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# Heterogenization of Metalorganic Catalysts of Olefin Polymerization and Evaluation of Active Site Non-Uniformity

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**Summary:** Heterogenized activators – "support-$H_2O/AlR_3$" (where R=Me, iBu, support=montmorillonite, zeolite), synthesized directly on the support, form with metallocenes metal alkyl complexes highly active in olefin polymerization without the use of commercial methylaluminoxane (MAO). It was shown by the method of temperature programmed desorption with the application of mass-spectrometry (TPD-MS) that the aluminumorganic compound in support-$H_2O/AlR_3$ is in general similar to the structure of commercial MAO. The heterogenization of Zr-cenes on support-$H_2O/AlR_3$ is accompanied by the appearance of the energy non-uniformity of active sites. The activation energy of thermal destruction of active Zr-C bonds in the active sites of prepared catalysts changes in the range from 25 to 32 kcal/mol.

**Keywords:** activator; metallocene; olefin polymerization; support

## Introduction

The catalytic properties of the heterogenized metallocene catalysts of the olefin polymerization depend on many factors and first of all on the method of heterogenization and on the nature of the activator.

We synthesized directly on the surface of the support the heterogenized activator by partial hydrolysis of aluminumalkyl by water contained in a support (support-$H_2O/AlR_3$).[1-3] Similar way is tested now also by other investigators.[4-7] In this paper the structure of products of partial hydrolysis of aluminumalkyl by the support water was compared with the commercial MAO structure, the properties of support-$H_2O/AlR_3$/Zr-cene catalysts in the ethylene and

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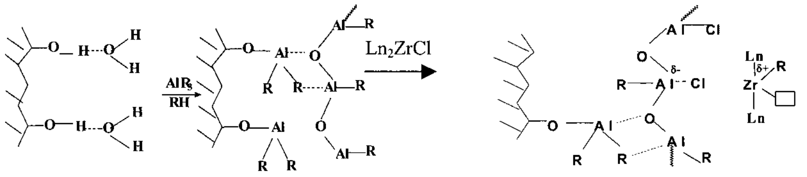
propylene polymerization were investigated, and the active site non-uniformity of supported metallocene catalysts was evaluated.

## Results and Discussion

We used as supports zeolite (ZSM-5), which has very stable skeleton structure, and the layered silicate montmorillonite (MMT). The distinctive feature of these supports is a very high mobility of internal water. $AlMe_3$ and $AliBu_3$ were used for the treatment of supports. The products of partial hydrolysis of aluminumalkyl, heterogenized on the surface, activate different metallocenes in the ethylene and propylene polymerization without the use of commercial MAO:



The activities of these catalysts are close to the activities of corresponding homogeneous systems with MAO. [3,8-10] The data, presented in Table 1, illustrate this for the propylene polymerization with the catalyst based on zeolite as a support and the data of Table 2 – for

Table 1. Propylene polymerization with $ZSM\text{-}5(H_2O)/AlMe_3$/Zr-cene and homogeneous Zr-cene-MAO* catalysts

| Catalyst | Zr wt % | $\frac{[Al]}{[Zr]}$ | T, $^0C$ | $A^a$ | $\overline{M}_W$ $10^{-3}$ | $\frac{\overline{M}_W}{\overline{M}_n}$ | $T_m$ $^0C$ | $\lambda^b$, % | $I_{iso}{}^c$ % |
|---|---|---|---|---|---|---|---|---|---|
| $ZSM\text{-}5(H_2O)/AlMe_3/$ $Et[Ind]_2ZrCl_2$ | 0,012 | 5540 | 40 | 19800 | 40 | 13,4 | 124 | 55 | 82 |
| $ZSM\text{-}5(H_2O)/AlMe_3/$ $Et[Ind]_2ZrCl_2$ | 0,015 | 4350 | 40 | 9170 | 43 | 8,8 | 123 | 50 | 82 |
| $ZSM\text{-}5(H_2O)/AlMe_3/$ $Et[Ind]_2ZrCl_2$ | 0,018 | 5000 | 75 | 13160 | $1,5^d$ | - | wax | - | 10 |
| $Et[Ind]_2ZrCl_2$-MAO | $0,026^e$ | 1720 | 75 | 25000 | $2,0^d$ | - | wax | - | 15 |

[a] A=activity, kgPP/molZr·$[C_3H_6]$·h; [b] polymer cristallinity; [c] PP isotacticity by Luongo method; [d] $M_n$; [e] mmol/l.

Table 2. Ethylene polymerization with zirconocenes supported on MMT-$H_2O$/$AlR_3$

| Catalyst | $Q_{Zr}\times 10^6$, mol/g MMT | [Al]/ [Zr] | Tp, $^0$C | A$^a$ |
|---|---|---|---|---|
| $Cp_2ZrCl_2$ - MAO | 5,6×10$^{-5}$ mol/l | 1000 | 40 | 20800 |
| MMT-$H_2O$/$AlMe_3$- $Cp_2ZrCl_2$ | 4,6 | 1100 | 40 | 10000 |
| Et(Ind)$_2$ZrCl$_2$ - MAO | 4,0×10$^{-5}$ mol/l | 1100 | 40 | 26000 |
| MMT-$H_2O$/$AlMe_3$- Et(Ind)$_2$ZrCl$_2$ | 2,4 | 2000 | 40 | 14700 |
| MMT-$H_2O$/$AlMe_3$- Et(Ind)$_2$ZrCl$_2$ | 2,4 | 2270 | 55 | 21450 |
| MMT-$H_2O$/$AlMe_3$- Et(Ind)$_2$ZrCl$_2$ | 2,4 | 2000 | 65 | 54850 |
| MMT-$H_2O$/$AliBu_3$- Et(Ind)$_2$ZrCl$_2$ | 2,4 | 1400 | 65 | 17800 |

[a] A = activity, kg PE/mol Zr [$C_2H_4$] h

the ethylene polymerization with catalysts based on montmorillonite as a support. Polyethylene (PE) synthesized with the supported catalyst has a higher molecular weight, broader molecular weight distribution, higher melting point and degree of crystallinity than PE prepared with the suitable homogeneous catalyst (Table 3).

Table 3. Characteristics of PE prepared with the ZSM-5($H_2O$)/$AlMe_3$/$Cp_2ZrCl_2$ catalyst and the $Cp_2ZrCl_2$-MAO homogeneous system (polymerization conditions: T=34°C, [$C_2H_4$]=0,054 mol/l).

| Catalyst | [Zr], wt.% | [Zr]/[Al] | $M_w$ | $M_w/M_n$ | Crystallinity, % | $T_m$ $^0$C |
|---|---|---|---|---|---|---|
| ZSM-5($H_2O$)/$AlMe_3$/$Cp_2ZrCl_2$ | 0,07 | 4600 | 202750 | 22,7 | 85 | 133 |
| ZSM-5($H_2O$)/$AlMe_3$/$Cp_2ZrCl_2$ | 0,21 | 440 | 150500 | 18,7 | 80 | 136 |
| ZSM-5($H_2O$)/$AlMe_3$/$Cp_2ZrCl_2$ + MAO | 0,16 | 470$^{a)}$ | 52800 | 18 | 76 | 123 |
| $Cp_2ZrCl_2$ - MAO | 0,18$^b$ | 400 | 57538 | 4,6 | 72 | 121 |

[a] [Al]/[Zr]=[$AlMe_3$ ]/[Zr]+[MAO]/[Zr] =350 +50; [b] mmol/l.

It is interesting that addition of free MAO into the reaction zone during polymerization of ethylene with the prepared heterogenized catalyst is accompanied by the decrease of molecular weight and melting point. [8] As seen from gel chromatogram (Figure 1), two products with different molecular weights are present in the polymer in this case. PE contains a fraction with lower molecular weight which is absent in the polymer, synthesized without additional MAO. This means that the active sites in the prepared supported catalysts

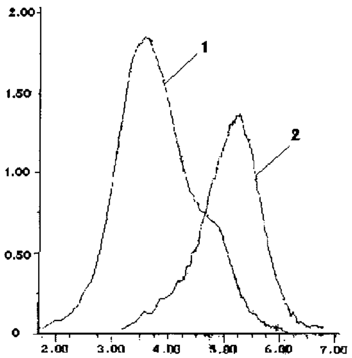


Figure 1. Gel-chromatograms of PE prepared with (1) ZSM-5($H_2O$)/$AlMe_3$/$Cp_2ZrCl_2$ and (2) ZSM-5($H_2O$)/$AlMe_3$/$Cp_2ZrCl_2$+MAO catalysts.

are located mainly on the surface during polymerization. Under the action of free MAO, the leaching of part of active sites from the catalyst surface into solution takes place.

The heterogenized products of partial hydrolysis of $AliBu_3$ activate metallocenes also. With the used Zr-cene, the supported catalyst exhibits in this case the lower activity in comparison with the catalyst containing the activator prepared with $AlMe_3$ (Table 2).

The specific activity of the catalyst depending on the content of Zr-cene in a supported catalyst has a maximum in the region of the low surface concentration of Zr-cene (Figure 2).[10] Similar dependence is typical for many immobilized catalysts of olefin polymerization, including the supported catalysts of Ziegler-Natta type. One of the possible reasons for the reduction in the activity of supported catalyst with an increase of Zr content is the decrease of Al/Zr ratio. With a decrease of Al/Zr ratio, the fraction of more active catalytic complexes, containing the several molecules of co-catalyst, decreases. Besides, on the surface of support-$H_2O$/$AlR_3$, there are the sites of different activity towards Zr-cene, and only a part of them is able to form with Zr-cene the centers of high activity in olefin polymerization.

It was observed that the order of polymerization rate with respect to the monomer concentration changes from 2 to 1 both in the ethylene and propylene polymerization (Figure 3).[10] This allows to suggest that two olefin molecules are involved in the monomer insertion into the active site occurring in the transition state, as in the olefin polymerization with homogeneous catalysts and the heterogeneous Ziegler-Natta catalysts.

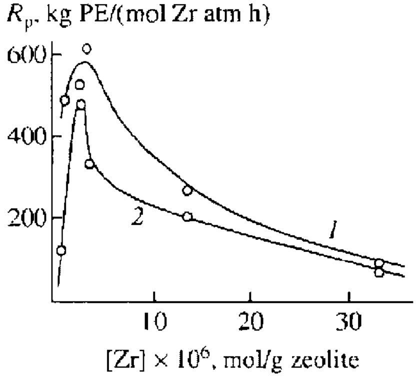


Figure 2. Effect of zirconocene concentration on the rate of ethylene polymerization with ZSM-5-$H_2O$/$AlMe_3$/$Cp_2ZrCl_2$; polymerization conditions: T = 34°C;. [$C_2H_4$] = 0.054 mol/l, [Al] = 4 mmol/g zeolite; 1- maximum rate; 2- stationary rate.

The structure of products of partial hydrolysis of $AlMe_3$ by the water of a support was compared with the structure of solid commercial MAO. For this we investigated the thermal destruction of both aluminumorganic compounds by the method of temperature programmed desorption with mass-spectrometric analysis of gaseous products (TPD-MS). [3,11]

The results showed that the composition of the desorption products arising by the thermal destruction of both compounds is identical and corresponding to the different fragments of

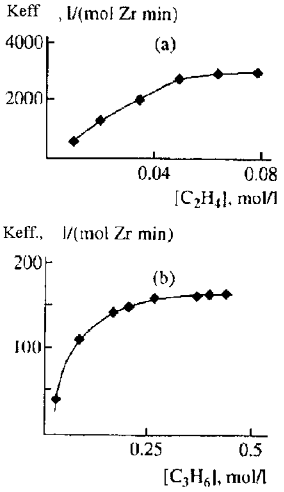


Figure 3. The effective rate constant of (a) ethylene and (b) propylene polymerization with the ZSM-5-($H_2O$)/$AlMe_3$/Et(Ind)$_2$ZrCl$_2$ as a function of monomer concentration. Polymerization conditions: T= 40°C; [Zr] = 0.05 wt.%; Al/Zr=1400.

MAO molecule. Moreover, the TPD spectra for the same fragments, arising from both compounds, are in general similar (Figures 4-6). This allows to conclude that the structure of the prepared heterogenized co-catalyst is close to the commercial MAO structure. [12,13]

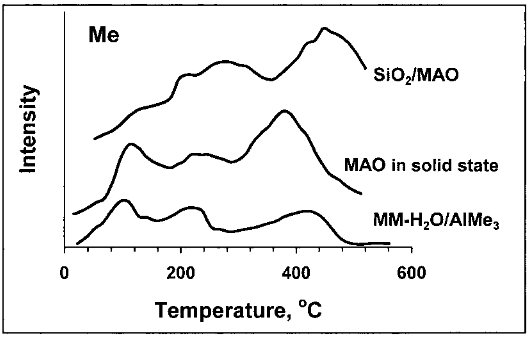


Figure 4. The curves of TPD for m/z=15.

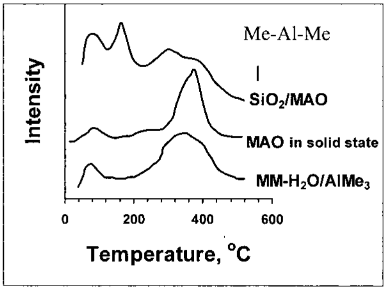


Figure 5.The curves of TPD for m/z=57.

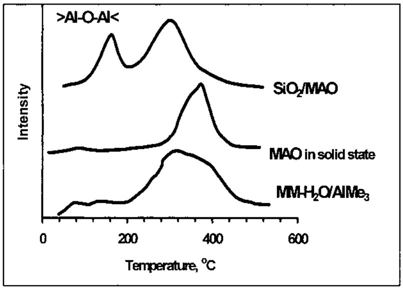


Figure 6. The curves of TPD for m/z=70.

At the same time we found out that after the supporting on the surface of dehydrated $SiO_2$, the commercial MAO looses part of the most active Me-groups. As seen from Figure 4, in TPD spectrum, which characterizes the detachment of methyl groups from the different fragments of MAO molecule, the maximum at low temperature is practically absent for $SiO_2$/MAO sample. It is important to note that the contributor of the recorded methyl groups is the thermal destructed MAO, and not $AlMe_3$. $AlMe_3$ is present in the tested samples, however the methyl groups, arising from the $AlMe_3$ destruction, are not registered by the method of mass-spectrometry.[14] The observed fact can be the reason why MAO, supported on the dehydrated $SiO_2$, does not activate the metallocene, and addition of free MAO or other aluminumalkyl is needed to produce the active heterogenized catalysts.

The initial stages of the ethylene polymerization with solid homogeneous $Cp_2ZrCl_2$/ MAO complex and with the heterogenized MMT-$H_2O/AlMe_3/Cp_2ZrCl_2$ catalyst were studied by the method of TPD-MS.[3,11] The method allows to record the evolution of short hydrocarbon molecules as a result of thermal destruction of Zr-C bonds in the living active sites depending on linear heating of sample. The results show the uniformity of active sites of homogeneous $Cp_2ZrCl_2$/MAO complex even in solid state (Figure 7a): there is only one narrow peak in the high temperature range on the TPD curve.

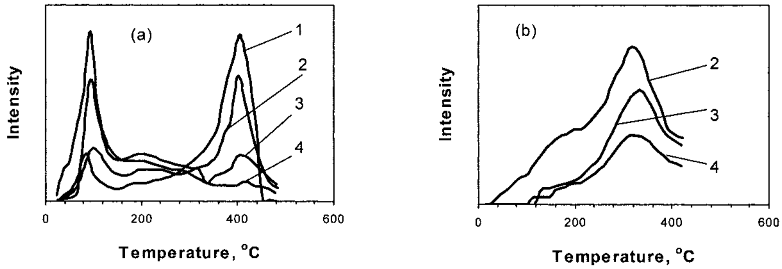
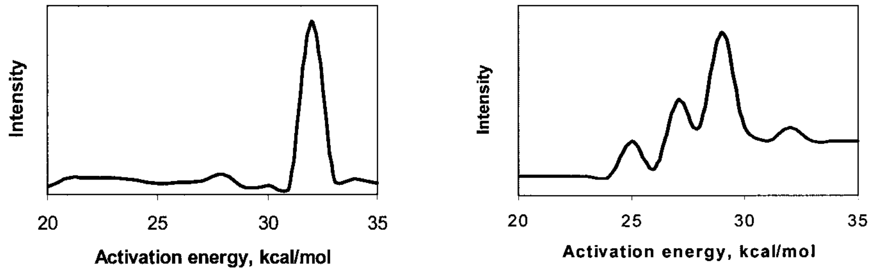


Figure 7. The TPD curves from solid $Cp_2ZrCl_2$-MAO complex (a) and the supported MM-$H_2O/AlMe_3/Cp_2ZrCl_2$ catalyst (b) after ethylene polymerization (ethylene pressure = 0,40kPa, temperature=20°C) for m/z of: 70 (1), 98 (2), 154 (3), 182 (4).

Meanwhile in the heterogenized MMT-$H_2O/AlMe_3/Cp_2ZrCl_2$ catalyst, several active sites with different activation energies of thermal destruction of the active Zr-C bonds are generated, according to data of Figure 7b: the maximum on the TPD curve in the same temperature range is broad and has a complicated shape. On the base of TPD-MS data, the distribution of active sites over activation energy of thermal destruction of Zr-C bonds for both investigated catalysts was calculated (Figure 8a,b). The activation energy of thermal destruction of Zr-C bonds in active sites is about 32 kcal/mol for the solid homogeneous $Cp_2ZrCl_2$/ MAO catalyst and changes in the range from 25 to 32 kcal/mol for the heterogenized MMT-$H_2O/AlMe_3/Cp_2ZrCl_2$ catalyst.



a. b.

Figure 8. Calculated energy spectra of active sites for m/z=98 for solid $Cp_2ZrCl_2$-MAO complex (a) and the supported MMT-$H_2O/AlMe_3/Cp_2ZrCl_2$ catalyst (b).

## Conclusion

The heterogenized activators – "support-$H_2O/AlR_3$", obtained directly on the surface, form with metallocene metal alkyl complexes which are active in olefin polymerization without use of commercial MAO. The aluminumorganic compound in the activator support-$H_2O/AlR_3$ is similar in general to the structure of commercial MAO. At the same time, it was found out that the commercial MAO, supported on the dehydrated $SiO_2$, looses part of the most active methyl-groups and obviously along with this, the ability to alkylate metallocenes. The heterogenization of Zr-cenes on support-$H_2O/AlR_3$ is accompanied by the appearance of the energy non-uniformity of active sites. The activation energy of thermal destruction of active Zr-C bonds in the active sites of the prepared heterogenized catalyst changes in the range from 25 to 32 kcal/mol.

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