Study of energy distribution of active sites in heterogeneous Ziegler-Natta catalysts

Lyudmila A. Novokshonova[1,*], Natalia Yu. Kovaleva[1], Yurii A. Gavrilov[1],
Vadim G. Krasheninnikov[1], Ilia O. Leipunskii[2], Alexey N. Zhigach[2],
Michail N. Larichev[2], Michail V. Chebunin[2]

[1] Institute of Chemical Physics RAS, Kosygin St 4, 117977 Moscow, Russia
[2] Institute of Energy Problems of Chemical Physics RAS, Leninsky pr. 38, bd. 2, 117977 Moscow, Russia

Summary

New method of investigation of active sites non-uniformity was developed. The method is based on mass-spectrometric study of temperature programmed desorption (TPD) products from the catalyst surface at initial stages of olefin gas-phase polymerization. The conditions of polymerization allowed to obtain the short macrochains on catalyst surface. Two well-resolved intense maxima in the temperature ranges of 180-210°C and 280-320°C on the TPD curves from $SiO_2/TiCl_4/AlEt_2Cl$ catalyst surface after polymerization were observed in a result of thermal destruction of active Ti-C bonds and the evolution of hydrocarbon molecules of different length (up to 14 monomer units in chain). One may conclude that in this catalyst there are at least two types of active sites varying in the activation energy of thermal destruction of Ti-C bonds. The distribution of active sites over activation energy of Ti-C bond thermal destruction was calculated.

Introduction

The non-uniformity of active sites is an important feature of heterogeneous catalysts of olefin polymerization. The non-uniformity of active sites leads to the broadening of molecular weight distribution (1-3), non-uniformity of copolymers in composition (4,5).

The surface non-uniformity of Ziegler-Natta catalysts was studied by CO-inhibition of the polymerization rate (2,6-8). By this method Keii (2) has shown a surface heterogeneity of the propagation rate constant for propylene polymerization. At step-wise inhibition of active sites the average value of the propagation rate constant decreased from 238 dm³/mol·s to 4.3 dm³/mol·s for TiCl₃/ AlEt₂Cl at temperature of

---

* Corresponding author

40 °C and from 4300 dm³/mol·s to 80 dm³/mol·s for TiCl₄ /MgCl₂ / C₆H₅COOC₂H₅ / AlEt₃ at temperature of 38 °C. The distribution of the propagation rate constant was described in terms of a distribution of the activation energy for the macrochain growth (2). Also shown is an increase in the value of activation energy of propylene polymerization on TiCl₃/AlEt₂Cl at step-wise poisoning of more active sites by CO from 8.5 kcal/mol for not inhibited polymerization to 10.8 kcal/mol and 14.6 kcal/mol at degree of polymerization rate inhibition (R_i/R_o) of 0.34 and 0.13 respectively (9).

In the paper the new method of investigation of active site non-uniformity was developed. The method is based on mass-spectrometric study of products of temperature programmed desorption (TPD) from the catalyst surface at initial stages of olefin polymerization. By this method the hydrocarbon (polyolefin) molecules released in thermal degradation of active "Ti-polymer chain" bonds are recorded when polymer chains are very short. Linear heating of the samples gives the information describing the energy distribution of active sites. With the developed method the initial stages of ethylene polymerization on SiO₂/TiCl₄/AlEt₂Cl catalyst were investigated. The energy distribution of active sites for this catalyst was obtained.

Experimental

Preparation of the catalyst.

The SiO₂/TiCl₄/AlEt₂Cl catalyst was obtained by sequential adsorption of catalyst components in MacBain balance device (10). First TiCl₄ was adsorbed and then AlEt₂Cl. The amount of chemisorbed TiCl₄ was equal to 1 μmol/m². The excess of TiCl₄ and then the excess of AlEt₂Cl were pumped out from the surface. The mole ratio Al/Ti in catalyst complex produced on the surface was equal to 1,5. The active sites of SiO₂/TiCl₄/AlEt₂Cl catalyst are formed by alkylated Ti(III) located separately on the aerosil surface by chemical bonding through oxygen (10). The pre-formed catalyst was distributed in vacuum into microflasks for the study of ethylene polymerization by TPD method. The catalyst in each microflask was weighted and equal to 0.001-0.007 g.

The temperature programmed desorption / mass-spectrometric study (TPD / MS).

The products of temperature programmed desorption from the catalyst surface were studied by mass-spectrometry prior to and after polymerization using programmed linear heating of the samples. The sample of catalyst was placed in special cell connected directly with mass-spectrometer MI-1201. The gas-phase polymerization was carried out also in this cell. The samples investigated were heated with the rate of 9.4 grad per minute from the room temperature to 500° C temperature. A continuous cyclic scanning of mass-spectra in the range of m/z=10-270 (10–400 in some experiments) were used. The ratio m/z is the mass to ion charge ratio; as z in our experiments was equal to one, this ratio characterizes ion mass. The time of mass-spectrum registration was less then 0.5 minute. Two series of experiments were carried out: the TPD products were investigated prior to and

after ethylene polymerization. The additional amount of AlEt$_2$Cl was not injected. The polymerization was conducted at ethylene pressure of $6.5 \cdot 10^{-2}$-2.6 kPa and room temperature. The polymerization time was 2-10 minutes.

Results and discussion

TPD prior to the polymerization.

The experiments with adsorption of lowmolecular hydrocarbons such as decane and hexadecane at pure SiO$_2$ surface (without catalyst) and with subsequent their temperature programmed desorption were previously carried out. The evolution of adsorbed hydrocarbons occurs in this case at the temperature of about 100 °C and there is no evolution in the range of more high temperatures.

The curve 1 in Fig. 1 shows a typical curve of thermal desorption from pre-formed SiO$_2$ / TiCl$_4$ / AlEt$_2$Cl catalyst.
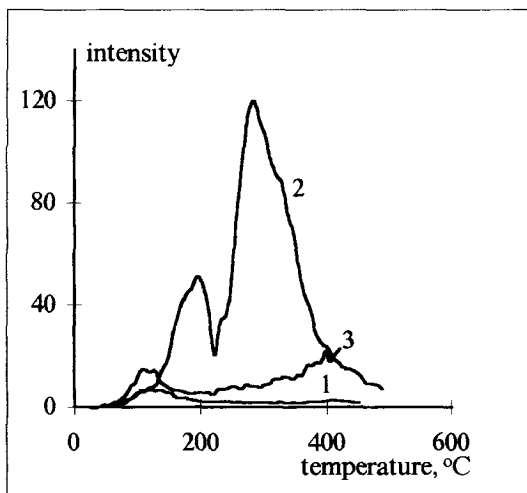

Fig.1. Curves of TPD from the surface of pre-formed catalyst prior to and after ethylene polymerization for m/z=140 as a typical representative of C$_n$H$_{2n}$ row (unsaturated hydrocarbons).
1 - pre-formed catalyst prior to polymerization;
2 - the catalyst after ethylene polymerization; polymerization conditions: room temperature, ethylene pressure 2.15 kPa, polymerization time 5 min.
3 - the catalyst after ethylene polymerization when polyethylene had already M$_n$=20000.

Titanium and aluminum compounds are not observed in the spectrum. A weak low temperature maximum on thermal desorption curves is observed at 120°C for a number of mass-spectral lines with m/z = 29-265. The maximum is associated with a desorption of physically adsorbed products. A set of mass-spectral lines with m/z, multiple to 14 (m/z=14·n) is observed. The intensity of the lines decreases quickly with an increase in "n". These lines may be attributed to the unsaturated hydrocarbons C$_n$H$_{2n}$ (11). The hydrocarbons were obtained by polymerization of ethylene, evolved in reaction of the Si-O-TiCl$_3$ catalyst with adsorbed AlEt$_2$Cl. The hydrocarbons obtained are physically adsorbed.

Besides the low temperature peak, a weak maximum in the temperature range of 400-450 °C is observed. This peak is typical for a row of lines within m/z=27-208. An exact periodicity with an increment 14 for m/z that is typical for linear hydrocarbons is not observed. It seams, the products of thermal destruction of hydrocarbons are observed. Some of these lines may be attributed to C$_n$H$_{2n+2}$ chains (11), where 4<n<12 (Fig. 2, curve 1).
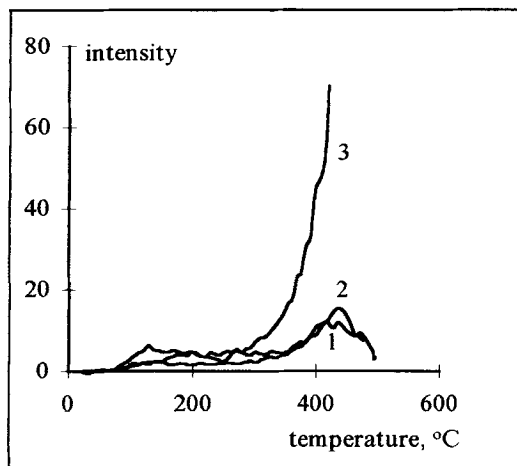
Fig. 2. Curves of TPD from the surface of pre-formed catalyst prior to and after ethylene polymerization for $m/z=142$ as a typical representative of C_nH_{2n+2} row (saturated hydrocarbons).
1 - pre-formed catalyst prior to polymerization;
2 - the catalyst after ethylene polymerization; polymerization conditions are the same as in Fig. 1;
3 - the catalyst after ethylene polymerization when polyethylene had already $M_n=20000$.

The evolve of organic compounds in the temperature range of 210-230° C was very low.

TPD from a catalyst after polymerization.

The ethylene polymerization was carried out at low pressure and room temperature for a short time to produce the short macromolecules on catalyst surface and small amount of polymer. At monomer pressure of 2.15 kPa the amount of polyethylene was equal to 0.7-0.8% of the catalyst weight. The average lifetime of growing chains calculated by us from dependence of average-number degree of polymerization on polymerization time in ethylene polymerization with used catalyst at room temperature and ethylene pressure of 2.15 kPa covers not less than 45 min.

The spectra of TPD products from the sample after polymerization are significantly different from those of the initial catalyst and from results of TPD of hydrocarbons (decane and hexadecane) adsorbed at surface of pure SiO_2 (without catalyst) in the temperature ranges of 180—210 °C and 280—320 °C. Two intense maxima for $m/z=27-252$ are observed at temperatures 180-210 °C and 280-320 °C. The TPD curve for $m/z=140$ is presented in Fig. 1 (curve 2). The curve 2 is typical for the m/z range of 27-252. The plot of three-dimensional TPD surface for the lines with $m/z=14 \cdot n$ and $n=5-16$, is shown in Fig. 3. These two maxima seem to be a weakly resolved superposition of several maxima, the relative intensities of which change with an increase of m/z. At higher m/z the resolution of the peaks is improved.

The most intense lines may be attributed to a family of unsaturated hydrocarbons with a general formula C_nH_{2n} with $n>3$. The maximum value of "n" was not determined. However, we can conclude that n_{max} is not less than 28. When the mass-spectral scanning range was elevated up to $m/z=400$ the line with $m/z=392$ (the highest belonging to $m/z=14 \cdot n$ family) was observed. The intensities of this line was 5 times higher than the noise level. The lines of this family with a probability more than 95% correlate with each other.
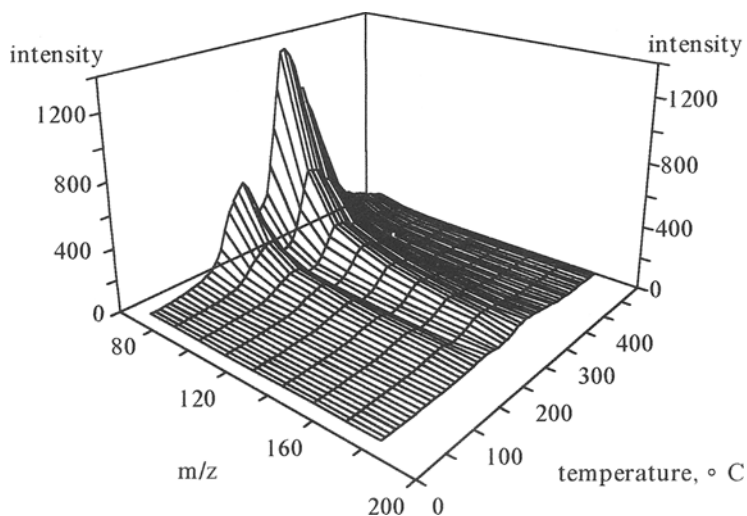
Fig. 3. Three-dimensional plot showing curves of thermal programmed desorption after ethylene polymerization for mass-spectral lines with m/z=14n (where n=5-16).

The intensity of the maximum at 280-320 °C is significantly (2.3 times) higher at n<14 than that of the lower temperature maximum. This ratio of the intensities rises up to 3.1 times at n=19.

The intensities of TPD curves at 120 °C and 400-450 °C (Fig. 1, curve 2) are relatively low. Low temperature maximum is associated with a desorption of physically adsorbed hydrocarbon molecules. High temperature maximum may be attributed to the thermal destruction of polyethylene which usually begins at temperature higher than 350 °C (12). Actually, TPD spectra of high-molecular polyethylene (M_n=20000) synthesized on the same catalyst show an intense evolution at temperature higher than 350 °C for lines with m/z up to 244 (Fig. 1, curve 3 and Fig. 2, curve 3).

The presence of two well-resolved maxima of TPD at 180-210° C and 280-320 °C from the catalyst surface after ethylene polymerization are due to evolution of hydrocarbon molecules with different lengths in a result of thermal destruction of Ti-C bonds in active sites. Mass-spectra of TPD products allowed to identify the molecules with masses up to 400, that corresponds to 14 monomer units of polyethylene chains.

The results enable to conclude that in SiO_2/$TiCl_4$/$AlEt_2Cl$ catalyst there are at least two types of active sites varying in the activation energy of thermal destruction of Ti-C bonds. Complex shape of both maxima indicates, that there is a distribution of activation energy for both of centre types.

The amount of saturated hydrocarbons in the products of thermal desorption is significantly less than that of unsaturated ones. This conclusion is illustrated by a comparison of the curve 2 in Fig. 1 and the curve 2 in Fig. 2.

The thermal destruction of metal-carbon bonds may occur both the radical mechanism and the β–elimination of hydrogen ion (13,14). The data for the initial polymerization stages show that the thermal destruction products contain mainly unsaturated hydrocarbons with a small amount of saturated products. Thus, β–elimination is the prevailing mechanism of thermal destruction of Ti-C bonds in the case being considered.

Based on the experimental dependence of evolution rate of desorption products on temperature, the activation energy of thermal destruction of "Ti-polymer chain" bonds in active centres were calculated in the assumption that the active site distribution over activation energy is continuous. The results obtained for $A=10^8$ are submitted in Fig. 4. The energy spectrum (Fig. 4) calculated for $SiO_2/TiCl_4$ /$AlEt_2Cl$ catalyst consists of two groups of energy peaks. The average values of thermal destruction energies of "Ti-polymer chain" bonds in these two groups of active sites differ about 1.5 times.
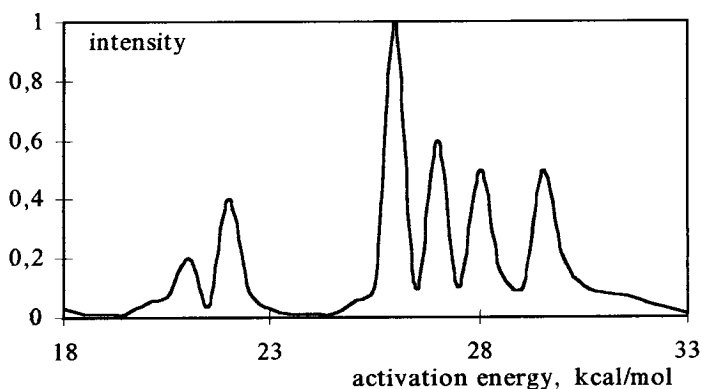

Fig. 4. Energy spectrum calculated on the base of TPD experimental data assuming the continuous active site distribution over activation energies of thermal destruction of Ti-C bonds.

Conclusion

The new method of investigation of active site non-uniformity was developed. The method is based on mass-spectrometric study of temperature programmed desorption (TPD) products from the catalyst surface at initial stages of olefin polymerization. The method allows to obtain the information concerning the energy non-uniformity of active sites in tirms of a distribution of active sites over activation energy of Mt-C bond thermal destruction.

Acknowledgement

References

1. Clark A, Bailey GC (1963) J. Catal. 2: 230
2. Keii T, Doi Y, Suzuki E, Tamura M, Murata M, Soga K (1984) Macromol. Chem. 185: 1537
3. Kissin YV (1993) Macromol. Chem., Makromol. symp. 66: 83
4. Kissin YV (1974) Adv. Polym. Sci. 15: 91
5. Yechevskaya LG, Bukatov GD, Zakharov VA (1991) Macromol. Chem. 192: 2865
6. Tait P. J. T., (1988) in Transition metals and Organometallics as catalysts for olefin polymerization. Springer-Verlag, Berlin, Heidelberg, p. 309
7. Shiono T, Ohgizama M, Soga K (1993) Macromol. Chem. 194: 2075
8. Gavrilov YuA, Novokshonova LA (1982) Proceedings of III-USSR Conference on the Mechanism of catalytic reactions., Novosibirsk, 1: 128
9. Novokshonova L.A., Gavrilov Yu.A., Krasheninnikov V.G., (February1990) 7-th International Microsymposium "Advance in the Field of ionic Polymerization", Berlin, p.8
10. Kovaleva NYu, Krasheninnikov VG, Gavrilov YuA, Novokshonova LA (1989) Polimery 34: 283
11. Cornu A, Massot R, (1966) Compilation of Mass-spectral Data. Heyden & Scns LTD, Press Universitaires de France
12. Lipatov YuS, Nesterov AE, Gritsenko TM, Veselovskii RA (1971) Spravochnik po chimii polimerov. Naukova Dumka, Kiev
13. Henrici-Olive G, Olive S (1977) Coordination and catalysis. Verlag Chemie, Weineim, New-York
14. Green ML N (1968) Organometallic Compounds. vol.2, Methuen, London EC4