

Kinetic Features of Ethylene Polymerization Over Supported Catalysts [2,6-Bis(imino)pyridyl Iron Dichloride/Magnesium Dichloride] with AlR_3 as an Activator

TATIANA B. MIKENAS, VLADIMIR A. ZAKHAROV, LYUDMILA G. ECHEVSKAYA, MIKHAIL A. MATSKO

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Science, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia

Received 13 April 2007; accepted 1 June 2007

DOI: 10.1002/pola.22245

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effects of polymerization temperature, polymerization time, ethylene and hydrogen concentration, and effect of comonomers (hexene-1, propylene) on the activity of supported catalyst of composition $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ ($\text{L} = 2,6\text{-bis[1-(2,6-dimethylphenylimino)ethyl] pyridyl}$) and polymer characteristics (molecular weight (MW), molecular-weight distribution (MWD), molecular structure) have been studied. Effective activation energy of ethylene polymerization over $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ has a value typical of supported Ziegler–Natta catalysts (11.9 kcal/mol). The polymerization reaction is of the first order with respect to monomer at the ethylene concentration >0.2 mol/L. Addition of small amounts of hydrogen (9–17%) significantly increases the activity; however, further increase in hydrogen concentration decreases the activity. The IRS and DSC analysis of PE indicates that catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ has a very low copolymerizing ability toward propylene and hexene-1. MW and MWD of PE produced over these catalysts depend on the polymerization time, ethylene and hexene-1 concentration. The activation effect of hydrogen and other kinetic features of ethylene polymerization over supported catalysts based on the Fe (II) complexes are discussed. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 5057–5066, 2007

Keywords: hydrogen activation; Iron (II) complex; kinetics (polym.); MgCl_2 supported catalysts; molecular weight distribution/molar mass distribution; polyethylene (PE)

INTRODUCTION

During the last few years, intensive research has focused on late transition metal complexes as catalysts for the polymerization of olefins with the pioneering works by Brookhart, Gibson, and coworkers.^{1–8}

A series of works on synthesis and testing of supported catalysts based on bis(imino)pyridyl complexes of iron chlorides, mainly on oxide supports, was published.^{9–17} These catalysts were shown to possess high and stable activity with AlR_3 as an activator and to be free of MAO.

Earlier we have reported the data on the highly active and stable supported catalysts $\text{LFeCl}_2/\text{MgCl}_2\text{-AlR}_3$ ($\text{L} = 2,6\text{-bis(imino)pyridine}$) and the effect of catalyst composition (content of iron, composition of AlR_3 cocatalyst) on the catalyst performance in ethylene polymerization.^{18,19}

Correspondence to: T. B. Mikenas (E-mail: Mikenas@catalysis.nsk.su)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 45, 5057–5066 (2007)
© 2007 Wiley Periodicals, Inc.

In this article, we present the additional kinetic data on the effect of polymerization temperature, polymerization time, ethylene and hydrogen concentration, and effect of comonomer (propylene, hexene-1) on the activity and polyethylene properties (molecular weight (MW), molecular weight distribution (MWD), and molecular structure). These data were used to suggest a mechanism explaining the activation effect of hydrogen and other kinetic features in ethylene polymerization over supported iron catalyst.

EXPERIMENTAL

LFeCl_2 ($\text{L} = 2,6\text{-bis}[1\text{-(2,6-dimethylphenylimino)ethylpyridyl}]$) was prepared according to the literature procedures.³

Highly dispersed activated MgCl_2 has been prepared according to ref. 20 at interaction of magnesium with excess of $n\text{-BuCl}$ ($n\text{-BuCl/Mg} = 3$) in heptane at 98 °C. Surface area of MgCl_2 is 80 m^2/g .

Supported catalysts have been prepared by interaction of LFeCl_2 solution in methylene chloride with the slurry of MgCl_2 support in heptane at ambient temperature for 1 h. Then hydrocarbons were decanted and catalysts were washed with heptane.

The polymerization runs were carried out in a reactor of 0.85 L capacity equipped with magnetic stirrer and jacket for temperature control at a constant ethylene pressure (1.5–10 bar), with heptane (200 mL) as a solvent, at 60–90 °C; the catalyst concentration was 0.02–0.04 g/L, with triisobutylaluminum (TIBA) as cocatalysts at concentration 6 mmol/L, for 10–60 min. Hydrogen (0.5–2 bar) was added at polymerization as a chain-transfer agent.

MWD measurements were performed using a WATERS-150 °C instrument in conjunction with a Differential Viscometer (Viscotek Model 100). Run conditions were as follows: temperature 140 °C; 1,2,4-trichlorobenzene as a solvent at a flow rate of 1 cm^3/min . Four mixed bed TSK-gel columns (GMHXL-HT, Tosoh) were used. Conventional ($\log\{\text{MW}\}$ -retention volume) and universal calibrations ($\log\{\text{MW} \times [\eta]\}$ vs. retention volume) were made using narrow Polystyrene standards and PE standards. We registered good correspondence of Conventional and Universal calculation data; here we present the results of GPC using Conventional calibration.

The IR spectra of polymer films were recorded with a BOMEM-MB-102 FTIR spectrometer. The content of CH_3 groups and double bonds in PE was calculated from IR spectra as described in ref. 21.

Differential scanning calorimetry (DSC) measurements were made using Netzch DSC 204 F4 Phoenix instrument at heating rate of 10 °C/min according to ASTM D 3417-83 and ASTM D 3418-82 methods.

The melt index (MI) measurements were made according to ASTM D 1238 (conditions 190/5).

RESULTS

Effect of Polymerization Temperature

Data on the effect of polymerization temperature on the catalytic properties of catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-AlR}_3$ are listed in Table 1. Activity increases as the polymerization temperature is elevated in the range of 60–90 °C. In contrast to the homogeneous catalysts of $\text{LFeCl}_2\text{-AlR}_3$ composition, supported catalysts are highly active and stable even at elevated temperatures (80–90 °C). Effective activation energy (E_a) of ethylene polymerization over catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-AlR}_3$ calculated from the data of Table 1 is 11.9 kcal/mol.

The value of MI of PE increases, accordingly, the MW decreases at elevation of polymerization temperature. Polyethylene produced over catalyst ($\text{LFeCl}_2/\text{MgCl}_2\text{-AlR}_3$) has a broad MWD ($M_w/M_n = 13\text{--}16$; Experiments 2–4, Table 1) over the entire range of polymerization temperatures.

Table 1. Effect of the Polymerization Temperature (T) on the Activity, MW, and MWD of PE^a

Run	T (°C)	Maximal Activity (kg of PE/g of Fe h mol of C_2H_4)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n
1	60	1145	—	—
2	70	1500	415	14.3
3	80	3230	270	13.3
4	90	3730	160	16.1

^a Polymerization condition: catalyst contains 0.6 wt % of Iron, 5 bar of C_2H_4 , 0.5 bar of H_2 , TIBA as cocatalyst, a TIBA concentration of 6 mmol/L, $\text{Al/Fe} = 750$ (Molar), and 1 h.

Table 2. Effect of Ethylene Concentration, Hydrogen Content, and Polymerization Duration on the Activity and Molecular Structure of PE

Run ^a	C ₂ H ₄ Pressure (bar)	H ₂ Pressure (bar)	Time (min)	Activity ^b (Kg of PE/g of Fe h Bar of C ₂ H ₄)	MN × 10 ⁻³ (g/mol)	M _w × 10 ⁻³ (g/mol)	M _w /M _n	CH ₃ /Polymer Chain	C=C ^c /Polymer Chain
1	1.5	0	60	70	22	190	8.7	0.8	0.9
2	3	0	60	180	27	269	9.9	0.6	1.7
3	5	0	60	164	27	311	11.4	0.4	1.8
4	10	0	60	194	22	321	14.9	0.5	1.5
5	5	0	10	70	19	202	11.0	1.2	1.2
6	5	0	60	120	23	344	15.0	0.5	0.8
7	5	0.5	60	200	20	270	13.0	—	—
8	5	1.0	10	160	14	116	8.2	1.1	0.9
9	5	1.0	60	200	20	317	16.0	0.6	0.9
10	5	2.0	60	115	10	158	15.0	—	—

^a Catalysts contain 0.33 wt % of Iron (Runs 1–4) and 0.85 wt % of Iron (Runs 5–10), polymerization at 80°C, a TIBA concentration of 6 mmol/L, Al/Fe = 1200 (molar).

^b Average activity.

^c Terminal vinyl group RC=CH₂ (909 cm⁻¹ bound in IR-spectra).

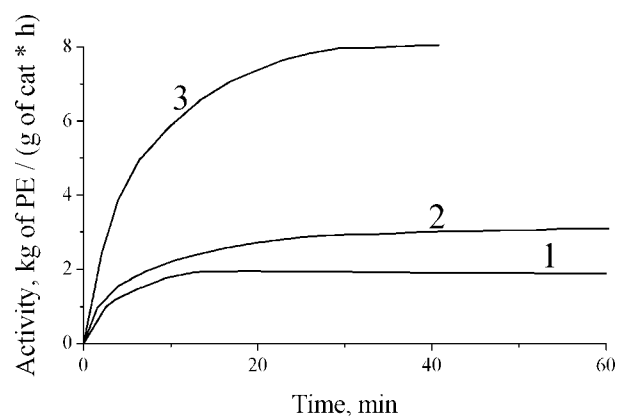
Effect of Ethylene Concentration

Data on the effect of ethylene concentration (pressure) on the activity and molecular structure of PE are presented in Table 2 and Figures 1–3. Note that activity rises sharply as ethylene pressure increases from 1.5 to 3 bar (Table 2, Runs 1 and 2). The catalyst activity is directly proportional to ethylene pressure in the range of 3–10 bar (Fig. 2) (activity referred to 1 bar of C₂H₄ does not change, Table 2, Runs 1–4). According to the data obtained, in the range of ethylene pressures 3–10 bar, the rate of polymerization is of the first order with respect to monomer.

The data of Table 2 and Figure 2 show that raising the ethylene pressure from 1.5 to 5 bar leads to an increase in the weight-average molecular weight (M_w). Upon further rising of ethylene pressure up to 10 atm, the M_w value remains virtually unchanged. Note that an increase in ethylene pressure from 1.5 to 10 bar results in MWD broadening (the M_w/M_n value increases from 8.7 to 14.9) due to increasing the fraction of high-molecular part of PE (Fig. 3).

As noted earlier,¹⁹ PE produced with catalyst LFeCl₂/MgCl₂-TIBA has an increased content of terminal vinyl groups, which proves that β-hydride chain transfer is the main chain-transfer reaction in ethylene polymerization. Using the GPC data for the number-average molecular weight (M_n) MN and IRS data for the contents

of methyl and vinyl end groups (Table 2), we estimated the amount of terminal vinyl and methyl groups per polymer molecule for polymers synthesized with catalyst LFeCl₂/MgCl₂-TIBA at different ethylene pressures. The polymer obtained at a low ethylene pressure (1.5 bar) has approximately 1 methyl and 1 vinyl end group per polymer chain (Table 2, Run 1). Raising the pressure increases the content of terminal vinyl end groups up to 1.5–1.8 C=C per polymer chain, and decreases the content of methyl end groups (0.4–0.6 CH₃ per chain).

**Figure 1.** Kinetic profile of ethylene polymerization over LFeCl₂/MgCl₂-TIBA catalyst at different ethylene pressure: 3 bar (1), 5 bar (2), 10 bar (3) (for the polymerization conditions, see Table 2).

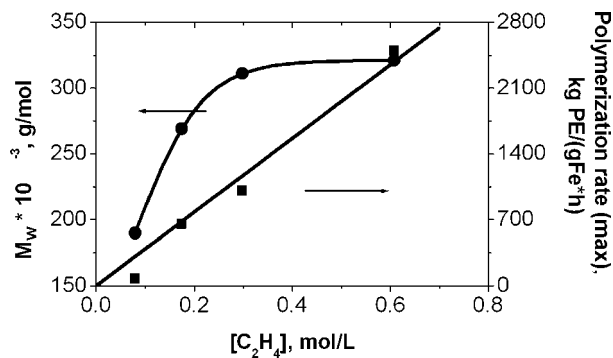


Figure 2. Effect of ethylene concentration on the polymerization rate and molecular weight (M_w) of polyethylene (for the polymerization condition, see Table 2, Runs 1–4).

Effect of Hydrogen

It is known that hydrogen is used to control the MW of PE over supported catalysts of various compositions. Note that catalytic activity generally decreases when hydrogen is introduced even in small amounts (5–10% vol.) at ethylene polymerization with supported Ziegler–Natta catalysts containing titanium and vanadium compounds as active components.^{22–24} The data presented earlier¹⁹ shows that the presence of hydrogen increases the activity for ethylene polymerization over catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-AlR}_3$. In this work, we used a wider range of hydrogen concentration to study ethylene polymerization with this catalyst. As seen from Table 2, the addition of 9–17% vol. of hydrogen to the feed mixture increases the activity of catalyst $\text{LFeCl}_2/\text{MgCl}_2$ (cf. Experiments 6 and 7 with 9 in Table 2). Note that in the indicated range of

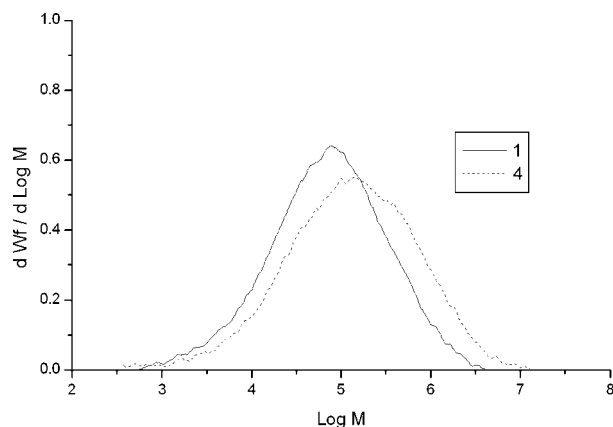


Figure 3. Effect of ethylene pressure on the MWD of PE (for the polymerization conditions, see Table 2, Runs 1 and 4).

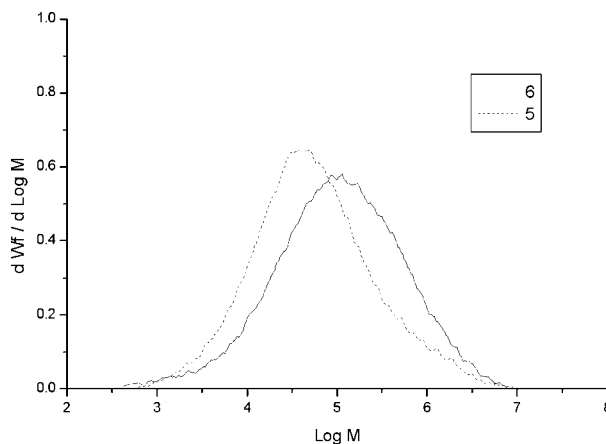


Figure 4. Effect of polymerization duration on the MWD of PE (for the polymerization conditions, see Table 2, Runs 5 and 6).

hydrogen concentration (9–17% vol.), there is a weak effect of hydrogen concentrations on values of number-average MW of PE (M_n). Thus, when hydrogen serves as an activator for catalyst $\text{LFeCl}_2/\text{MgCl}_2$, it is not an efficient transfer agent of polymer chain. An increase in hydrogen concentration to 30% vol. deteriorates the catalyst activity to the level observed without hydrogen and decreases the MW of PE (Table 2, Run 10). Similar effect concerning the hydrogen activation of catalysts based on bis(imino)pyridyl complexes of iron chlorides supported on oxides was reported in ref. 25. Addition of small amounts of hydrogen significantly increases the activity; however, further increase in hydrogen concentration decreased the activity.

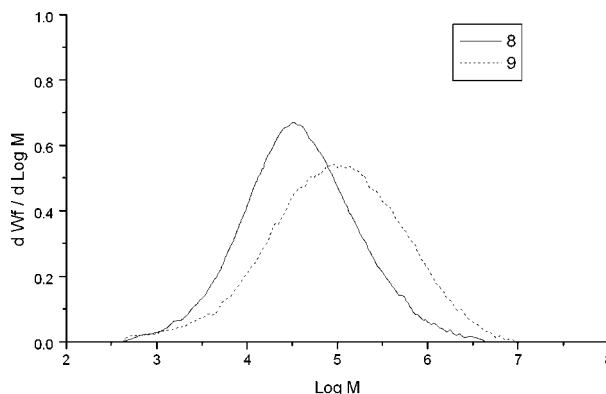


Figure 5. Effect of polymerization duration on the MWD of PE (for the polymerization conditions, see Table 2, Runs 8 and 9).

Table 3. Data on the Copolymerization of Ethylene with Hexene-1 Over LFeCl₂/MgCl₂ Catalyst^a

Run	PH ₂ (bar)	[C ₆ H ₁₂] (mol/L)	Time (min)	V ^b	MI(5) (g/10min)	CH ₃ /1000°C	(C=C) ^c /1000°C
1	0	0	60	73	0.08	0.6	0.40
2	0	0.4	60	28	0.33	0.7	0.7
3	0.5	0	60	107	0.15	0.8	0.44
4	0.5	0.4	30	107	1.2	1.1	0.70
5	0.5	0.8	28	103	2.5	1.4	0.70
6	0.5	1.4	30	73	1.25	0.8	0.39

^a Polymerization conditions: 5 bar of ethylene, 70°C, a TIBA concentration of 6 mmol/L, catalyst contains 0.6% wt % of Iron.^b Average activity: kg of PE/g of Fe h bar of C₂H₄.^c Terminal vinyl group RC=CH₂ (909 cm⁻¹ bound in IR-spectra).

Effect of Polymerization Time

As seen from Table 2, the catalyst activity increases as the polymerization time increases from 10 to 60 min (cf. Experiments 5 and 6 and Experiments 8 and 9 in Table 2). This is caused by the occurrence of the initial accelerating stage in the kinetic curves of polymerization (Fig. 1), with the polymerization rate attaining its maximum at coming to a plateau only 15–30 min after the reaction onset. MW of PE also increases with the time of ethylene polymerization, both in the absence and in the presence of hydrogen. Broadening of PE MWD (M_w/M_n) occurs at increasing the polymerization time due to shifting the peak maximum to the high MW region (Figs. 4 and 5). Similar data on the effect of polymerization time on MW and MWD were obtained with homogeneous bis(imino)pyridyl complexes of Fe(II)³ and with Fe(II) complexes supported on silica gel, which was modified with partially hydrolyzed MAO.²⁵

Polymers produced in a short polymerization time have a close number of terminal methyl and vinyl groups (approximately one group per polymer chain, Table 2). Similar data were

obtained for PE synthesized at a low pressure (1.5 bar) (Table 2). As the reaction time increases, MW of PE increases and the content of methyl groups in polymer decreases (approximately to 0.5 CH₃ per polymer chain), with retained content of vinyl end groups (approximately one C=C per chain) (Table 2). The effect of decreasing the content of methyl end groups at increased polymerization time was observed also with a homogeneous system based on bis(imino)pyridyl complexes of Fe(II).³

Copolymerization of Ethylene with α -Olefins Over Catalyst LFeCl₂/MgCl₂ + Al(*i*-Bu)₃

Data on the activity of catalyst LFeCl₂/MgCl₂ + AlR₃ in homo- and copolymerization of ethylene with hexene-1 and propylene as well as data on the molecular structure of the polymers produced are presented in Tables 3 and 4. Previously,^{26–31} the comonomer effect was shown to occur with supported titanium- and vanadium-magnesium catalysts; it consists in increased activity at copolymerization of ethylene with α -olefins. In contrast to supported Ziegler type

Table 4. Effect of α -Olefin on Polymers Characteristics

Run ^a	T (°C)	α -Olefin	[C ₆ H ₁₂] (mol/L)	V ^b	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	CH ₃ /chain	C=C ^c /chain	T_m^d (°C)	X^d (%)
1	80	—	0	120	18	235	13.2	1.4	0.9	137.3	75.9
2	80	C ₆ H ₁₂	0.6	126	11	94	8.7	1.2	0.8	136.3	77.9
3 ^e	70	C ₃ H ₆	(35%) ^f	23	7.0	40	5.7	5.5	0.33	—	—

^a Polymerization conditions: 5 bar of ethylene, 0.5 bar of hydrogen, a TIBA concentration of 6 mmol/L, and 1 h.^b Average activity: kg of PE/g of Fe h bar of C₂H₄.^c Terminal vinyl group RC=CH₂ (909 cm⁻¹ bound in IR-spectra).^d Melting points (T_m) and crystallinity values (X) are from the second heating scans.^e Polymerization without hydrogen.^f [C₃H₆] in feed mixture.

catalysts, the introduction of hexene-1 decreases the activity of catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-AlR}_3$ for ethylene polymerization without hydrogen (Table 3, Experiments 1 and 2). In ref. 25, bis(imino)pyridyl complexes of Fe(II) supported on oxides completely deactivated in ethylene polymerization without hydrogen at the addition of hexene-1. At ethylene copolymerization with hexene-1 in the presence of hydrogen, activity of catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-AlR}_3$ remains unchanged as compared with homopolymerization of ethylene at a concentration of hexene-1 in the polymerization medium equal to 0.4–0.8 M (Experiments 3–5 in Table 3).

The IRS analysis of polymers shows that the introduction of hexene-1 to ethylene polymerization, both with and without hydrogen, does not lead to a noticeable increase in the content of methyl groups in the polymer (Tables 3 and 4). Homo- and copolymers have nearly equal amounts of methyl groups calculated per polymer chain (Table 4, Experiments 1 and 2); that is, hexene-1 is not incorporated into the polymer chain. This conclusion is confirmed also by the DSC data (Table 4). The polymer obtained in the presence of hexene-1 has the same melting point (136–137 °C) and high crystallinity (77.9%) as homopolymer (cf. Experiments 1 and 2 in Table 4). Besides, similar to ethylene homopolymers, the polymers produced with hexene-1 have a high content of terminal vinyl groups (0.5–1.0 C=C per 1000 °C). All polymers obtained over catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ have a very low content of vinylidene groups (<0.03 C=C per 1000 °C).

However, hexene-1 and propylene are efficient transfer agents of polymer chain: its addition upon ethylene polymerization significantly decreases the PE MW (Table 4). The introduction of hexene-1 results in shifting the MWD curve to the region of low MWs and narrowing of MWD (Fig. 6).

Ethylene copolymerization performed with propylene in the absence of hydrogen over catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ showed the same peculiarities as the copolymerization with hexene-1: a sharp drop in activity for homopolymerization, a sharp decrease in the MW, and narrowing of PE MWD (Table 4, Experiment 3). Note that copolymerization conditions were chosen so as to provide the formation of a copolymer over titanium–magnesium catalysts that contains 35% mol of propylene (the propylene content in a feeding mixture was 35% mol). However, catalyst $\text{LFeCl}_2/\text{MgCl}_2$ produced a powder polymer with the propylene content of only ~0.3% mol.

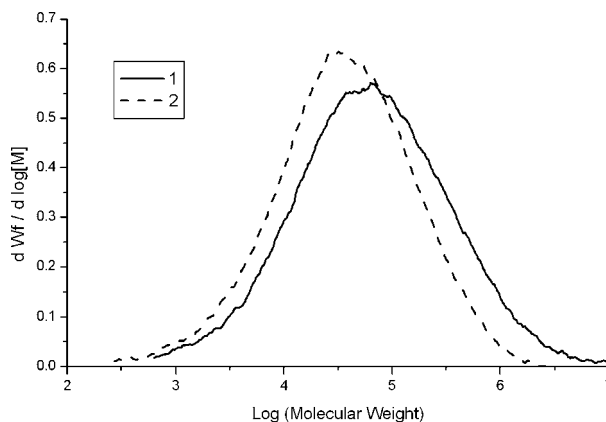


Figure 6. Effect of hexene-1 adding into ethylene polymerization on the MWD of PE (for the polymerization conditions, see Table 4, Runs 1 and 2).

DISCUSSION

The data presented above and the earlier published data¹⁹ show that the catalysts for ethylene polymerization, bis(imino)pyridyl complexes of iron dichloride supported on magnesium chloride, are similar to the Ziegler–Natta catalysts supported on MgCl_2 in the pattern of active site formation: active sites form upon interaction of LFeCl_2 with Lewis acid sites of magnesium chloride adsorption and are activated during ethylene polymerization by aluminum–organic cocatalysts (AlR_3), which are typical of the Ziegler catalysts. These catalysts are highly active and stable at elevated temperatures of polymerization. Effective activation energy of ethylene polymerization over $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ has a value typical of supported Ziegler–Natta catalysts (11.9 kcal/mol). The polymerization reaction is of the first order with respect to monomer at the ethylene concentration >0.2 mol/L.

On the other hand, ethylene polymerization with catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ has some kinetic features and peculiarities of molecular structure of the polymers to be obtained:

- Catalysts containing LFeCl_2 show an increased activity upon introduction of hydrogen in the ratio $\text{H}_2/\text{C}_2\text{H}_4 = 0.1\text{--}0.2$ (mol), in contrast to conventional supported catalysts based on titanium and vanadium compounds, which are deactivated by addition of hydrogen.
- Unlike Ti- and V/Mg-catalysts, which are activated by the introduction of comono-

mers (propylene, hexene-1, etc.) to ethylene polymerization, the addition of hexene-1 results in a sharp decrease in the activity of catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ at polymerization without hydrogen. The catalyst activity does not change with respect to ethylene homopolymerization, when copolymerization of ethylene and hexene-1 is carried out in the presence of hydrogen at concentrations of hexene-1 up to 0.8 M, further increase in the concentration of hexene-1 decreasing the activity. A sharp drop in the activity of catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ is observed also with propylene used as a comonomer (polymerization without hydrogen).

- Catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ has a very low copolymerizing ability toward propylene and hexene-1; the number of methyl branches in polymer, the melting point and crystallinity of polymers do not show essential changes upon introduction of comonomer.
- Polyethylene produced with $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ has the following features:
 - A high content of terminal vinyl groups (0.7–1.8 C=C per polymer chain).
 - A broad MWD; the value of M_w/M_n varies with polymerization conditions from 6 to 23.
- MW and M_w/M_n values of PE produced over $\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$ depend on the polymerization time and ethylene concentration and increase with these parameters.
- As the MW of PE increases (at increasing reaction time or ethylene pressure), the content of methyl groups in polymer decreases, while the content of vinyl end-groups does not change or increases.
- MW and M_w/M_n values of PE decrease when propylene or hexene-1 is introduced to polymerization.

As noted earlier, polymers produced with catalysts containing homogeneous complexes of Fe(II) ($\text{LFeCl}_2\text{-MAO-Al(i-Bu)}_3$)³ and supported complexes of Fe(II) ($\text{LFeCl}_2/\text{MgCl}_2\text{-Al(i-Bu)}_3$)¹⁹ have a high content of terminal vinyl groups. At ethylene polymerization with these systems, β -hydride chain transfer to a metal or a monomer contributes significantly to the reactions of polymer chain restriction. In this case, the ratio of saturated and unsaturated terminal groups in polymers varies with polymerization conditions (time and ethylene pressure). The authors of

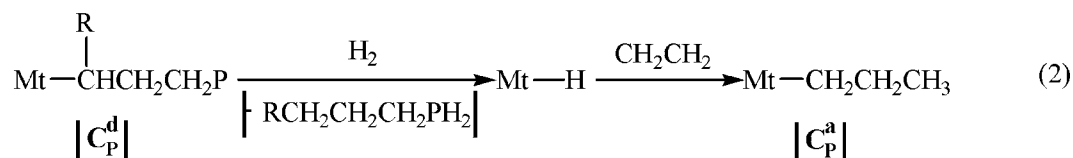
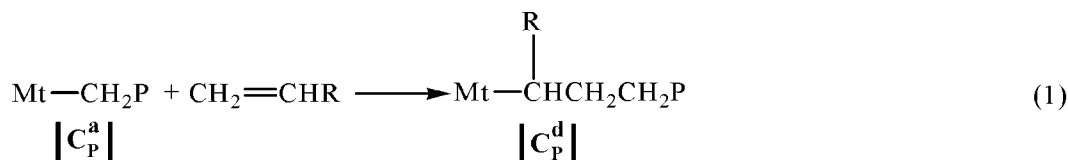
ref. 3 explained this fact by variation in the rate ratio of transfer reactions with aluminum–organic compound (yielding CH_3 end groups) and β -hydride transfer reactions (vinyl end groups). The second explanation of this fact proposed by the authors of ref. 32 is that two types of active centers of a different chemical nature are formed in the interaction between 2,6-bis(imino)pyridyl complexes of iron and aluminum–organic compound. Different centers in the latter catalyst systems respond differently to reaction conditions, such as the reaction duration, the ethylene concentration, and so forth, produce the low-MW fraction and the high-MW fraction of polyethylene.

A typical feature of catalysts containing LFeCl_2 as the active component is that they increase their activity upon hydrogen introduction to polymerization (at a ratio of $\text{H}_2/\text{C}_2\text{H}_4 = 0.1\text{--}0.2$ (mol)).^{19,25,33,34}

Activation by hydrogen is known to occur not only with $\text{LFeCl}_2/\text{MgCl}_2\text{-AlR}_3$ catalysts, but also with titanium–magnesium catalysts used for polymerization of propylene and other higher olefins. To interpret this effect, two schemes are discussed in the literature.^{35–40}

1. In the absence of hydrogen, a part of active sites (C_p^d) turns into a “sleeping” state after 2,1-addition of α -olefin (C_p^d) to the polymer chain, because steric constraints prevent incorporation of the next molecules of α -olefins. Addition of hydrogen and/or ethylene increases the catalyst activity for propylene polymerization. Molecules of hydrogen or ethylene can enter such “sleeping” sites, turning them into the active state; the introduction of hydrogen leads to chain transfer accompanied by the formation of Mt-H bond, and the introduction of ethylene causes a growth of polymer chain (reaction 2) (Scheme 1).
2. According to the second scheme, the “sleeping” sites arise from the formation of π -allyl complexes of propylene or other α -olefins with active polymerization sites (Scheme 2).

In this case, π -allyl complex (b) forms by reaction 3 with polymer chain transfer, while regeneration of the active polymerization site occurs upon interaction of complex (b) with hydrogen to give hydride iron complex (c) on which α -olefin is coordinated (reaction 4). Further insertion of



Scheme 1. Deactivation of active sites via 2,1-insertion of α -olefins and reactivation of a “sleeping” sites by hydrogen.

α -olefin (or ethylene) along Fe—H bond (reaction 5) results in the formation of active site (d).

As noted earlier, catalysts $\text{LFeCl}_2/\text{MgCl}_2\text{-Al}(\text{i-Bu})_3$ produce polyethylene with a broad MWD, β -hydride chain transfer to a metal (Fe) or a monomer being the main polymer chain transfer reactions. This yields PE molecules of different MWs (oligomers among them) containing vinyl end groups. Such unsaturated compounds that are formed during polymerization or introduced additionally (propylene, hexene-1) may block a part of active sites. This leads, for instance, to a sharp drop in activity that occurs upon addition of propylene or hexene-1 (Tables 3 and 4).

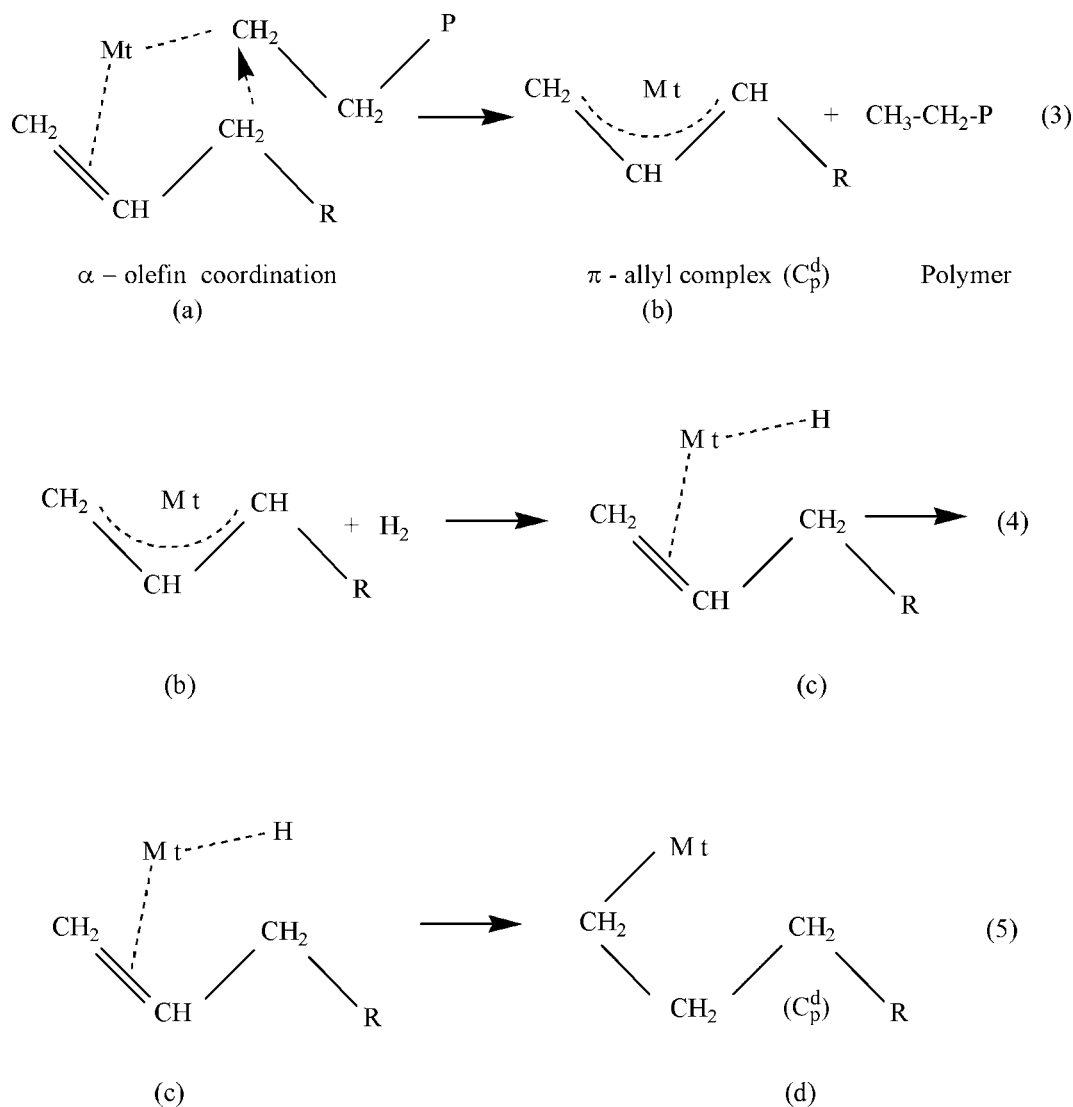
Earlier, using the radiochemical data to estimate the number of growth sites and the growth rate constant for supported catalysts containing bis(imino)pyridyl complexes of iron dichloride, we assumed^{33,34} that a part of active sites in these catalysts may be blocked as a result of 2,1-insertion of ethylene oligomers that form in polymerization, turning into a “sleeping” state (reaction 1). Hydrogen molecules can be incorporated into such “sleeping” sites, making them active (reaction 2).

The probability that a part of active sites may deactivate by the earlier mechanism (2,1-insertion of oligomers along the Fe–polymer bond) can be supported by the data reported in ref. 40. A study by Fink and Babik⁴¹ on the structure and distribution of propylene dimers obtained with various bis(imino)pyridyl iron complexes showed a high (>90%) probability of 2,1-insertion of propylene into Fe – iso-propyl bond at oligomerization of propylene, using iron complexes of LFeCl_2 composition ($\text{L} = 2,6\text{-bis[1-(2,6-$

dimethylphenylimino)ethyl]pyridyl) in combination with a boric activator and $\text{Al}(\text{i-Bu})_3$.

New data obtained in our study on the effect of hydrogen and hexene-1 concentrations and polymerization time on the MW, MWD and the structure of polymers suggest that the second scheme of catalyst $\text{LFeCl}_2/\text{MgCl}_2\text{-Al}(\text{i-Bu})_3$ deactivation in ethylene polymerization and its activation upon hydrogen introduction is also quite probable. The second scheme assumes the π -allyl mechanism of the “sleeping” sites formation due to blocking of active polymerization sites by high-molecular olefins, which may add to the active site as a result of 1,2 or 2,1-addition. In this case, the formation of π -allyl complex is accompanied with termination of polymer chain (reaction 3). This reaction can be confirmed by the data of Table 3 (cf. Experiments 1 and 2): the introduction of hexene-1 in the absence of hydrogen increases MI (decreases the MW) even to a greater extent than in the presence of hydrogen but without hexene-1 (Experiment 3). According to reaction 4, addition of hydrogen leads to hydrogenolysis of π -allyl complex and reactivation of the active site, however, this is not accompanied by polymer chain transfer. Presumably, this is why the MW of PE changes only slightly upon variation in hydrogen concentration in the case of catalyst activation by hydrogen (Experiments 6, 7, and 9 in Table 2).

An increase in hexene-1 concentration in the presence of hydrogen increases the number of blocking events (reaction 3) (with polymer chain transfer) and the number of activation events (reaction 4); thus, the MW of PE decreases upon simultaneous introduction of hexene-1 and hydrogen.



Scheme 2. Reactivation of active sites via the formation of π -allyl complexes with α -olefins and reactivation of a “sleeping” sites by hydrogen.

As mentioned earlier, MW depends on the polymerization time. It can be assumed that early in the polymerization the concentration of low-molecular oligomers is rather high, and these oligomers, similar to hexene-1, are blocking and transferring the polymer chain by reactions 3 and 4, thus decreasing the molecular weight of PE. Note that the addition of hexene-1 leads to narrowing of PE MWD; at a short polymerization time this also gives PE with a narrow MWD (cf. Experiments 1 and 2 in Table 4 and Experiments 5 and 8 in Table 2).

Therefore, analysis of the data obtained gives ground to conclude that β -hydride chain transfer at polymerization over iron–magnesium catalysts produces unsaturated oligomers, which may

block a part of active sites via the formation of π -allyl complexes with polymer chain transfer (Scheme 2, reaction 3). Hydrogen addition leads to reactivation of the active sites by reaction 4 accompanied with the formation of active polymerization site.

REFERENCES AND NOTES

- Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J Am Chem Soc* 1998, 120, 4049.
- Small, B. L.; Brookhart, M. *J Am Chem Soc* 1998, 120, 7143.
- Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.;

- McTavish, S. J.; Redshaw, C.; Solan, G. A.; Stromberg, S.; White, A. J. P.; Williams, D. J. *J Am Chem Soc* 1999, 121, 8728.
4. Bennett, A. M. A. (to DuPont Co.). U.S. Pat. 5,955,555(1999).
5. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew Chem Int Ed Engl* 1999, 111, 448.
6. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew Chem Int Ed Engl* 1999, 38, 428.
7. Kumar, K. R.; Sivaram, S. *Macromol Chem Phys* 2000, 201, 1513.
8. Talsi, E. P.; Babushkin, D. E.; Semikolenova, N. V.; Zudin, V. N.; Panchenko, V. N.; Zakharov, V. A. *Macromol Chem Phys* 2001, 202, 1816.
9. Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P.; Babushkin, D. E.; Sobolev, A. P.; Echevskaya, L. G.; Khysniyarov, M. M. *J Mol Catal A* 2002, 182/183, 283.
10. Kimberley, B. S.(to BP Chemicals Co.). WO99/46304 (1999).
11. Maddox, P. J.(to BP Chemicals Co.). WO 00/55216 (2000).
12. Kimberlay, B. S.(to BP Chemicals Co.). U.S. Pat. 6,472,341(2002).
13. Schmidt, R.; Welch, M. B.; Palackal, S. J.; Alt, H. G. *J Mol Catal A* 2002, 179, 155.
14. Kaul, F. A. R.; Puchta, G. T.; Schneider, H.; Biehlert, F.; Mihalios, D.; Herrmann, W. A. *Organometallics* 2002, 21, 74.
15. Ma, Z.; Ke, Y.; Wang, H.; Guo, C.; Zhang, M.; Sun, W.-H.; Hu, Y. *J Appl Polym Sci* 2003, 88, 466.
16. Huang, R.; Liu, D.; Wang, S.; Mao, B. *Macromol Chem Phys* 2004, 205, 966.
17. Huang, R.; Kukalyekar, N.; Koning, C. E.; Chadwick, J. C. *J Mol Catal A* 2006, 260, 135.
18. Zakharov, V. A.; Bukatov, G. D.; Barabanov, A. A.; Mikenas, T. B.; Echevskaya, L. G. In *Current Achievements on Heterogeneous Olefin Polymerization Catalysts*; Terano, M., Ed.; Japan Advanced Institute of Science and Technology, Sankeisha: Nagoya, 2004; pp 23–28.
19. Mikenas, T. B.; Zakharov, V. A.; Echevskaya, L. G.; Matsko, M. A. *J Polym Sci A: Polym Chem* 2005, 43, 2128–2133.
20. (a) Zakharov, V. A.; Mikenas, T. B.; Makhtarulin, S. I. *Rus. Pat.* 1121835(1987). ;(b) Zakharov, V. A.; Mikenas, T. B.; Makhtarulin, S. I. *Chem Abstr* 1988, 108, 38594.
21. Echevskaya, L. G.; Zakharov, V. A.; Golovin, A. V.; Mikenas, T. B. *Macromol Chem Phys* 1999, 200, 1434.
22. Spits, R.; Pasquet, V.; Patin, M.; Guyot, A. In *Ziegler Catalysts*; Fink, G.; Mulhaupt, R., Eds.; Springer-Verlag: Berlin, Heidelberg, 1995; p 401.
23. Karol, F. G.; Cann, K. J.; Zoeckler, M. T. In *Proceedings of the Symposium on Novel Preparation and Conversion of Light Olefins*, Miami beach meeting, Miami, USA, September 10–15, 1989; pp 602–608.
24. Kissin, Y. V.; Mink, R. I.; Nowlin, T. E.; Brandolini, A. J. *Top Catal* 1999, 7, 69.
25. Schmidt, R.; Welch, M. B.; Palackal, S. J.; Alt, H. G. *J Mol Catal A* 2002, 179, 155.
26. Tait, P. J. T. In *Transitional Metals and Organometallics as Catalysts for Olefin Polymerizations*; Kaminsky, W.; Sinn, H., Eds.; Springer-Verlag: New York, 1988; p 309.
27. Soga, K.; Yanagihara, H.; Lee, D. *Makromol Chem* 1989, 190, 995.
28. Gul'tseva, N. M.; Ushakova, T. M.; Aladyshev, A. M.; Raspopov, L. N.; Meshkova, I. N. *Vysokomol Soedin, Ser A (Rus)* 1991, 33, 1074.
29. Zakharov, V. A.; Echevskaya, L. G. *Vysokomol Soedin B (Rus)* 1997, 39, 1396.
30. Bukatov, G. D.; Zakharov, V. A.; Echevskaya, L. G. In *Transitional Metals and Organometallics as Catalysts for Olefin Polymerizations*; Kaminsky, W.; Sinn, H., Ed.; Springer-Verlag: New York, 1988; p 101.
31. Echevskaya, L. G.; Matsko, M. A.; Mikenas, T. B.; Nikitin, V. E.; Zakharov, V. A. *J Appl Polym Sci* 2006, 102, 5436.
32. Kissin, Y. V.; Quian, C.; Xie, G.; Chen, Ya. *J Polym Sci A: Polym Chem* 2006, 44, 6159.
33. Barabanov, A. A.; Bukatov, G. D.; Zakharov, V. A.; Semikolenova, N. V.; Mikenas, T. B.; Echevskaja, L. G.; Matsko, M. A. *Macromol Chem Phys* 2006, 207, 1368.
34. Zakharov, V. A.; Semikolenova, N. V.; Mikenas, T. B.; Barabanov, A. A.; Bukatov, G. D.; Echevskaya, L. G.; Mats'ko, M. A. *Kinet Katal (Engl)* 2006, 47, 303.
35. Chadwick, J. C.; Mieldema, A.; Sudmeijer, O. *Macromol Chem Phys* 1994, 195, 167.
36. Busico, V.; Cipullo, R.; Corradini, P. *Macromol Chem Rapid Commun* 1992, 13, 15.
37. Bukatov, G. D.; Goncharov, V. S.; Zakharov, V. A. *Macromol Chem Phys* 1995, 196, 1751.
38. Guyot, A.; Spitz, R.; Dassaud, J. P.; Gomez, C. *J Mol Catal* 1993, 82, 29.
39. Jeske, C.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J Am Chem Soc* 1985, 107, 8091.
40. Chadwick, J. C.; Morini, G.; Baltontin, G.; Camurati, I.; Heere, J. J. R.; Mingozi, I.; Testoni, F. *Macromol Chem Phys* 2001, 202, 1995.
41. Fink, G.; Babik, S. T. *Kinet Katal* 2006, 47, 201.