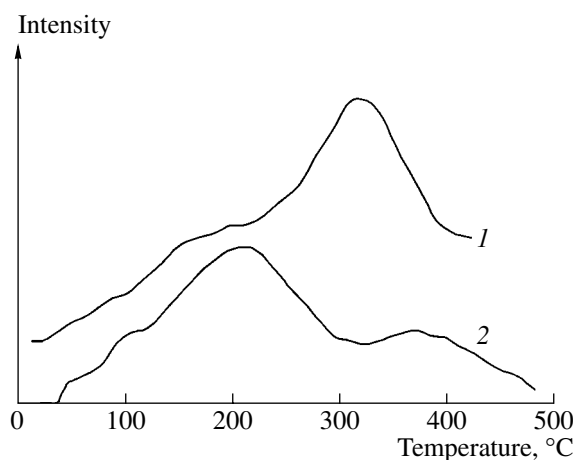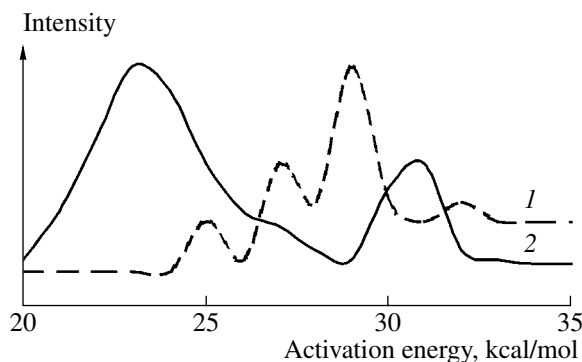
activation energy of the thermal destruction of active Zr–C bonds in the MMT-$H_2O/AlMe_3/Me_2Si(Ind)_2ZrCl_2$ and MMT-$H_2O/AlMe_3/Cp_2ZrCl_2$ catalysts after ethylene polymerization. Clearly, the energy distribution of active sites in the catalysts supported on MMT-$H_2O/AlMe_3$ depends strongly on the nature of metallocene. Most of the surface alkylmetal complexes in the catalyst containing the *ansa*-metallocene $Me_2Si(Ind)_2ZrCl_2$ are characterized by a lower activation energy of Zr–C bond destruction (~23 kcal/mol) than most of these complexes in the Cp_2ZrCl_2-based catalyst (~29 kcal/mol).

Thus, the heterogenized alkylaluminoxanes prepared in situ on the support surface by the partial hydrolysis of AlR_3 with the constitutional water of the support are effective activators for metallocenes. The metal–alkyl complexes formed by heterogenized isobu-

tylaluminoxane in MMT-H_2O/Al(i-Bu)$_3$ and the *ansa*-metallocene $Me_2Si(Ind)_2ZrCl_2$ are more active in propylene polymerization than their counterparts formed by MAO in MMT-H_2O/AlMe$_3$. The thermal decomposition of isobutylaluminoxane molecules in MMT-H_2O/Al(i-Bu)$_3$, studied by TPD–MS, begins at a lower temperature and is more complicated than MAO decomposition. As demonstrated by the TPD–MS study of the early stages of the gas-phase polymerization of ethylene and propylene, the heterogeneity and energy distribution of active sites in a heterogenized metallocene catalyst depends strongly on the nature of metallocene in the catalyst. The energy spectra of the active sites of the MMT-H_2O/AlMe$_3$/$Me_2Si(Ind)_2ZrCl_2$ and MMT-H_2O/AlMe$_3$/Cp_2ZrCl_2 catalysts are presented in terms of the distribution of Zr–C bonds by the activation energy of their thermal destruction.

ACKNOWLEDGMENTS

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