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Kinetic regularities of ethylene oligomerization in the presence of the catalytic system Cr^{III}—AlR_3—2,5-dimethylpyrrole—modifying agent

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The influence of temperature, ethylene pressure, and mole ratios THF : Cr and CCl_4 : Cr on the kinetics of ethylene oligomerization in the presence of the catalytic system $Cr(acac)_3$—$AlEt_3$—2,5-dimethylpyrrole—modifying agent (THF and CCl_4 as modifying agents) was studied. The selectivity to hex-1-ene for ethylene oligomerization reaches 86 wt.%.

Key words: ethylene, chromium, catalytic system, oligomerization, polymerization.

Linear α-olefins (LAO) find wide use as comonomers and monomers in co- and polymerization reactions. They are also valuable plasticizers and solvents. Over the last 15—20 years, the selective oligomerization of ethylene to higher α-olefins (but-1-ene, hex-1-ene, oct-1-ene) attracts attention of largest chemical companies producing olefins and related polymers.

Presently, the demand for but-1-ene is covered by the industrial process of selective dimerization of ethylene to but-1-ene (see Refs 1 and 2), but the scale of production of hex-1-ene and oct-1-ene remains yet insufficient. Special attention is given to hex-1-ene, because it finds wide use in the synthesis of linear medium- and low-density polyethylenes (PE), polyhexene, and other chemical products.

The formation of hex-1-ene in small amounts was first observed when PE was obtained in the presence of chromium catalysts.[3] Later the polycomponent homo- and heterogeneous catalytic systems (CS) based on the Cr^{III} derivatives of pyrrole and organoaluminum compounds for the selective oligomerization of ethylene to hex-1-ene were developed.[4—6] Selective ethylene oligomerization proceeds in the presence of various homogeneous catalysts consisting of transition metals (Cr^{III}, Ti^{IV}, Ni^{II}), mono-, bi-, or tridentate organic ligands, and organoaluminum compounds (AlR_3 (R = Et, Bu^i) and methylalumoxane (MAO)). The results of studies of the activity and selectivity of these catalysts were described.[7—9] The catalytic systems may contain additional components (modifying agents) favoring an increase in the selectivity of formation higher LAO.[10—12]

The selectivity and catalytic activity of various catalysts of ethylene oligomerization to higher α-olefins were studied in detail, but the data on the kinetic regularities of this reaction are scarce. For example, single kinetic curves describing ethylene oligomerization in the presence of the CS can be found in literature: $[(Me_3SiC_5H_3CMe_2C_6H_3Me_2)TiCl_3)]$—MAO at 30 °C and ethylene pressure 1.5 MPa,[13] $CrCl_3 \cdot 3THF$—MAO at 20 °C and 0.1 MPa,[14] $Cr(acac)_3$—PNP—MAO (PNP is bis(diphenylphosphino)isopropylamine) at 30—45 °C and 3—4.5 MPa,[15] $CrCl_3 \cdot 3THF$—PNP—$Al(C_6F_5)_3$ at 45 °C and 4.0 MPa,[16] and bis(2-dodecylsulfanylethyl)amine—$CrCl_3$—MAO at 70 °C and 0.1 MPa.[17] The kinetic model for the selective oligomerization of ethylene predominantly to hex-1-ene in the presence of the system $CrCl_3 \cdot 3THF$—PNP—$AlEt_3$ was proposed.[18] However, the data on the kinetics of ethylene oligomerization by the Cr^{III} compounds with pyrrole derivatives are lacking so far.

In the present work, we report for the first time the kinetic regularities of ethylene oligomerization using the CS $Cr(acac)_3$—$AlEt_3$—2,5-dimethylpyrrole (2,5-DMP) in the absence and in the presence of modifying agents (THF and CCl_4) at temperatures ranging from 40 to 80 °C and at pressures as high as 1.0—3.0 MPa. Activity and selectivity of the catalyst are also described.

Experimental

All procedures with solvents and catalyst components were carried out in standard Schlenk flasks under argon. Heptane,

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toluene, and THF were purified and dried by standard procedures. 2,5-Dimethylpyrrole, $Cr(acac)_3$, and $AlEt_3$ (Sigma—Aldrich) were used without preliminary purification. The prepared solutions with a certain concentration of the CS components were stored under an inert atmosphere.

For the preparation of the catalyst, a solution of $Cr(acac)_3$ (0.04 g, 0.1 mmol) in toluene (10 mL) was mixed with a solution of 2,5-DMP (0.03 mL, 0.30 mmol) in heptane (6.5 mL) in a Schlenk flask. The obtained light violet mixture was stirred for 5 min. A mixture of the cocatalyst $AlEt_3$ (0.28 mL, 2.03 mmol) and the corresponding modifying agent (0.2 mmol of CCl_4 and/or 0.3—1.2 mmol of THF) was prepared in another Schlenk flask. The colored mixture formed was diluted with heptane (10 mL) and stirred for 5 min. The prepared mixtures of the CS components were successively introduced into the reactor at a pressure of ethylene of 0.6 MPa.

The selective oligomerization of ethylene was carried out in a 0.2-L temperature-controlled reactor of stainless steel. A magnetic stirrer was used. The reaction temperature was maintained with a thermostat, which supplied a heat carrier into the reactor jacket. Prior to each experiment, the reactor was thoroughly cleaned and dried by evacuation for 30 min at 90 °C. The solvent and the CS components were injected into the reactor using a special metallic syringe, while an ethylene pressure of 0.6 MPa was set in the reactor. The ethylene pressure was brought to a specified value. Ethylene was continuously fed into the reaction zone. The duration of all experiments was 60 min. Then the reaction of ethylene oligomerization was terminated, the reactor was cooled with flowing cold water, and the residual pressure was released to the atmosphere. From the reaction mixture consisting of the liquid and solid (polymeric) phases a small portion of the liquid phase was taken. A 5% aqueous HCl was added to this portion in order to deactivate the catalyst components.

Then the quantitative analysis of the liquid phase to the content of higher LAO was carried out with a CHROM 5 gas chromatograph equipped with a flame-ionization detector and a glass packed column (length 2400 mm, internal and external diameters 3 and 5 mm, respectively), the sorbent was 15% CARBOWAX 1500 on CHEZASORB AW, the temperature of the thermostat was 80 °C, and the temperature of the evaporator and detector was 220 °C. Chromatograms were recorded and processed using a Multichrom apparatus-program complex.

Results and Discussion

Search for optimum conditions for ethylene oligomerization. There are two published reports on ethylene polymerization in the presence of the CS $Cr(acac)_3$—$AlEt_2Cl$ (see Ref. 19) and $Cr(acac)_3$—MAO (see Ref. 20). As shown in the latter case, ethylene polymerization at 50 °C, an ethylene pressure of 0.1 MPa, and a mole ratio of Al : Cr = 50 has a low rate (279 (g of PE) $(g\ Cr)^{-1}\ h^{-1}$) to form PE with a broad bimodal molecular weight distribution (MWD). When $AlEt_3$ or $AlBu^i{}_3$ is used instead of MAO at the mole ratio Al : Cr = 10, no ethylene oligo- or polymerization is observed at all. To check this unusual result, we studied the oligomerization of ethylene using the CS $Cr(acac)_3$—$AlEt_3$ (**CS1**) in the presence and absence of various modifying agents. Already the first experiments showed that at the ratio Al : Cr = 10 the pressure increase to 1—3 MPa activates the CS $Cr(acac)_3$—$AlEt_3$ and induces the formation of PE. It was established that at the optimum mole ratio Al : Cr = 20 up, to 3 wt.% of higher α-olefins, but-1-ene and hex-1-ene are observed along with the formation of PE (Table 1 and Fig. 1, curve *1*). The polymerization kinetics has a pronounced non-stationary nature, indicating the fast decay of active sites.

In order to change the direction of polymerization toward the formation of higher α-olefins, we studied the CS $Cr(acac)_3$—$AlEt_3$—2,5-DMP (**CS2**) using the pyrrole-substituted ligand. The typical kinetic curve for ethylene consumption in the presence of this CS is shown in Fig. 1, curve *2*. As can be seen from Fig. 1, the oligomerization of ethylene for 1 h is characterized by the quasi-stationary rate. Unlike the two-component **CS1**, 11.0 wt.% of the polymer and 89 wt.% of higher α-olefins, but-1-ene (52.2 wt.%) and hex-1-ene (36.9 wt.%), are formed in the presence of the **CS2** (see Table 1).

Various electron-donor compounds (for example, ethers, amines, *etc.*) that block the active sites responsible for polymer formation are used to decrease the rate of polymer formation in the reaction of selective ethylene dimerization to but-1-ene in the presence of the CS $TiOBu_4$—$AlEt_3$.[21] The same effect could be observed for the CS containing the Cr^{III} complexes. However, as experimentally shown, the introduction of THF into the **CS2** $Cr(acac)_3$—$AlEt_3$—2,5-DMP does not suppress the polymer formation. An increase in the mole ratio THF : Cr from 3 to 12 causes a twofold decrease in the activity of the CS in the presence of THF (**CS3**) and an increase in the selectivity to hex-1-ene from 48 to 72 wt.% (see Table 1).

The introduction of halides (C_2Cl_6, CH_2Cl_2, $C_2H_3Cl_3$, *etc.*) into the CS enhances the yield of oligomers.[10—12] At 120 °C and an ethylene pressure of 5.0 MPa in the presence of the CS 2-ethylhexanoatechromium(III)-1,2,3,4,5-pentaphenyl-1,3-cyclepentadiene—$AlEt_3$ (mole ratio

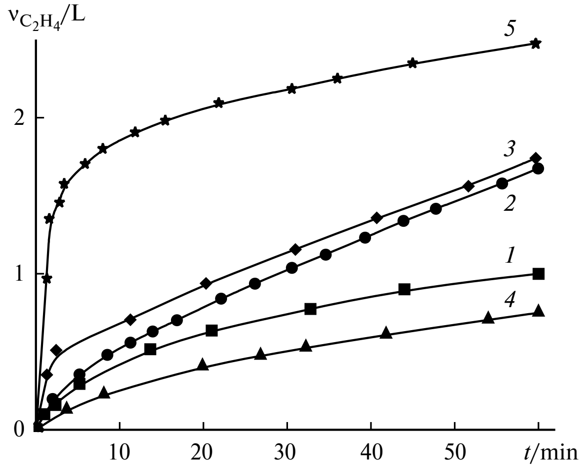

Fig. 1. Kinetic curves of ethylene consumption in the presence of the catalytic systems **CS1** (*1*), **CS2** (*2*), **CS3** (*3*), **CS4** (*4*), and **CS5** (*5*). Here and in Figs 2 and 3, $v_{C_2H_4}$ is the volume of ethylene absorbed during the reaction.

Table 1. Activity and selectivity of ethylene oligo- and polymerization in the presence of various CS[a]

Entry	Mole ratio[b] Cr : Al : L : THF : CCl_4	T/°C	P/MPa	PE		But-1-ene	Hex-1-ene	Activity of CS, (g of hex-1-ene) (g of $Cr)^{-1}$ h^{-1}
				g	wt.%	wt.%		
				$Cr(acac)_3$—$AlEt_3$ (**CS1**)				
1	1 : 20	80	3	1.32	97.0	2.5	0.5	8
				$Cr(acac)_3$—$AlEt_3$—2,5-DMP (**CS2**)				
2	1 : 20 : 3	80	3	0.23	11.0	52.1	36.9	150
				$Cr(acac)_3$—$AlEt_3$—2,5-DMP—THF (**CS3**)				
3	1 : 20 : 3 : 3	80	3	0.28	14.4	37.8	47.8	200
4	1 : 20 : 3 : 6	80	3	0.26	13.4	27.0	59.6	175
5	1 : 20 : 3 : 12	80	3	0.24	22.9	5.0	72.1	100
				$Cr(acac)_3$—$AlEt_3$—2,5-DMP—CCl_4 (**CS4**)				
6	1 : 20 : 3 : 2	80	3	0.45	51.7	1.1	47.2	80
				$Cr(acac)_3$—$AlEt_3$—2,5-DMP—THF—CCl_4 (**CS5**)				
7	1 : 20 : 3 : 3 : 2	80	3	0.42	14.5	—[c]	85.5	500
8	1 : 20 : 3 : 6 : 2	80	3	0.47	25.5	—[c]	74.5	300
9	1 : 20 : 3 : 12 : 2	80	3	0.49	27.3	—[c]	72.7	250
10	1 : 20 : 3 : 3 : 2	60	3	0.50	12.6	—[c]	87.4	700
11	1 : 20 : 3 : 3 : 2	40	3	0.75	15.1	0.2	84.7	810
12	1 : 20 : 3 : 3 : 2	40	2	0.49	20.1	0.1	79.6	370
13	1 : 20 : 3 : 3 : 2	40	1	0.36	31.0	—[c]	68.1	150

[a] Reaction conditions: [Cr] = 1.8 mmol L^{-1}, heptane (55 mL), duration 60 min.

[b] L is 2,5-DMP. The ratio of the corresponding components of the CS is presented.

[c] The content of but-1-ene in the reaction products was not determined.

1 : 3 : 90), the additive of C_2Cl_6 increases the selectivity to hex-1-ene from 60.5 to 89 wt.% and enhances the catalytic activity from 4670 to 23 100 g (g of $Cr)^{-1}$ h^{-1} (see Ref. 12). The yield of the polymer during ethylene oligomerization decreases from 6.5 to less than 1.5 wt.%. The effect of CCl_4 on the catalytic activity in the presence of the **CS4** is illustrated by the data in Table 1. The experimental results obtained using the **CS4** indicate that only the selectivity to hex-1-ene increases (compared to the **CS2**), whereas the polymer content increases noticeably and the activity of the catalyst decreases. The combined use of the modifying agents CCl_4 and THF was demonstrated for the **CS5** (see Table 1). For example, when CCl_4 with a small mole ratio THF : Cr = 3 was introduced the oligomerization rate was sharply increased within the first minutes from 200 to 500 (g of hex-1-ene) (g of $Cr)^{-1}$ h^{-1}. This shows that the reaction kinetics has pronounced non-stationary nature. Then the reaction rate decreased slowly. As should be expected, an additive of CCl_4 also affected the selectivity of the reaction, which increased approximately twofold; however, the amount of the polymer mixture remained unchanged. The further study of the ethylene oligomerization kinetics was carried out in the presence of the most active catalytic system **CS5** $Cr(acac)_3$—$AlEt_3$—2,5-DMP—THF—CCl_4 with the mole ratio of components 1 : 20 : 3 : 3 : 2.

Influence of the ethylene pressure and temperature on the kinetics of ethylene oligomerization. It could be assumed that the use of the organic ligand (in our case, 2,5-DMP) and non-hydrolyzed alkylaluminum $AlEt_3$ improves the thermal stability of the CS. In fact, in accord with the published data[22] obtained for the CS $CrCl_3 \cdot 3THF$—$(Ph_2P)_2N(Pr^i)P(Ph)N(Pr^i)H$—$AlEt_3$ in a toluene medium with an induction period of 36 min, we also could not observe an induction period within 5—10 min after the beginning of the reaction (Fig. 2). Depending on the initial temperature of the reaction, up to 50—70% of the total amount of reacted ethylene were absorbed within the first 5 min. For a short time the temperature in the reactor reaches a value that is 5—10 °C higher than the specified temperature and that additionally affects the thermal stability of the active sites, leading to their deactivation.

An increase in the ethylene concentration in the reaction zone by the pressure increase in the reactor accelerates the oligomerization in the initial period during which the oligomerization rate decreases insignificantly (see Fig. 2). This indicates that the reaction of irreversible decay of active sites does not control the process of formation of higher α-olefins.

The calculation shows that the reaction order to the ethylene pressure (*i.e.*, with respect to the ethylene con-

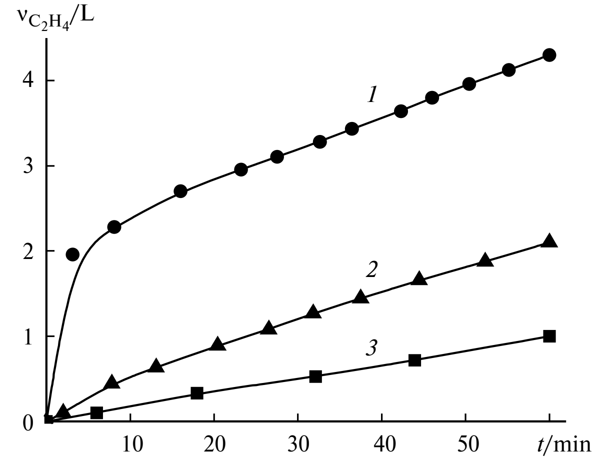

Fig. 2. Kinetics of ethylene oligomerization at an ethylene pressure of 3 (*1*), 2 (*2*), and 1 MPa (*3*). Temperature is 40 °C.

centration) in this period is 1.64. The study of the temperature and pressure effect on ethylene oligomerization in cumene medium in the presence of the CS Cr(acac)$_3$—(Ph$_2$P)$_2$N(Pr^i)—MAO showed[15] that the reaction order to ethylene is 1.57 and the CS is thermally unstable at $T \leq 45$ °C. The study of ethylene oligomerization on other Cr^{III} complexes showed[3,23] that the reaction order to ethylene changes from 1.5 to 2.

The study of the temperature effect on the kinetics of ethylene oligomerization showed that, in the presence of our CS, no induction period is observed and the oligomerization reaction begins immediately after delivery of Cr(acac)$_3$ (Fig. 3). At the temperature higher than 40 °C, the activity of the catalytic system decreases. The reaction rate constant $k_{1.64}$ calculated for 313 K is equal to $6.17 \cdot 10^{-3}$ L mol^{-1} s^{-1}.

In this report we were able to describe kinetic regularities of the oligomerization of ethylene in the presence of the catalytic systems Cr(acac)$_3$—AlEt$_3$, Cr(acac)$_3$—AlEt$_3$—2,5-DMP, and Cr(acac)$_3$—AlEt$_3$—2,5-DMP—modifying agent (THF and/or CCl$_4$). It was found that the CS Cr(acac)$_3$—AlEt$_3$—2,5-DMP—THF—CCl$_4$ (mole ratio of the components 1 : 20 : 3 : 3 : 2) exhibited the highest selectivity and activity at 40 °C and an ethylene pressure of 3 MPa. The yield of hex-1-ene was 86 wt.% of the amount of reacted ethylene, and the activity of the CS reached a value of 810 (g of hex-1-ene) (g of Cr)$^{-1}$ h^{-1}.

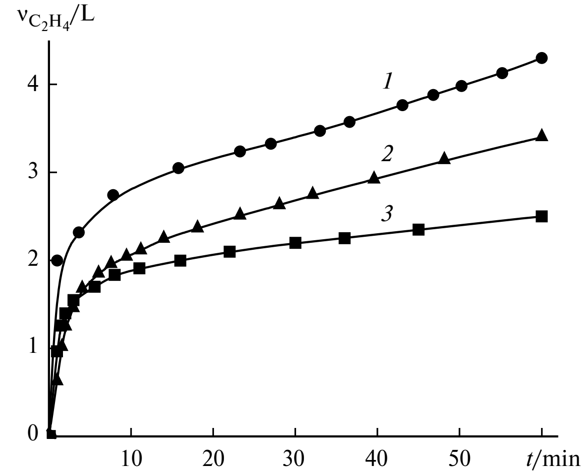

Fig. 3. Kinetics of ethylene oligomerization at temperatures 40 (*1*), 60 (*2*), and 80 °C (*3*). Ethylene pressure is 3 MPa.

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