

Study of the ethylene polymerization over homogeneous and supported catalysts based on 2,6-bis(imino)pyridyl complexes of Fe(II) and Co(II)

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Abstract

The kinetic data on ethylene polymerization over homogeneous catalysts based on 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridineiron(II) and cobalt(II) chlorides (LMCl_2 , $\text{M} = \text{Fe, Co}$) with different aluminium-organic activators (MAO , AlMe_3 , $\text{Al}(i\text{-Bu})_3$) are reported. LFeCl_2 is very effective with AlMe_3 and $\text{Al}(i\text{-Bu})_3$ as activator and LCoCl_2 is highly active in the presence of AlMe_3 . For MAO as activator, the activity depends on the content of free AlMe_3 in MAO . Maximal activity has been found for MAO completely purified from free AlMe_3 . According to ^1H and ^2H NMR study, formation of the similar neutral intermediates of the type $[\text{LFe(II)Me}(\mu\text{-Me})_2\text{AlMe}_2]$ have been detected for $\text{LFeCl}_2/\text{AlMe}_3$ and $\text{LFeCl}_2/\text{MAO}$ catalysts. In the system $\text{LCoCl}_2/\text{MAO}$, the complex of the type LCo(II)Me(X)MAO ($\text{X} = \text{Me}$ or Cl) with terminal Co-Me group is detected. Interaction of LCoCl_2 with AlMe_3 results in the formation of diamagnetic Co(I) species.

Highly active supported catalysts $\text{SiO}_2/\text{LFeCl}_2 + \text{AlR}_3$ and $\text{SiO}_2/\text{MAO}/\text{LFeCl}_2$ have been prepared. In contrast to homogeneous systems, the supported catalysts are stable at elevated temperatures of polymerization (70°C) and produce high molecular mass polyethylene with improved morphology. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 2,6-Bis[1-(2,6-dimethylphenylimino)ethyl]pyridineiron(II) and cobalt(II) chlorides; Ethylene polymerization; Homogeneous and supported catalysts; Trialkylaluminiums; Methylaluminoxane; NMR spectroscopy of intermediates

1. Introduction

Recently, new catalysts based on 2,6-bis(imino)pyridyl complexes of iron(II) and cobalt(II) has been discovered [1,2]. At activation with methylaluminoxane (MAO), these complexes proved to be extremely

active homogeneous catalysts for ethylene polymerization to linear polyethylene.

More detailed kinetic data on the effect of complexes LMCl_2 composition [$\text{L} = 2,6\text{-bis(imino)pyridyl}$; $\text{M} = \text{Fe, Co}$] and polymerization conditions over the catalysts activity and polymer molecular mass are given in Refs. [3,4]. It was shown that the catalysts activity and the polymers molecular mass essentially depend over the ligand L composition and, particularly, on the substituents in the aryl groups of a ligand. Iron-based complexes exhibited higher activity

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in comparison with that of the cobalt complexes and lead to formation of polyethylene (PE) with higher molecular mass. It should be mentioned that according to the data of Ref. [4], polymers with broad and in some cases bimodal, molecular mass distribution are formed at ethylene polymerization over the catalysts ($\text{LFeCl}_2 + \text{MAO}$). This fact evidences that these catalysts contain several types of active centres and cannot be referred to the group of “single site catalysts”. It was proposed [1–4] that generation of the active sites in these systems occur according to the same scheme, as it was accepted for metallocene-based catalytic systems: by formation of the ion pair at the interaction of bis(imine)pyridyl complexes of Fe and Co with MAO via the reaction (1).



Later, the data were obtained showing that aluminium trialkyls (AlMe_3 , $\text{Al}(i\text{-Bu})_3$) can also be the effective activators for bis(imine)pyridyl $\text{Fe}(\text{II})\text{Cl}_2$ [5,6]. These results makes doubtful the proposed reaction (1) on formation of the ion intermediates as the active sites of these catalysts.

By means of ^1H and ^2H NMR, we have studied the structure of the intermediates formed at bis(imine)pyridyl $\text{Fe}(\text{II})\text{Cl}_2$ interaction with different activators (MAO and AlMe_3) [6]. It was shown that in the both cases, the intermediates represented by neutral complex $[\text{LFeMe}\cdot\text{AlMe}_3]$ with close or identical structures were formed. Possibly these intermediates are the straight precursors of the active sites of these catalysts.

In this paper, the additional kinetic data on ethylene polymerization with LFeCl_2 , activated with different aluminium-organic activators (AAs) and the new data, obtained at ethylene polymerization over LCoCl_2 with different AA, are reported. Using ^1H and ^2H NMR spectroscopy, the structure of the intermediates formed at 2,6-bis(imine)pyridyl $\text{Co}(\text{II})\text{Cl}_2$ interaction with different AAs were investigated and the obtained results were compared with those for the catalytic system $\text{LFeCl}_2 + \text{AA}$. By grafting of LFeCl_2 on the silica, highly effective supported catalysts were prepared and tested at ethylene polymerization. The kinetic data on ethylene polymerization with the supported catalysts were compared with that for the corresponding homogeneous systems.

2. Experimental

Methylene chloride, methylene chloride- d_2 and toluene- d_8 were dried over P_2O_5 and distilled. Toluene was dried over molecular sieves (4 Å), purified by refluxing over sodium metal and distilled in dry argon. The prepared solvents were stored and handled in vacuum. All experiments were carried out in sealed high vacuum systems using breakseal techniques.

2,6-Bis[1-(2,6-dimethylphenylimino)ethyl]pyridine-iron(II) (LFeCl_2) and cobalt(II) (LCoCl_2) chlorides were prepared according to Ref. [4]. Silica Davison 952 (surface area $260\text{ m}^2/\text{g}$) was used as the support.

2.1. MAO and AlMe_3 samples preparation

MAO-1: the commercial sample purchased from Witco as toluene solution (total Al content 1.8 M). This sample contains ca. 0.5 M of Al as AlMe_3 .

MAO-2 has been prepared by vacuum distillation of MAO-1 at 20°C . The obtained solid product was dissolved in toluene (total Al content is 0.1 M and Al as AlMe_3 is 0.01 M).

MAO-3 has been prepared by vacuum distillation of MAO-1 at 50°C . Total Al content in the prepared solutions was 0.1 M and Al as $\text{AlMe}_3 \cong 0.001\text{ M}$.

AlMe_3 (TMA): according to ^1H NMR data, the liquid fraction, separated by MAO distillation, contains only AlMe_3 (Al content: 0.4 M). This fraction was used as TMA sample.

$\text{Al}(\text{CD}_3)_3$ - CD_3 -labelled AlMe_3 (99% D) was prepared from 99% D-labelled CH_3I by consequential treatments with Al metal at 80°C and Na metal in $\text{C}_{12}\text{H}_{26}$ at 100°C and then distilled in vacuum.

2.2. Preparation of LFeCl_2 (LCoCl_2)/MAO and LFeCl_2 (LCoCl_2)/ AlMe_3 samples and NMR measurements

The weighted amount of complex LFeCl_2 (LCoCl_2) was placed inside the dried and argon-filled NMR tube, equipped with fine glass breakseals. The system with complex was vacuumed to 2×10^{-2} Torr and sealed off the vacuum line. Calculated quantities of needed solvents (d_8 -toluene or CD_2Cl_2) and solutions of MAO-2 (AlMe_3) were transferred under vacuum into the NMR tube and mixed with complex at

appropriate temperature. For NMR spectra registration, the NMR tubes were sealed off from the system.

In the samples prepared with complex LFeCl_2 , the total concentration of Fe was 0.001–0.0003 M, and that of Al was 0.5–3 M (Al/Fe ratios were in the range 50–1000).

Total concentration of Co in $\text{LCoCl}_2/\text{MAO-2}$ catalytic systems was 0.003 M, and that of Al was 0.1–0.3 M, whereas Al/Co ratio was in the range 30–100. For the systems $\text{LCoCl}_2/\text{AlMe}_3$, the Al/Co ratio was varied from 5 to 50.

The ^1H NMR and ^2H NMR spectra were recorded at 400.13 and 61.4 MHz, respectively, on a Bruker MSL-400 spectrometer in 5 and 10 mm tubes. The following operating conditions were used: sweep width 125 kHz (^2H and ^1H); spectrum accumulation frequency 20 Hz (^1H), 2.5 Hz (^2H); number of scans 5000–20,000 (^1H and ^2H); 20–40° pulse at 5 μs (^1H), 10 μs (^2H). The chemical shifts were calculated from the signals of residual CH_2Cl_2 (δ 5.27) and $\text{CHD}_2\text{C}_6\text{D}_5$ (δ 2.10 (CH_3)) in deuterated solvents.

2.3. Preparation of supports

- (a) *Dehydroxylated silica samples*: the sample of silica was calcined at 450 °C for 3–4 h and dehydroxylated for 4 h under vacuum at the desired temperature.
- (b) *MAO (TMA) modified silica samples*: the sample of silica dehydroxylated at 450 °C was treated by toluene solution of MAO-1 or TMA at the ratio [Al]:[OH] = 10 (molar). The suspension was stirred at 20 °C for 30 min. Then the liquid fraction

was decanted, the solid part was washed up three times with toluene and dried at room temperature under vacuum.

2.4. Preparation of the supported catalysts

The solution of complex LFeCl_2 in CH_2Cl_2 (0.1 mmol Fe/g of support) was added to the support sample. The resulting suspension was stirred at 20 °C for 30 min. Then the liquid fraction was decanted, the solid part was washed up for three times with CH_2Cl_2 and dried in vacuum at room temperature. The Fe and Al contents were determined by AES-ICP.

2.5. Polymerization studies

2.5.1. Polymerization over homogeneous systems

Ethylene polymerization was performed in a steel 1 l autoclave. Complex LFeCl_2 or LCoCl_2 (0.001 g, 2.0×10^{-6} mol) was introduced into the autoclave in a vacuum sealed glass ampoule. Autoclave was evacuated at 50 °C cooled down to 20 °C and then charged with solution of calculated amount of co-catalyst in toluene (150 ml). After setting up the polymerization temperature (35 °C) and the required ethylene pressure (2 or 5 bar), the reaction was started by breaking off the ampoule with complex. The experimental unit was equipped with automatic computer-controlled system for the ethylene feed, maintaining the required pressure, recording the ethylene consumption and providing the kinetic curve output both in the form of a table and as a graph.

Table 1
Data on the ethylene polymerization over catalyst LFeCl_2 with different AAs

Experiment No.	AA	Al/Fe (mol)	Activity ^a (kg PE/mol Fe min bar)	MI (2.16) ^b (g/10min)
1	MAO-1	500	200	13.4
2	MAO-2	500	48	–
3	MAO-3	500	440	8.3
4	AlMe_3	500	450	>120
5	AlMe_3	250	66	50
6	AlMe_3	100	18	–
7	$\text{Al}(i\text{-Bu})_3$	500	375	<0.03
8	$\text{Al}(i\text{-Bu})_3$	100	<10	–

^a Polymerization at 35 °C, in toluene, for 15 min; $[\text{Fe}] = 1.4 \times 10^{-5}$ M, at ethylene pressure 2 bar.

^b MI of polymer at load 2.16 kg.

2.5.2. Polymerization over supported catalysts

For polymerization runs with the supported catalysts, the same experimental unit as for the homogeneous catalysts was used. 0.05–0.15 g of the prepared catalyst was introduced into the autoclave in a vacuum sealed glass ampoule. Autoclave was evacuated at 70 °C, cooled down to 20 °C and then charged with calculated amount of co-catalyst ($\text{Al}(i\text{-Bu})_3$) and heptane (150 ml). After setting up the polymerization temperature (70 °C) and the ethylene pressure (4 bar), the reaction was started by breaking off the ampoule with the catalyst, this moment being the starting point of polymerization rate counting.

The detailed polymerization conditions used are given in Tables 1, 2 and 4.

3. Results and discussions

3.1. Ethylene polymerization over homogeneous catalysts LFeCl_2 and LCoCl_2 : the effect of AAs

Data on the activity at ethylene polymerization over the catalysts LFeCl_2 and LCoCl_2 with different AAs are presented in Tables 1 and 2 and Fig. 1. The kinetic

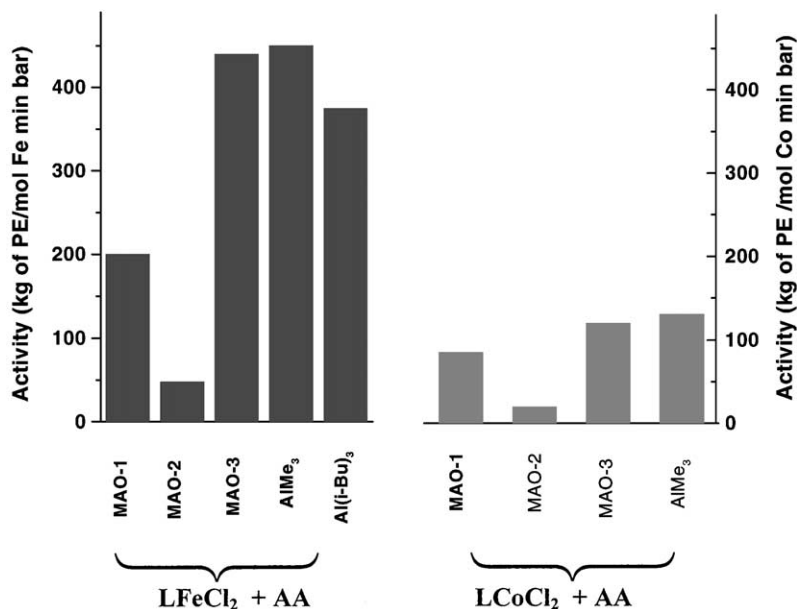


Fig. 1. The comparison of LFeCl_2 and LCoCl_2 activities at ethylene polymerization with different activators (Al/Fe = 500, molar).

Table 2

Data on the ethylene polymerization over catalyst LCoCl_2 with different AAs

Experiment no.	AA	Al/Co (mol)	Activity ^a (kg PE/mol Co min bar)
1	MAO-1	500	85
2	MAO-2	500	20
3	MAO-3	500	120
4	AlMe_3	500	130
5	AlMe_3	250	80
6	AlMe_3	100	16
7	$\text{Al}(i\text{-Bu})_3$	500	1

^a Polymerization at 35 °C, in toluene, for 15 min; $[\text{Co}] = 1.4 \times 10^{-5}$ M, at ethylene pressure 5 bar.

curves of ethylene polymerizations with these catalytic systems are shown in Figs. 2 and 3.

The catalyst LFeCl_2 activated with aluminium trialkyls (AlMe_3 (TMA) and $\text{Al}(i\text{-Bu})_3$ (TIBA)) exhibited high activity (Table 1, exp. 4 and 7). The activity value depends on the ratio AlR_3/Fe and drastically decreases at lowering of the ratio $\text{Al}/\text{Fe} < 500$. When MAO samples were used as co-catalysts, the activity of the system strongly depended on free TMA content in MAO sample. It is known that the commercial

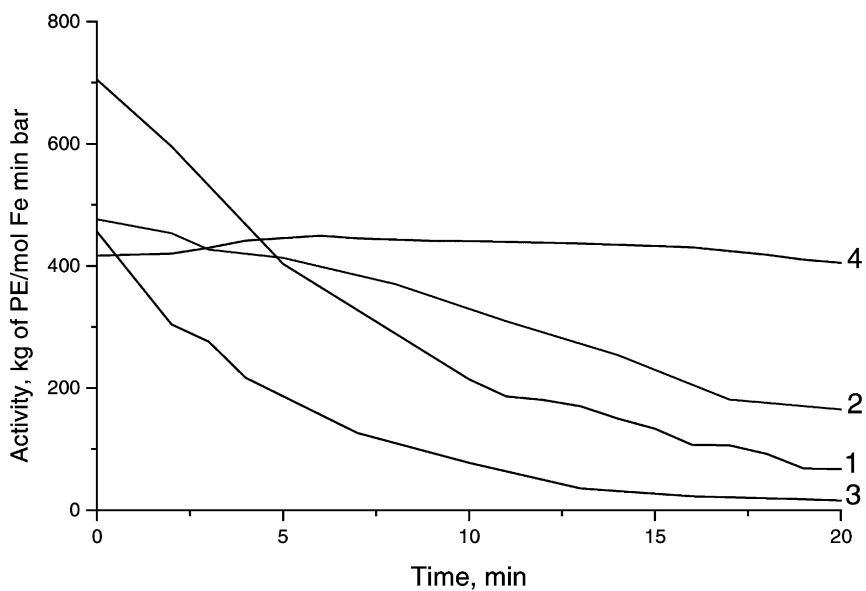


Fig. 2. The kinetic curves for polymerization over LFeCl_2 with different AAs (Table 1): (1) TMA (exp. 4); (2) TIBA (exp. 7); (3) MAO-1 (exp. 1), (4) MAO-3 (exp. 3).

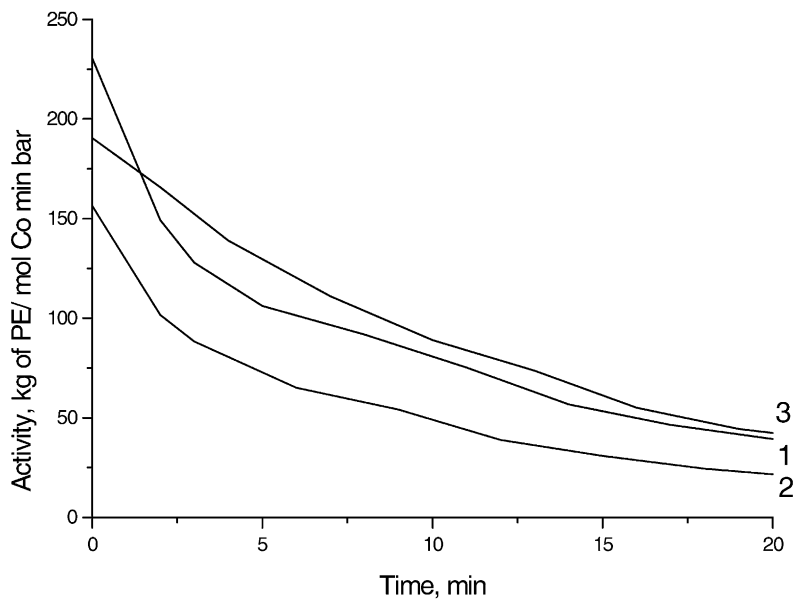


Fig. 3. The kinetic curves for polymerization over LCoCl_2 with different AAs (Table 2): (1) TMA (exp. 4); (2) MAO-1 (exp. 1); (3) MAO-3 (exp. 3).

samples of MAO (MAO-1 here) contains the sufficient amount of free TMA (28% of Al in MAO-1). The activity of the catalyst $\text{LFeCl}_2 + \text{MAO-1}$ was found to be lower than that of the system $\text{LFeCl}_2 + \text{AlR}_3$ (Table 1, exp. 1, 4, 7). The removal of the major part of free TMA from MAO-1 (sample MAO-2, TMA content: 10% of total Al) resulted in dramatic fall in catalytic activity (Table 1, exp. 2). On further purification of MAO from free TMA (MAO-3 sample, TMA content $\cong 1\%$ of total Al), the activity grew up again (Table 1, exp. 3).

In case of the catalysts $\text{LCoCl}_2 + \text{AA}$ (AA = MAO or TMA), the effect of AA over the catalyst activity was close to that observed for the system $\text{LFeCl}_2 + \text{AA}$ (Tables 1 and 2, Fig. 1), but the catalyst $\text{LCoCl}_2 + \text{TIBA}$ was almost inactive at molar ratio $\text{Al/Co} = 500$. On the whole, the catalysts $\text{LCoCl}_2 + \text{AA}$ are less active than $\text{LFeCl}_2 + \text{AA}$ catalytic systems (Fig. 1).

In the presence of the co-catalysts MAO-1, TMA and TIBA, the catalytic systems on the base of LFeCl_2 are unstable: their activity sharply decreases in 15–30 min of polymerization at 35°C (Fig. 2, curves 1 and 2). When MAO-3 was used as co-catalyst, the stability of the catalytic system increases (Fig. 2, curve 4). The catalysts $\text{LCoCl}_2 + \text{AA}$ are also unstable and noticeably deactivates in the course of polymerization at 35°C (Fig. 3). In this case, the stability of the system does not increase when MAO-3 was used as co-catalyst (Fig. 3, curve 3).

AA composition has the pronounced effect over the molecular mass (melt index, MI) of the polymers, produced with the catalysts $\text{LFeCl}_2 + \text{AA}$. On comparison of the data obtained using TMA and TIBA as co-catalysts, this effect is particularly pronounced. TMA is much more effective chain transfer agent than TIBA, and with TMA as co-catalyst low molecular mass PE with very high MI is produced (Table 1, exp. 4, 5, 7).

The molecular mass of polymers obtained over the catalysts $\text{LCoCl}_2 + \text{AA}$ was noticeably lower than that produced with $\text{LFeCl}_2 + \text{AA}$ systems. It was impossible to measure MI of polymers produced with cobalt-based catalysts even at the load of 2.16 kg.

Polymers obtained with $\text{LFeCl}_2 + \text{AA}$ and $\text{LCoCl}_2 + \text{AA}$ catalytic systems are highly linear. According to IR and ^{13}C NMR spectroscopic data, they contain only terminal vinyl and methyl groups. The molecular structure of well soluble in hydrocarbons,

low molecular mass polymer sample prepared with $\text{LCoCl}_2 + \text{TMA}$ catalyst (Table 2, exp. 4) was investigated by high temperature ^{13}C NMR spectroscopy. According to the NMR data, the polymer sample contains only terminal vinyl and methyl groups in the ratio 1:1 (10 $\text{CH}_3/1000\text{ C}$ and 11 $\text{CH}_2=\text{CHR}/1000\text{ C}$). The value of average molecular mass (M_n), calculated according to these data, is 1330. Good correspondence between the content of the terminal methyl and vinyl groups evidences that in this system, the process of polymer chain transfer with TMA (usually very effective chain transfer agent) is practically negligible. At the same time, the reaction of β -hydride chain transfer is very effective in this system and leads to the formation of highly linear PE with low molecular mass and with the ratio of terminal vinyl and methyl groups 1:1.

For PE sample prepared over the catalyst $\text{LFeCl}_2 + \text{MAO-1}$ at the polymerization temperature 70°C , the molecular structure of the fraction soluble in boiling *n*-heptane (10.2 wt.% of total PE sample) was investigated by ^{13}C NMR. This PE sample contains only terminal methyl and vinyl groups (6.7 $\text{CH}_3/1000\text{ C}$ and 2.7 $\text{CH}_2=\text{CHR}/1000\text{ C}$; $M_n = 3000$). The measured ratio of terminal groups evidences that in this catalytic system, the reaction of chain transfer with TMA, contained in MAO-1, proceeds too.

Thus, homogeneous catalysts based on LFeCl_2 and LCoCl_2 are very active at ethylene polymerization in the presence of aluminium trialkyls as co-catalysts. When MAO is used for activation, the catalytic activity of this system strongly depends upon free TMA content in MAO sample. In the presence of MAO sample rigorously purified from free TMA, the catalysts exhibited maximal activity and increased stability at polymerization.

3.2. ^1H and ^2H NMR spectroscopic characterisation of intermediates in $\text{LMCl}_2/\text{MAO}(\text{AlMe}_3)$ ($M = \text{Fe}, \text{Co}$) catalytic systems

3.2.1. $\text{LFeCl}_2/\text{MAO}(\text{AlMe}_3)$ systems

We have shown previously that the same intermediates of the type $\text{LFe}(\text{II})(\text{Me})(\mu\text{-Me})_2\text{AlMe}_2$ are formed in $\text{LFeCl}_2/\text{MAO}$ and $\text{LFeCl}_2/\text{AlMe}_3$ catalytic systems [6]. However, stability of intermediates in $\text{LFeCl}_2/\text{AlMe}_3$ system is far less than that of intermediates formed in the presence of MAO. The catalyst productivity of $\text{LFeCl}_2/\text{MAO}$ system dramatically

decreases with the diminishing AlMe₃ content in the composition of MAO. In this work, we have revealed that further decrease of AlMe₃ content in MAO gives rise to the sample denoted as MAO-3 with the best co-catalytic activity towards LFeCl₂ and LCoCl₂ pre-catalysts (Tables 1 and 2). The reason of this nonlinear behaviour is not entirely clear. However, according to the kinetic data, catalytic system LFeCl₂/MAO-3 is the most stable and relatively slow loses in its initial activity. Using ¹H NMR spectroscopy, we have compared LFeCl₂/MAO-2 and LFeCl₂/MAO-3 catalytic systems and have revealed no essential difference in the structures and concentrations of the observed intermediates. Thus, the same reactive species (neutral complexes of the type LFe(II)(Me)(μ-Me)₂AlMe₂ or LFe(II)(Cl)(μ-Me)₂AlMe₂) are formed in LFeCl₂/AlMe₃, LFeCl₂/MAO-2 and LFeCl₂/MAO-3 catalytic systems. Probably, these species are more stable in the samples with minimal AlMe₃ content.

3.2.2. LCoCl₂/MAO(AlMe₃) systems

The ¹H NMR spectrum of complex LCoCl₂ (0.003 M solution in CD₂Cl₂) (Fig. 4a, Table 3) shows six rather narrow ($\Delta\nu_{1/2} = 20\text{--}50$ Hz) paramagnetically shifted peaks that can be unambiguously assigned on the basis of integration and proximity to the paramagnetic centre (δ , -20°C , CD₂Cl₂, 138.4 (2H, Py-H_m) (**A**); 47.3 (1H, Py-H_p) (**B**); 5.8 (4H, Ar-H_m) (**C**); -1.65 (6H, N = C (Me)) (**F**); -16.2 (2H, Ar-H_p) (**E**); -38.3 (12H, Ar-Me) (**D**)).

Just after the addition of MAO-2 to the solution of LCoCl₂ in d₈-toluene at -20°C ([LCoCl₂] = 0.003 M, Al/Co = 50), all signals of LCoCl₂ dramatically change their positions and the new broad signal at 178 ppm (3H) (**X**) is observed (Fig. 4b). This means that the new complex **1** is formed upon interaction of LCoCl₂ with MAO. It is worth noting that because of solubility and stability problems, ¹H NMR spectrum of LCoCl₂ (Fig. 4a) was recorded in CD₂Cl₂ and that

of **1** in d₈-toluene (Fig. 4b). However, when going from CD₂Cl₂ to d₈-toluene as a solvent, the chemical shifts of **1** change insignificantly. All peaks of the initial tridentate arylimine ligand, except for the peak **C** of Ar-H_m protons (4H), masked by intense resonance of MAO, can be observed in the ¹H NMR spectrum of **1** (δ , -20°C , d₈-toluene, 51.2 (1H, Py-H_p) (**B**); 22.1 (2H, Py-H_m) (**A**); 12.3 (2H, Ar-H_p) (**E**); -26.6 (12H, Ar-Me) (**F**); -32.4 (6H, N=C (Me)) (**D**); (Fig. 4b, Table 3)). Thus, the arylimine ligand of LCoCl₂ remains intact upon formation of complex **1**.

The ²H NMR spectrum of the system LCoCl₂/Al(CD₃)₃/MAO-2 at -20°C exhibits one signal at 178 ppm ($\Delta\nu_{1/2} = 700$ Hz) (Fig. 4c). The position of this peak is the same as that of the peak **X** in ¹H NMR spectrum (Fig. 4b). Thus, the peak **X** arises from methylation of LCoCl₂ by MAO or AlMe₃. For comparison, ²H NMR spectrum of LFe(II)(Me)(μ-Me)₂AlMe₂ at -30°C displays relatively sharp peak at 45 ppm ($\Delta\nu_{1/2} = 50$ Hz) from terminal AlMe₂ moiety and that at 610 ppm ($\Delta\nu_{1/2} = 500$ Hz) assigned to bridging Fe-Me-Al groups [6]. Large chemical shift and line width of the peak **X** in the spectrum of complex **1** evidence that it belongs to methyl group directly bound to cobalt atom. Chemical shifts of complex **1** are characteristic for mononuclear paramagnetic cobalt(II) species. Integration of the peak **X** shows that it belongs to one Co-Me moiety. So, the intermediate **1** can be proposed as mononuclear paramagnetic complex of cobalt(II) containing initial tridentate ligand and Co-Me moiety.

The reaction of LCoCl₂ with AlMe₃ or Al(CD₃)₃ (in toluene at -60 to $+10^\circ\text{C}$ at the molar ratio of Al/Co = 5/50) results in its immediate conversion into cobalt species different to complex **1** formed in CoCl₂/MAO-2 system (Table 3). These species display ¹H NMR peaks (-60°C) in the range -2 to $+12$ ppm that is typical for diamagnetic cobalt(I) species [7,8]. The detailed assignment of the ¹H NMR

Table 3
¹H NMR chemical shifts (δ , ppm) for LCoCl₂ with MAO-2 and TMA

	T (°C)	A (Py-H _m)	B (Py-H _p)	C (Ar-H _m)	D (Ar-Me)	E (Ar-H _p)	F N=C (Me)	X (Co-Me)
LCoCl ₂	-20	138.4	47.3	5.8	-38.3	-16.2	-1.65	N/o
LCoCl ₂ + MAO-2	-20	22.1	51.2	-	-26.6	12.3	-32.4	178
LCoCl ₂ + AlMe ₃	-20	11.3	19.5	-	2.0	-	-3.5	-

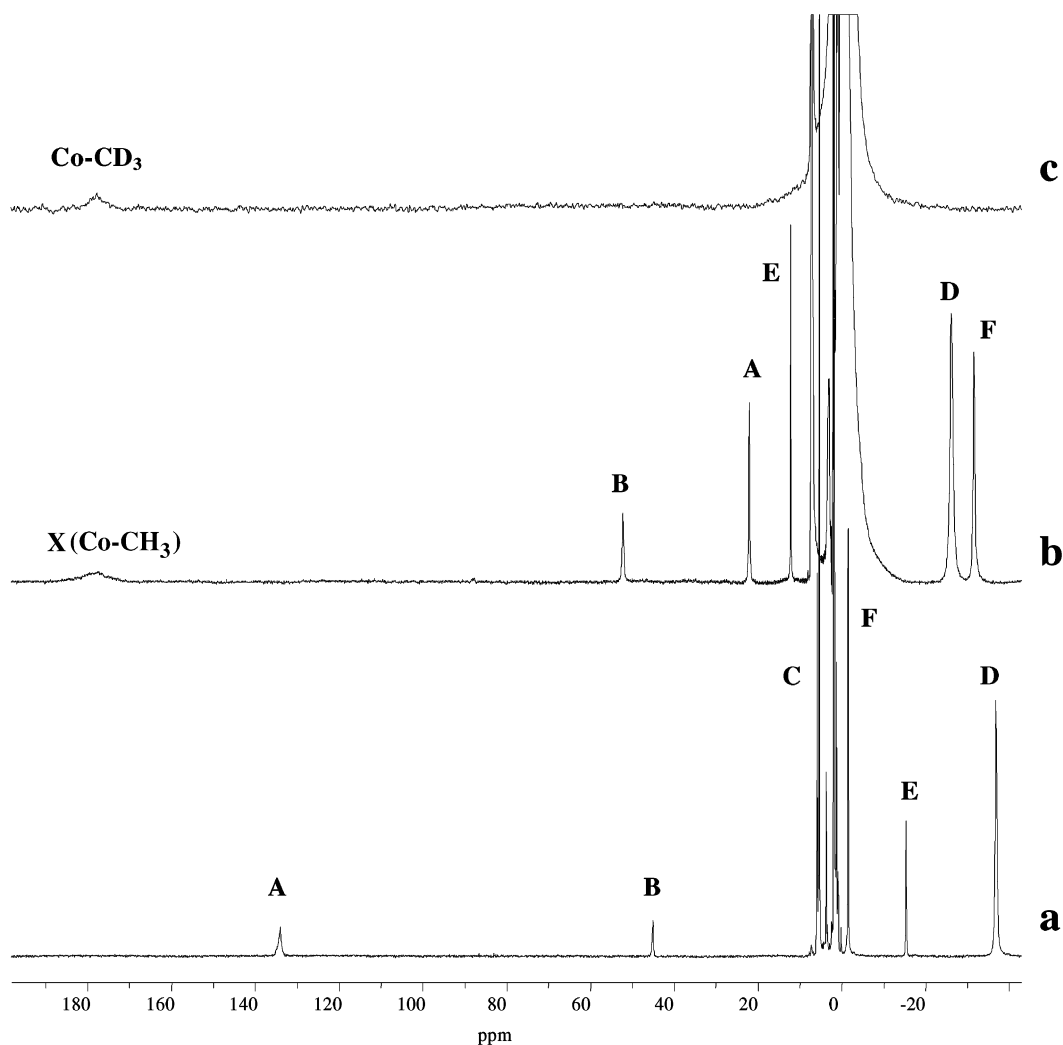


Fig. 4. NMR spectra of LCoCl_2 and $\text{LCoCl}_2 + \text{MAO-2}$ (signals assignment according to Table 3): (a) LCoCl_2 (^1H , CD_2Cl_2 , -20°C); (b) $\text{LCoCl}_2 + \text{MAO-2}$ (^1H , d^8 -toluene, -20°C); (c) $\text{LCoCl}_2 + (\text{deuterated MAO-2})$ (^2H , d^8 -toluene, -20°C).

resonances of cobalt species formed in $\text{LCoCl}_2/\text{AlMe}_3$ system is still not completed. However, it is evident that strictly different intermediates are formed upon activation of LCoCl_2 with MAO and AlMe_3 . In the first case complex of cobalt(II) incorporating ligand L and Co–Me moiety predominates in solution, whereas in the second case complexes of cobalt(I) are formed.

To explain the stability towards reduction of cobalt(II) moiety in complex **1**, formed in the catalytic system $\text{LCoCl}_2/\text{MAO}$, with respect to $\text{LCoCl}_2/\text{AlMe}_3$

system, it can be proposed that the intermediate **1**, probably, contains MAO as one of the ligands. Based on this assumption and the above ^1H and ^2H NMR data for the system $\text{LCoCl}_2/\text{MAO}$, the composition of complex **1** can be proposed as $\text{L}(\text{Me})\text{Co}(\text{II})\text{Cl}\cdot\text{MAO}$ or $\text{L}(\text{Me})\text{Co}(\text{II})\text{Me}\cdot\text{MAO}$.

Thus, in contrast to iron based catalysts, different intermediates are formed in $\text{LCoCl}_2/\text{MAO}$ and $\text{LCoCl}_2/\text{AlMe}_3$ systems, though we have not found the noticeable difference in their catalytic properties.

3.3. Ethylene polymerization over the supported catalysts $\text{LFeCl}_2/\text{SiO}_2$ (SiO_2/MAO , $\text{SiO}_2/\text{AlR}_3$)

Silica is the most widely used support for preparation of supported catalysts (for instance, metallocene based catalysts). As it was shown above, different types of aluminium-organic compounds (AA = AlR_3 , MAO) can be used for activation of bis-(imine)pyridyl iron and cobalt complexes. Considering these results, we have to prepare the series of supported catalysts with the composition $\text{LFeCl}_2/\text{SiO}_2$ (AA), where AA was introduced into the composition of support. Data on the composition and activity at ethylene polymerization of the prepared supported catalysts are given in Table 4. In exp. 1, silica, dehydroxylated at 800 °C under vacuum was used as the support. In exp. 2–4, the supports were prepared by interaction of silica, dehydroxylated at 450 °C, with AA and thorough washing from the excess of AA. All catalysts were prepared by treatment of the supports with the excess of LFeCl_2 and carefully washed from unadsorbed iron complex. In all prepared catalyst samples the content of LFeCl_2 , strongly bounded with the support surface, was rather low (0.05–0.14 wt.% of Fe). The supported catalysts prepared using silica, modified with AA as supports, were active at ethylene polymerization without additional activation with aluminium organic co-catalyst (TIBA) (Table 4, exp. 2, 3, 4), among them the system $\text{LFeCl}_2/\text{SiO}_2/\text{MAO}$ exhibited the highest activity (80 kg of PE/mol Fe min bar). Thus, the active species of supported $\text{LFeCl}_2/\text{SiO}_2/\text{AA}$ catalysts are formed at

LFeCl_2 interaction with the surface alkylaluminium compounds.

The catalyst with the most simple composition prepared on the base of dehydroxylated silica (Table 4, exp. 1) should be marked especially: its activity in presence of co-catalyst TIBA was higher than that of the catalysts prepared using silica samples modified with TMA or TIBA (Table 4, exp. 2, 3).

The kinetic curves of the ethylene polymerization over the homogeneous $\text{LFeCl}_2 + \text{TIBA}$ and the supported catalytic systems $\text{LFeCl}_2/\text{SiO}_2 + \text{TIBA}$ are compared in Fig. 5. The homogeneous catalyst shows very high initial activity but it sharply falls down in the course of polymerization even at the polymerization temperature 35 °C (Fig. 5, curve 1). The increase of polymerization temperature up to 70 °C resulted in more sharp deactivation of the homogeneous catalyst (Fig. 5, curve 2). At the same time, the supported catalyst exhibits high and stable activity at the polymerization temperature 70 °C that provide high polymer yield at the elevated polymerization temperatures.

The activity of supported catalyst $\text{LFeCl}_2/\text{SiO}_2$ is effected by the composition of the aluminium organic co-catalyst. When TMA was used for the catalyst activation, the activity was two to three times higher than that in the presence of TIBA (correspondingly, 170 and 62 kg of PE/mol Fe bar min, in toluene). It should be noted, that the catalyst retains its high stability at 70 °C.

The data on the composition and activity at ethylene polymerization of the supported catalysts prepared

Table 4
Data on the composition and activity at ethylene polymerization of the supported catalysts $\text{LFeCl}_2/\text{silica}$

Experiment no.	Support	Composition of catalysts (wt.%)		TIBA ^a	Activity ^b (kg PE/mol Fe min bar)	MI (5) ^c (g/10 min)
		Al	Fe			
1	SiO_2^{d}	–	0.13	+	52.0	0.04
2	$\text{SiO}_2/\text{AlMe}_3$	2.2	0.14	+	7.0	0.9
3	$\text{SiO}_2/\text{Al}(i\text{-Bu})_3$	2.0	0.06	–	10.5	0.11
				+	22.0	
4	SiO_2/MAO	5.0	0.05	–	10.3	0.13
				+	54.0	
				–	80.0	

^a TIBA as co-catalyst in polymerization, Al/Fe = 400.

^b Polymerization at 70 °C, in heptane, 4 bar of C_2H_4 , for 1 h.

^c MI of polymer at load 5 kg.

^d SiO_2 has been dehydroxylated by heating at 800 °C under vacuum.

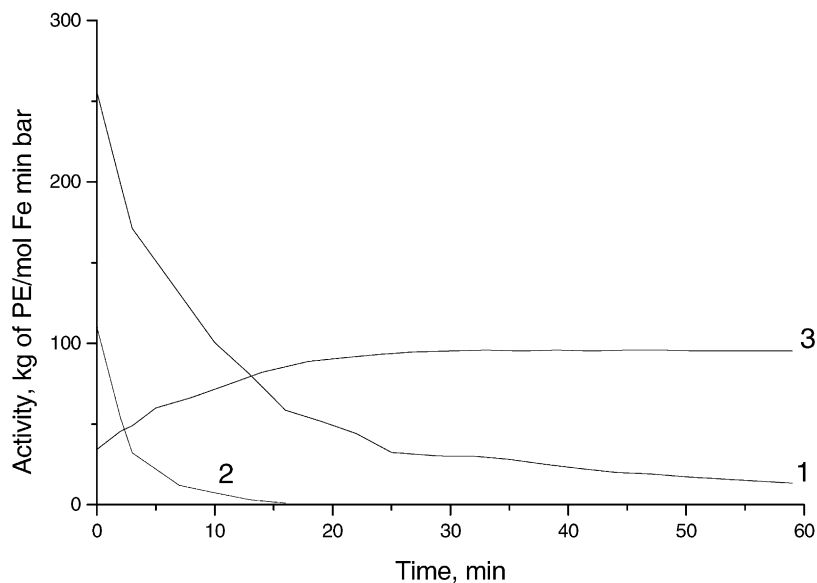


Fig. 5. The kinetic curves of ethylene polymerization over homogeneous and supported LFeCl₂: (1) homogeneous LFeCl₂ + TIBA (35 °C, heptane); (2) homogeneous LFeCl₂ + TIBA (70 °C, heptane); (3) supported SiO₂/LFeCl₂ + TIBA (70 °C, heptane).

using silica samples dehydroxylated at different temperatures are summarised in Table 5. It is known that the increase of the silica dehydroxylation temperature in the range 250–800 °C leads to the complete removal of hydrogen bonded hydroxyl groups with low reactivity and insignificant decrease of more reactive terminal OH-groups content. The obtained data show that the increase of silica dehydroxylation temperature has almost no effect on the amount of strongly adsorbed iron complex, whereas the activity of the supported catalysts slightly decreases (Table 5). In all the cases, the amount of strongly adsorbed LFeCl₂ was noticeably lower than the silica terminal OH-groups concentration ($(\text{OH})_t/\text{Fe} = 14\text{--}20$, Table 5). It can be proposed that fixation of iron complex on the silica

occurs by multiple bonding of LFeCl₂ with SiO₂ surface via interaction of pyridyl and phenyl groups of the ligand L with the OH-groups of silica. Possibly, the requirement of multiple bonding determines the low amount of LFeCl₂, strongly bound to the silica surface.

In contrast to homogeneous catalysts, polymerization over the investigated supported systems resulted in formation of PE with the improved morphology and high bulk density (Fig. 6). The spherical shape of the PE particles corresponded to that of the silica support is in accordance with the known replication effect.

Thus, using silica as the support, highly effective supported catalysts with the simple composition LFeCl₂/SiO₂ + AlR₃ can be prepared. In contrast to

Table 5

Data on the effect of silica dehydroxylation temperature (T_d) on the composition and activity of LFeCl₂/SiO₂ catalyst

Experiment no.	T_d (°C)	$[\text{OH}]_t^a$ (μmol/g)	[Fe] (wt.%)	$[\text{OH}]_t/\text{Fe}$ (mole)	Activity ^b (kg PE/mol Fe min bar)
1	250	410	0.12	20.0	70
2	450	335	0.10	18.6	64
3	800	329	0.13	14.3	52

^a Content of terminal Si–OH groups of silica.

^b Polymerization at 70 °C, in heptane, 4 bar of C₂H₄, for 1 h, TIBA as co-catalyst at Al/Fe = 420 (molar).

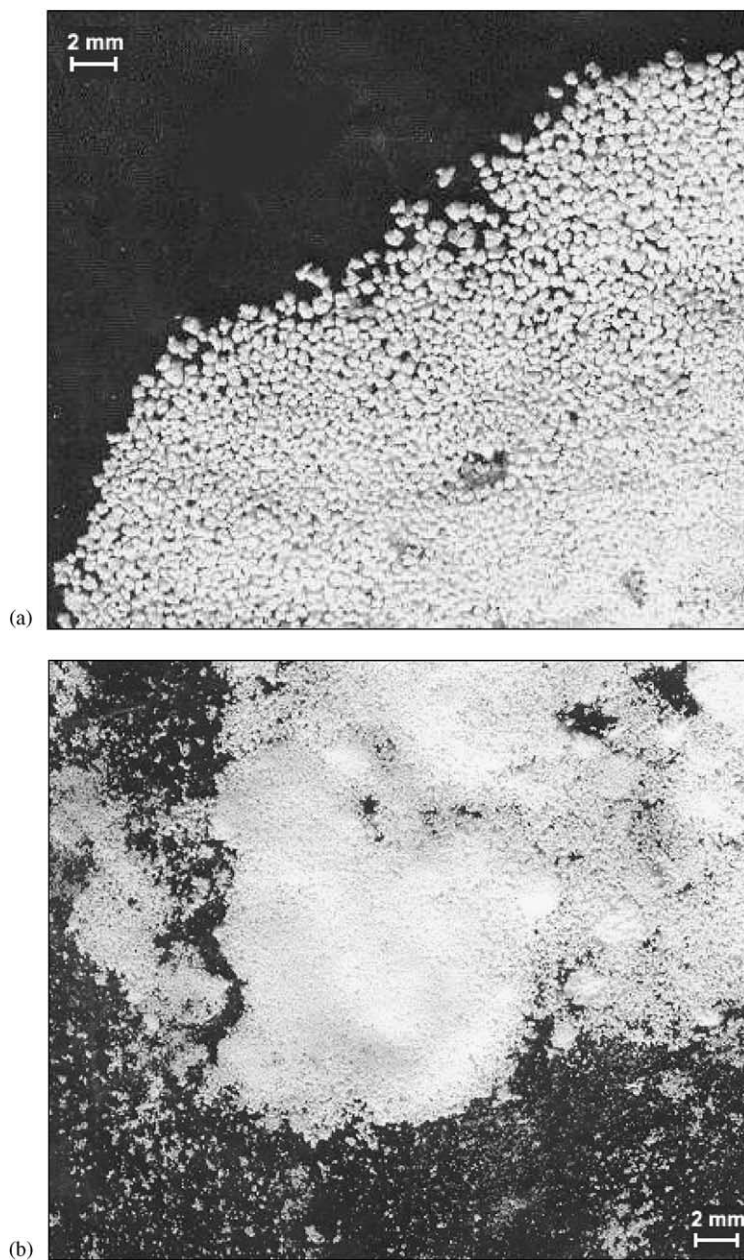


Fig. 6. PE samples obtained over the supported $\text{LFeCl}_2/\text{SiO}_2 + \text{Al}(i\text{-Bu})_3$ (a) and homogeneous $\text{LFeCl}_2 + \text{Al}(i\text{-Bu})_3$ (b) catalysts.

the homogeneous systems, the supported catalysts are stable at elevated temperatures of polymerization and produce high molecular mass linear PE with good morphology.

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