Regulation of molecular weight, molecular weight distribution and branching distribution in polyethylene produced by supported catalysts bearing bis(imino) pyridyl Fe(II) and N,N-α-diimine Ni(II) complexes

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ABSTRACT

For preparation of highly active supported catalyst with bis(imino)pyridyl Fe(II) complexes (Fe1, Fe2) and N,N-α-diimine complex of Ni (Ni3), silica modified with alumina (SiO2(Al)) was used as a support. Data on the possibility to regulate molecular weight (MW) and molecular weight distribution (MWD) of polyethylene (PE), produced over the supported catalyst Fe1/SiO2(Al)+TIBA by variation of polymerization temperature and the addition of hydrogen and hexene-1, are obtained. The prepared PE samples were characterized by Mw values varied from 80 to 350 kg/mol and various MMD (Mw/Mn=4.6-11.7).

By grafting on SiO2(Al) of two different iron bis(imino)pyridyl complexes, producing PE with diverse MW, bi-component catalyst was prepared. This catalyst generates linear PE with broad and bimodal MWD (Mw/Mn=33).

Fixation on SiO2(Al) of α-diimine Ni(II) pre-catalyst (Ni3), yielding high molecular weight branched PE at the ethylene homopolymerization, and bis(imino)pyridyl Fe(II) complex (Fe2) that forms lower molecular weight linear PE, affords formation of a new bi-component catalyst. The catalyst produces PE with broad MWD and high content of branches concentrated in high molecular weight PE fraction. Polyolefins J (2022) 9: 103-116

Keywords: Ethylene polymerization; supported catalysts; bis(imino)pyridyl complex of Fe; diimine complex of Ni; molecular weight distribution.

INTRODUCTION

Complexes of late transition metals (Ni(II), Fe(II), Co(II)) with bis(imino)pyridine ligands, discovered in 1998 [1-3], are considered to be one of the most promising families of post-metallocene catalysts for ethylene polymerization. The progress in this area has been reported in a number of recent reviews [4-8]. In this family of catalysts, complexes of Fe(II) gained extreme attention due to their high activity. Tuning the ligand structure in these complexes and polymerization conditions (ethylene pressure, polymerization temperature, composition of the activator) gives possibility to obtain products with different molecular weight (Mw) ranging from linear oligomers to linear high-molecular weight PE and with molecular-weight distribution (MWD) varying from typical single-site (Mw/Mn ≤ 2.5) to broad polymodal PEs (Mw/Mn > 20) [8-10]. In case of ethylene...
polymerization over homogeneous systems, involving bis(imino)pyridyl complexes of iron (LFeCl₂), some peculiarities are observed, that distinguish these catalysts from the systems based on metallocene complexes of Zr(IV) and Ti(IV): (i) homogeneous LFeCl₂ catalysts are highly active with aluminum tri-isobutyl (Al(i-Bu)₃) co-catalyst used instead of methylaluminoxane (MAO) [11-15]; (ii) in ethylene polymerization over these catalysts with both TIBA and MAO co-catalysts PE with broadened MWD (Mₕ/Mₙ >3) is formed [11-15]; (iii) with the introduction of α-olefin as a co-monomer into polymerization, branched polymer is not formed, being the evidence of very low co-polymerization ability of LFeCl₂ catalysts [15].

Because it was discovered that α-dimine Ni (II) complexes could effectively catalyze the polymerization of ethylene [16], these systems were extensively studied and developed significantly. The evolution of nickel complexes as the catalysts for ethylene polymerization is reflected in a number of recent research and review articles [17-27]. Some characteristic properties of Ni(II)-based catalysts can be emphasized: (i) homogeneous catalysts based on α-dimine complexes of Ni(II) are highly active in the ethylene polymerization when MAO, MMAO or Et₂AlCl are used as co-catalysts, (ii) Ni(II)-based catalysts produce polymers with narrow MWD (Mₚ/Mₙ ≈2) that indicate the single-site behavior of these pre-catalysts, (iii) the main difference of Ni(II)-based catalysts from that, based on Fe(II), is formation of highly branched PE in ethylene homopolymerization, (iv) the MW values of polymers, produced over Ni(II)-based catalysts can be regulated in a wide range, from oligomers [17, 18] to high molecular weight PE [21,25-27] by variation of the ligand composition in Ni(II) pre-catalyst.

Olefin polymerization processes in slurry and gas phase reactors require the use of catalysts in the supported form, therefore the development of supported catalysts bearing late transition metal complexes and study of their catalytic properties are significant points of interest [11, 28-37]. In most studies silica pretreated with MAO (SiO₂/MAO) was used for grafting of LFeCl₂ complexes with the additional use of MAO in polymerization as a co-catalyst [28, 30, 34].

Data on the catalysts, containing LFeCl₂ complexes supported on MgCl₂, are represented in refs. [38, 39]. It was shown that LFeCl₂ is tightly fixed on the surface on this support and thus obtained supported catalyst exhibited extremely high activity at polymerization in the presence of TIBA as co-catalyst [39].

The possibility to obtain the supported catalyst by anchoring of LFeCl₂ on silica, dehydroxylated at 800°C, was shown in ref. [11]. The catalyst was active in ethylene polymerization with TIBA as co-catalyst at 80°C. However, in this case low amount of complex is adsorbed on the support surface (the catalyst contained 0.1%wt. of Fe) and respectively, the catalyst exhibited rather low activity, calculated per average weight of the catalyst. Later it was shown [40] that substantial increase in the amount of iron complex, fixed on the surface of SiO₂, can be achieved through modification of silica surface by insertion of alumina in the oxide form (SiO₂(Al) supports). Such modification results in the formation of Lewis acidic sites (LAS) with different strength on the silica surface and complex LFeCl₂ is adsorbed on LAS with different strength. The catalysts with maximal activity were obtained using the support with the highest content of strong LAS. The above catalysts exhibited high activity, which was calculated both per the unit of fixed iron and per average weight of the catalyst (140 kg/g Fe h bar C₃H₄ and 428 g/g of cat h bar C₃H₄).

The supported diimine nickel catalysts have recently attracted much attention [26, 35-37]. Highly active heterogeneous catalysts were prepared via interaction of OH-group in the ligand of α-imino-ketone nickel complex with the silica surface. These catalysts were active in ethylene polymerization up to 100°C without any co-catalyst and produced high molecular weight PE with noticeable branching [26]. Ref. [37] reveals the preparation of heterogeneous catalysts with anilinonaphthoquinone complexes of Ni and Pd as active component and the study of their co-polymerization properties.

Earlier we have shown [41] that iminoacenaphthyl complex of Ni(II) (LacNiBr₂), similarly to the bis(imino)pyridyl complex of iron, can be fixed on the surface of SiO₂(Al). The prepared supported catalyst LacNiBr₂/SiO₂(Al) showed appreciable activity in the ethylene polymerization with TIBA as co-catalyst and produced branched PE, containing ≈ 40 CH₂/1000C.

As in the case of homogeneous catalysts, the molecular
weight of polymers, produced with the supported iron complexes, is mainly determined by the ligand structure of the complex used, whereas the data on the effect of polymerization conditions on the MW values are very scarce in the literature.

In the present work, we investigated the possibility to regulate the MW and MWD of PE, obtained with the catalytic system Fe1/SiO2(Al)+TIBA, through variation of polymerization parameters. For this purpose, we have studied firstly the effect of the ethylene pressure, hydrogen content in polymerization medium, the polymerization temperature and addition of α-olefin (hexene-1) on the MW and MWD of the resultant polymer. Secondly, to produce PE with broad and bimodal MWD, bi-component supported catalysts, bearing two bis(imino)pyridyl iron complexes or combination of N,N-α-diimine complex of Ni(II) and bis(imino)pyridyl iron complex, which produce PE with different MWs, were prepared and studied in ethylene polymerization.

EXPERIMENTAL

All experiments were carried out in sealed high vacuum systems using “break seal” techniques.

Catalyst preparation

For preparation of the support SiO2(Al), commercial sample of silica Davison 952 with the surface area 260 m²/g was used. The support SiO2(Al) was prepared as described in ref. [40].

2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine iron(II) dichloride (Fe1) and 2,6-bis[1-(2,6-dichloromethylphenylimino)ethyl]pyridine iron(II) dichloride (Fe2) were prepared according to ref. [3] and ref.[42], respectively (Scheme 1, A).

\[
\text{R}_1 \text{R}_2 = \text{Me, } \text{Fe1} \quad \text{R}_1 \text{R}_2 = \text{Cl, } \text{Fe2}
\]

1,4-Bis(2,4,6-trimethylphenyl)-2,3-dimethyl-1,4-diasabuta-1,3-dienyl nickel (II) dibromide (Ni3) was prepared as described in ref. [23] (Scheme 1, B).

The supported catalyst preparation

The sample of SiO2(Al) support was treated with a solution of Fe1 or Fe2 in CH2Cl2, taken in the amount needed for preparation of the catalyst with the desired iron content (0.5 and 0.25 wt%, respectively). The suspension was stirred at 20°C for 30 min, the liquid fraction was decanted, the solid part was twice washed up with CH2Cl2 and dried under vacuum up to the residual pressure of 2×10⁻² torr. The content of Al and Fe in the catalysts was determined by AES-ICP (2.5 wt.% of Al and 0.49 wt.% of Fe for Fe1/SiO2(Al) and 2.5 wt.% of Al and 0.25 wt.% of Fe for Fe2/SiO2(Al)).

Preparation of bi-component catalyst containing two bis(imino) pyridyl iron(II) complexes

The sample of SiO2(Al) support was treated with the solution of Fe1 in CH2Cl2, taken in the amount needed for obtaining of the catalyst with the iron content 0.25 wt.%. The suspension was stirred at 20°C for 30 min, the liquid fraction was decanted, the solid was twice washed up with CH2Cl2 and dried under vacuum. The prepared catalyst was treated with the solution of Fe2 in CH2Cl2, taken in the amount needed for obtaining of the catalyst with the iron content 0.25 wt.%. The obtained bi-component catalyst was twice washed up with CH2Cl2 and dried under vacuum up to the residual pressure of 2×10⁻² torr.

Preparation of bi-component catalyst containing α-diimine Ni(II) and bis(imino) pyridyl iron(II) complexes

The sample of SiO2(Al) support was treated with the solution of Ni3 in CH2Cl2, taken in the amount needed for preparation of the catalyst with Ni content 0.3 wt.%. The suspension was stirred at 20°C for 30 min, the liquid fraction was decanted, the solid was twice washed with CH2Cl2 and dried under vacuum. Thus prepared catalyst was treated with the solution of Fe2 in CH2Cl2, taken in the amount needed to obtain the catalyst with the iron content 0.1 wt.%. The catalyst was twice washed up with CH2Cl2 and dried under vacuum up to the residual pressure of 2×10⁻² torr.
Polymerization

Commercial sample of Al(i-Bu)3 (TIBA) was used as the co-catalyst (heptane solution, 0.035 M of Al). Ethylene polymerization was performed in a steel 0.5 L reactor. The catalyst (0.03 – 0.01 g) was placed into the reactor in a sealed glass ampoule. The reactor was evacuated at 80°C, cooled down to 20°C and charged with heptane (200 ml) and the solution of co-catalyst TIBA (7.5 mmol/l). After setting up the desired polymerization temperature, ethylene and hydrogen pressure was inserted into the reactor. Hexene-1 (0.6 mol/l) was introduced into the reactor in one portion before starting of the reaction. The reaction was started by breaking of the ampoule with the catalyst. During the polymerization, ethylene pressure and temperature were maintained constant by an automatic computer-controlled system. The polymerization rate (Rp) was determined by ethylene consumption a few seconds apart. After a prescribed time, the reactor was vented, the obtained solid product was separated and dried at ambient conditions to a constant weight. The detailed experimental conditions are given below in the footnotes of the tables.

Measurements of PE molecular weight (MW) and molecular weight distribution (MWD)

MWD measurements were performed using a high-temperature gel permeation chromatography (GPC) PL 220 system equipped with RI detector in 1,2,4-trichlorobenzene stabilized with 0.0125% BHT at a flow rate of 1 mL/min at 160°C. The polymers were analyzed using a set of Olexis columns. Samples were dissolved at a concentration of 0.5-2.5 mg/mL, depending on the molecular weights. Data collection and handling were carried out using Cirrus GPC Software and Multi Detector Software, and data were collected at 1 point per second. The instrument was calibrated using polyethylene and polystyrene standards with narrow MWD in the range 13200000 - 540 g/mol.

Separation of polymers into fractions with narrow MWD was performed using a PolymerChar fractionation station PREP mc2. 1 g of a sample was dissolved in a definite volume of o-xylene for 2 h, then a calculated amount of 2-(2-butoxyethoxy)-ethanol was added in a polymer solution to precipitate a part of polymer. The total volume of liquid (xylene and 2-(2-butoxyethoxy)-ethanol) was always 180 mL. Hot solution of the polymer was filtered into a collecting flask. The precipitated polymer was dissolved in a new portion of xylene; the precipitation-dissolution procedure was repeated to obtain 5 fractions with a narrow MWD: fractions 1-4 were obtained at 60vol.%, 50vol.%, 45vol.% and 41vol.% of 2-(2-butoxyethoxy)-ethanol in mixture with o-xylene, and the last fraction was washed with pure o-xylene. The total number of branches was determined by FTIR and 1H NMR spectroscopy [43,44] using a Shimadzu FTIR 8400 S IR spectrometer and a Bruker MSL-400 NMR spectrometer, respectively.

RESULTS AND DISCUSSION

Effect of polymerization conditions (ethylene pressure, hydrogen content, polymerization temperature and addition of hexene-1 into polymerization) on the catalyst activity, molecular weight and molecular weight distribution of the produced polyethylene

Effect of the ethylene pressure on the molecular weight of polyethylene

At the ethylene polymerization over both homogeneous and supported post metallocene catalysts in the absence of any additional agents of polymer transfer reactions the molecular mass of PE can be determined by the chain transfer reactions with ethylene, alumina organic co-catalyst and by the reaction of hydride transfer to the transition metal in the active center of the catalyst. Data on the effect of the ethylene pressure (the concentration) on the MW of the produced PE are the most important and reliable for determination of each transfer reaction contribution. In case of predominant contribution of the chain transfer reaction with ethylene into the MW of the resultant PE, the number-average molecular mass of PE (Mn) should be determined by the equation (1):

$$M_n = \frac{P_n}{V_{et}^{trans}} = \frac{K_p \cdot C_p \cdot C_m}{K_{et}^{trans} \cdot C_p \cdot C_m} \approx \frac{K_p}{K_{et}^{trans}}$$

(1)

Where Pn - polymerization degree; Vp - polymerization rate; Vet - rate of transfer reaction with ethylene; Kp - propagation rate constant; Ket - constant of chain transfer reaction with ethylene; Cp - concentration of the active centers and Cm - the ethylene concentration.
Thus, according to the equation (1), in case of predominant contribution of the chain transfer reaction with ethylene on the molecular weight of PE, the ethylene pressure does not affect the $M_n$ value of PE. Data on the molecular weight of PE samples, obtained over the supported catalyst Fe1/SiO2(Al) at various ethylene pressures (Table 1) show that with the increase in the ethylene pressure from 2.5 to 10 bar, $M_n$ values of the obtained polymers change insignificantly. It means that according to the equation (1), at ethylene polymerization over this catalyst the chain transfer reaction with ethylene is dominating one. The increase in $M_w$ values at the enhancement of the ethylene pressure (Table 1) probably correlates with broadening of MWD ($M_w/M_n$ values increase from 7.5 (2.5 bar of C2H4) to 10-11.6 (5-10 bar of C2H4)).

Thus, for regulation of MW of PE, produced with this supported catalyst, it is necessary to use additional chain transfer agents.

**Effect of hydrogen**

Earlier we have found that polymerization activity of Fe1, supported on SiO2 and MgCl2, at polymerization in the presence of hydrogen used as a chain-transfer agent, noticeably increases. [11, 39] In ref. [45] this “effect of hydrogen” was explained by reactivation of “dormant” active centers, formed due to the 2,1-insertion of low molecular weight oligomers (RCH=CH2) into the growing polymer chain. However, the effect of hydrogen concentration on the MW and MWD of the produced PE was not considered in these works. In case of the studied catalyst Fe1/SiO2(Al), similar effect of hydrogen on its activity is observed (Table 2 and Figure 1). It is seen that without H2 (Table 2, exp.1) the catalyst exhibits the lowest activity (18 Kg PE/g Fe•bar C2H4•h) and the highest stability (Figure 1, curve 1).

Addition of hydrogen into polymerization results in the increase in the catalyst activity by a factor of almost 7 (Figure 1, curve 2). The kinetic curve shows a noticeable increase in the initial activity of the catalyst, which gradually decreases, but keeps higher than that in the run without hydrogen (Figure 1, curve 1). With the increase in the amount of hydrogen, introduced into the reactor (Figure 1, curve 3), further grows of the catalyst activity is observed, but the kinetic curve in this case is less stable, demonstrating sharp increase in the activity in the first minutes of the reaction, which noticeably decreases with polymerization time. At further increase in the amount of hydrogen up to 2 bar, the catalysts activity decreases, when compared with the experiment where 1 bar is added (Table 2, exp.3), but in comparison with the polymerization run without hydrogen, the rate is more stable and much higher (in 5 times).

Data on the MW and MWD of PE samples, obtained at different hydrogen pressure, are plotted in Table 2 and Figure 2. With the increase in the amount of hydrogen in polymerization medium, the $M_w$ values of polymers decrease from 350 kg/mol to 83 kg/mol (exp.1 and 4). The catalyst Fe1/SiO2(Al) produces PE with a broad molecular weight distribution ($M_w/M_n$=10.0-6.4, $n$)

<table>
<thead>
<tr>
<th>Exp no</th>
<th>P(H2) bar</th>
<th>PE Yield gPE/g cat</th>
<th>Activity kgPE/gFe.barC2H4•h</th>
<th>$M_n$ kg/mol</th>
<th>$M_w$ kg/mol</th>
<th>$M_w/M_n$</th>
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<td>18</td>
<td>35</td>
<td>350</td>
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</tr>
<tr>
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<td>0.5</td>
<td>3010</td>
<td>120</td>
<td>24</td>
<td>230</td>
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<td>130</td>
<td>8.7</td>
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<tr>
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<td>2260</td>
<td>90</td>
<td>13</td>
<td>83</td>
<td>6.4</td>
</tr>
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</table>

(1) Polymerization at 80°C for 1 hour at the ethylene pressure 5 bar.
Regulation of molecular weight, molecular weight distribution and branching distribution in polyethylene produced by supported catalysts...

Table 2), evidencing the multisite nature of this catalyst. Data of Figure 2 show that contribution of the high molecular weight shoulder in the MWD curves decreases with the increase in hydrogen pressure. As the result, PE with more narrow MWD is formed ($M_w/M_n$ value decreases from 10 to 6.4 (Table 2, exps. 1 and 4)). These results confirm non-homogeneity of the active sites in this multisite catalyst, namely, the active sites, producing PE with high MW, are more active in the chain transfer reaction with hydrogen in comparison with those producing PE with low MW.

Thus, hydrogen is the effective chain transfer agent at ethylene polymerization over the catalytic system Fe1/SiO2(Al) with TIBA as co-catalyst and it is possible to obtain PE with $M_w$ values within the range 83-230 kg/mol at polymerization with different content of hydrogen. Note that the addition of hydrogen into polymerization results in the formation of PE with a narrow MWD.

Effect of the polymerization temperature

Earlier [46] data on the effect of the polymerization temperature in the region 35-70°C on the activity of the catalysts, prepared by supporting of Fe1 on SiO2 and MgCl2, were presented. It was shown that the increase in polymerization rate with the enhancement of the reaction temperature is determined both by the increase of propagation rate constant and the number of active centers.

In this work, data on the effect of polymerization temperature on the activity and molecular weight and MWD of PE, produced with the catalyst Fe1/SiO2(Al), were obtained (Table 3 and Figure 3). It is seen that in the polymerization runs without hydrogen, elevation of the temperature from 50°C to 80°C results in the increase in the catalyst polymerization rate and at 80°C the catalyst exhibits high and stable activity (Table 3, exp. 1 and 2 and Figure 3A). It should be noted that, homogeneous catalytic system Fe1 with co-catalyst TIBA has low thermal stability and is not active in the ethylene polymerization at temperature higher 50°C [11]. The increase in polymerization temperature from

<table>
<thead>
<tr>
<th>Exp. no</th>
<th>$T_{pol}$, °C</th>
<th>$P(H_2)$, bar</th>
<th>PE Yield(1) gPE/g cat</th>
<th>Activity(1) kgPE/gFe.barC2H4.h</th>
<th>$M_n$, Kg/mol</th>
<th>$M_w$, Kg/mol</th>
<th>$M_w/M_n$</th>
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<td>11.5</td>
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</table>

(1) Polymerization for 1 hour at the ethylene pressure 5 bar.
50 to 80°C weakly affects the MW of the produced PE ($M_w=340-350$ kg/mol). In case of polymerization in the presence of hydrogen, the increase in the polymerization temperature from 80 to 90°C weakly affects the catalyst activity and the shape of the kinetic curve (Table 3, exp.3 and 4 and Figure 3B). However, even at this relatively low increase in the reaction temperature, a noticeable decrease in the MW of polymer is observed. Apparently, in these experiments hydrogen is the main chain transfer agent and at the enlargement of the reaction temperature, the rate of the reaction of chain transfer with hydrogen increases to a greater extent than the rate of chain propagation reaction.

Thus, in polymerization with this supported catalyst, regulation of PE molecular mass by variation of the reaction temperature is effective only in the presence of hydrogen.

**Polymerization in the presence of hexene-1**

The peculiarity of the homogeneous catalytic systems with bis(imino)pyridine complexes of iron is theirs very low copolymerization ability and at the ethylene polymerization in the presence of hexene-1 linear polyethylene is formed [15].

Data on the effect of hexene-1 on the catalyst Fe1/SiO$_2$(Al) activity in ethylene polymerization without hydrogen and in the presence hydrogen and molecular-mass characteristics of the produced polymers are collected in Table 4 and Figure 4. In the presence of hexene-1, the activity of the catalyst slightly increases and linear PE, practically without branching, is formed. Data of IRS and DSC analysis of polymers, obtained in the ethylene polymerization with hexene-1 and without it, show that the PE samples were characterized by close terminal CH$_3$ groups content (0.9-1.2 CH$_3$/1000 C), melt temperature (140°C) and crystallinity (65-66%), typical for the ethylene homopolymers. Thus, in case of ethylene polymerization over this catalytic system in the presence of hexene-1, copolymerization process of ethylene with hexene-1 does not proceed. At the same time, we have found that the addition of hexene-1 into polymerization over the

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**Table 4. Data on the effect of hexene-1 in the ethylene polymerization on the catalyst activity and molecular weight characteristics of polymers.**

<table>
<thead>
<tr>
<th>Exp. no</th>
<th>Hexene-1 Mol/l</th>
<th>P(H$_2$) bar</th>
<th>PE Yield$^{(1)}$ gPE/g cat</th>
<th>Activity$^{(1)}$ kgPE/gFe.barC,H$_2$.h</th>
<th>$M_w$ Kg/mol</th>
<th>$M_w$ Kg/mol</th>
<th>$M_w/M_n$</th>
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<tr>
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<tr>
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<td>23</td>
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<td>6.1</td>
</tr>
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$^{(1)}$ Polymerization at 80°C for 1 hour at the ethylene pressure 5 bar.
catalyst FeI/SiO₂(Al) results in noticeable decrease in MW and narrowing of MWD of PE (Table 4, exps. 1 and 2, 3 and 4 and Figure 4). The MWD curves show that narrowing of MWD mainly occurs due to the decrease in contribution of the high-molecular weight component. Thus, the presented results indicate that at ethylene polymerization over the catalytic system FeI/SiO₂(Al) + TIBA in the presence of hexene-1, the latter acts as an additional chain-transfer agent, which results in the decrease in MW of the produced polymer. Data on the effect of hexene-1 on the MWD of produced PE (Figure 4) show non-homogeneity of the active cites in this catalyst in the chain transfer reaction with hexene-1. It is seen that predominantly the active sites, which produce PE with high molecular weight, are involved in this chain transfer reaction. It may be noted that earlier [47] in case of the ethylene-hexene-1 co-polymerization over supported Ziegler type titanium magnesium catalysts, it was observed that hexene-1 acts as an effective chain-transfer agent. It was found that, in comparison with homopolymer, the molecular mass of copolymer decreases, and polymer containing trans-vinylene groups (R-CH=CH-CH₂-P) was formed. The scheme of chain transfer process with participation of hexene-1 and formation of trans-vinylene groups in the polymer was proposed. This scheme includes the reaction of 2-1 incorporation of hexene-1 into the growing polymer chain that provokes the temporal stop of the chain propagation reaction. The transfer of the polymer chain occurs via the hydride transfer from the terminal butyl group of the polymer to the ethylene, coordinated on the active center. At that, the active center (=Ti-CH₂CH₃) is regenerated and polymer containing trans-vinylene group Bu-CH=CHCH₂P is formed.

Thus, at the ethylene polymerization in the presence of hexene-1 over the supported catalyst FeI/SiO₂(Al), hexene-1 acts as the effective transfer agent both in the presence and absence of hydrogen. Besides, introduction of hexene-1 into polymerization results in noticeable narrowing of MWD for the produced polyethylene (Mₘ/Mₙ value decreases from 10 to 6.7). So, the addition of hexene-1 into the ethylene polymerization provides additional possibilities for regulation of molecular mass and MWD of the resultant polymer. At the same time, α-olefin practically does not participate in co-polymerization with ethylene and in its presence linear polyethylene is formed.

**Preparation of polyethylene with bimodal molecular weight distribution and regulated branchings distribution over bi-component catalysts, containing bis(imino)pyridyl complexes of Fe(II) and α-diiimine Ni(II) complex**

As it was shown in ref. [40], by adsorption of bis(imino)pyridyl complex of iron on the supports SiO₂(Al), highly active catalysts with the increased loading of iron complex (up to 0.8 wt% of Fe) can be prepared. In this case, by adsorption of two different complexes, producing PE with diverse molecular
mass on SiO$_2$(Al) support, it is possible to prepare bi-component catalyst, producing PE with bimodal molecular mass distribution. For preparation of bi-component supported catalyst, we have selected the following iron complexes: (1) complex, used in the present work (Fe1); and (2) bis(imino)pyridyl complex with chloro-substituent in both α-positions of the aryl rings (Fe2). According to the data of ref. [42] in homogeneous polymerization the latter complex produces low molecular mass PE (13.3 kg/mol). It is possible to expect that the catalyst with Fe2 fixed on SiO$_2$(Al) will produce PE with lower molecular mass than that obtained using Fe1/SiO$_2$(Al) catalyst. By anchoring of Fe2 on SiO$_2$(Al) support, the corresponding catalyst was prepared and tested in ethylene polymerization. The obtained data on the activity and molecular mass characteristics of PE are compared with that obtained using Fe1/SiO$_2$(Al) catalyst (Table 5). Similarly to the studied Fe1 complex, Fe2 is tightly fixed on the surface of SiO$_2$(Al). Activity of the supported Fe2 in ethylene polymerization was close to that of the studied Fe1/SiO$_2$(Al) catalyst (Table 5, exps. 1 and 2). The polymer, obtained with Fe2/SiO$_2$(Al) has noticeably lower MW and more narrow MMD in comparison with PE sample produced by the catalyst with Fe1 complex as the active component (Table 5, exps. 1 and 2, Figure 5, curves 1 and 2).

The catalyst, prepared by treatment of the support SiO$_2$(Al) with both complexes [Fe1+Fe2], provides high PE yield (Table 5, exp. 3). In comparison with polymers, produced by the catalysts bearing individual iron complexes, PE sample obtained with bi-component catalyst is characterized by broader polydispersity (M$_w$/M$_n$=33) and GPC curve of this sample displays well-defined bimodality (Figure 5, curve 3). The position of MM peak maximums of this bimodal polymer corresponds to the position of MM peaks of polymers produced by the supported individual complexes (Figure 5, curves 1 and 2). The obtained results indicate that both active components of the supported catalyst [Fe1+Fe2]/SiO$_2$(Al) participate in polymerization and each of them produces PE with appropriate molecular mass.

The peculiarity of N,N-α-diimine Ni(II) complexes as homogeneous and supported catalysts is their ability to produce highly branched polyethylenes at ethylene homopolymerization with high activity [16-27, 35-37, 42]. According the data of ref. [42], supporting of iminoacenaphthyl Ni(II) complex on SiO$_2$(Al) results in formation of highly active catalyst that produces branched PE.

In the present study, we used the combination of α-diimine Ni (II) complex Ni3 and appropriate bis(imino)pyridyl complex of Fe(II) for preparation of a new supported bi-component catalyst to produce PE with controllable distribution of the branches. Data obtained for the mono-component supported catalysts with Fe2 and Ni3 complexes and bi-component catalyst, containing both complexes, are collected in Table 6.

![Figure 5](image)

**Figure 5.** MWD curves of polymers obtained over bis(imino) pyridyl complexes of iron, (1) Fe1; (2) Fe2; (3) [Fe1+Fe2] supported on SiO$_2$(Al).

(Numbers of the curves correspond to the experiment numbers in Table 5)

### Table 5. Data on the ethylene polymerization over mono-component and bi-component catalysts containing different bis(imino) pyridyl complexes of Fe(II) fixed on SiO$_2$(Al) and molecular weight characteristics of the produced PE.

<table>
<thead>
<tr>
<th>Exp. no</th>
<th>Content of Fe</th>
<th>PE Yield$^{(1)}$ gPE/g cat</th>
<th>Activity$^{(1)}$ kgPE/gFe.barC$_2$H$_4$.h</th>
<th>M$_n$ kg/mol</th>
<th>M$_w$/M$_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe1 0.5 %wt.</td>
<td>89 μmol/g</td>
<td>3010</td>
<td>120</td>
<td>230</td>
</tr>
<tr>
<td>2</td>
<td>Fe2 0.25 %wt.</td>
<td>45 μmol/g</td>
<td>1170</td>
<td>47</td>
<td>190</td>
</tr>
</tbody>
</table>

$^{(1)}$Polymerization at 80°C for 1 hour, ethylene pressure 5 bar, hydrogen pressure 0.5 bar.
Regulation of molecular weight, molecular weight distribution and branching distribution in polyethylene produced by supported catalysts...

and Figure 6. In ethylene polymerization at 50°C with TIBA as co-catalyst, the catalyst Ni3/SiO2(Al) shows reasonable activity (19 kg PE/g Ni h bar) and produces branched PE (CH3/1000 C=36) with narrow polydispersity (Mw/Mn=2.6) and Mw value of 210 kg/mol (Table 6, exp.1, Figure 6, curve 1). The catalyst Fe2/SiO2(Al) produces linear PE with noticeably lower MW (Table 6, exp.2). Bi-component catalyst, containing both Fe2 and Ni3 complexes, demonstrates activity close to that of the supported Ni complex (Table 6, exp.3). Polymer, produced with this bi-component catalyst, has broader MWD (Mw/Mn=5.9) and noticeable content of branches (CH3/1000 C=10). Comparison of MWD curves of polymers, obtained with mono-component and bi-component catalyst (Figure 6), shows that both components of the supported catalyst [Ni3+Fe2]/SiO2(Al) are active in polymerization and produce PE with characteristic molecular mass. According to the data of Table 6 and Figure 6, α-diamine complex of Ni(II) generates the high molecular mass fraction of the polymer, and, respectively, the branches are mainly concentrated in this fraction. To verify this supposition, the polymer, obtained with bi-component catalyst [Ni3+Fe2]/SiO2(Al) (Table 6, exp. 3), was separated into five fractions with narrow MWD and the branching content in each fraction was measured using FTIR or 1H NMR (Figure 7). The calculated MWD for the sum of fractions is in a good agreement with the MWD of initial polymer. The profile of the branching distribution (Figure 7) indicates that indeed, the main part of the branches is located in high molecular weight PE fraction produced with nickel component of the catalyst. Evidently, by variation of the active components composition and ratio, polymers with controllable bimodal MWD can be prepared, which open broad possibilities for production of polymers with controllable molecular mass distribution and branching distribution.

**CONCLUSION**

The catalyst supported with the composition Fe1/SiO2(Al) displays high activity in ethylene polymer-
ization at temperature 80°C with TIBA as cocatalyst (180 kg PE/g Fe.h.bar C₂H₄ or 0.9 kg PE/g cat.h.bar C₂H₄). We have shown the possibilities to control the molecular weight and molecular weight distribution of PE, produced at the ethylene polymerization over this catalyst, via variation of polymerization conditions.

It is found that hydrogen is the effective agent of chain transfer reaction at ethylene polymerization over this catalyst and variation of hydrogen content from zero to 30 % vol. in H₂/C₂H₄ gas phase, allows to obtain PE with Mw value within the range 350-83 kg/mol. It is worth noting that the addition of hydrogen into polymerization increases the catalyst activity about 4 times at optimal hydrogen content (10% vol. in gas phase). Molecular weight distribution of PE, produced without hydrogen, was broad (Mw/Mn=10.0) but became more narrow at a high hydrogen content (Mw/Mn=6.4).

At polymerization without hydrogen, the increase in polymerization temperature from 50 to 80°C practically does not affect Mw values. But in the case of polymerization in the presence of hydrogen, a small increase in the reaction temperature from 80 to 90°C causes a noticeable decrease in PE molecular weight probably because of strong effect of the temperature on the rate of the chain transfer reaction with hydrogen.

We have found first that introduction of hexene-1 into polymerization over the catalyst Fe1/SiO₂(Al) results in noticeable decrease in the molecular weight and narrowing of MWD of PE, produced at polymerization both in the presence and absence of hydrogen. Thus, hexene-1 acts as the effective agent in the polymer chain transfer reaction. At the same time, hexene-1 does not participate in copolymerization with ethylene and linear polyethylene is formed in its presence.

An important common peculiarity for the chain transfer reactions at the ethylene polymerization over the multisite catalyst Fe1/SiO₂(Al) with hydrogen and hexene-1 was found. The above chain transfer agents more effectively interact with the active centers of the catalyst, producing high molecular weight PE, and in both cases this results in formation of polymer with narrowed MWD.

In this work, we used an effective approach to produce polymers with bimodal MWD and PE with broad MWD and branching, concentrated in high molecular weight fraction of PE via preparation of two types of bi-component supported catalysts. We have prepared the supported bi-component catalyst, containing two bis(imino)pyridyl complexes of iron (II) with different substituents in the ligand L, which generates PE with diverse molecular masses: complex Fe1, producing PE with molecular mass Mw=230 kg/mol and complex Fe2, giving PE with molecular mass Mw=13 kg/mol. This bi-component catalyst gives PE with broad (Mw/Mn=33) and bimodal MWD. The position of peak maximums on the bimodal MWD curve corresponds to the position of MM peaks of polymers produced by separate supported mono-component catalysts, based on the complexes Fe1 and Fe2.

To obtain PE with broad MWD and containing branches in high molecular weight polymer fraction another bi-component catalyst composed of N,N-α-dimine complex of Ni(II) (Ni3) and Fe2, fixed on SiO₂(Al), was prepared. Both components of this catalyst proved to be active in ethylene polymerization and produce PE with appropriate molecular structure: α-dimine complex of Ni generates branched high molecular mass PE fraction, whereas bis(imino)pyridyl complex of Fe gives linear PE with low MW.

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CONFLICTS OF INTEREST
The authors declare that they have no conflicts of interest.

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