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Enhancement of Catalytic Activity for Selective Oligomerization of Ethylene by Microwave Treatment

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Abstract—It has been found that the activity of a catalyst for selective oligomerization (trimerization) of ethylene based on a chromium salt and organoaluminum compounds (OACs) can be substantially enhanced by the microwave irradiation of organoaluminum compounds directly prior to mixing them with the chromium salt and a pyrrole ligand. The effects of irradiation conditions and the nature of the reagents used have been studied. The catalyst obtained according to an optimal procedure outperforms known analogs in activity.

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The production of ethylene copolymers that involve 1–2 to 8–10% light α-olefins, mainly, hexene-1 and octene-1 in their manufacture is currently increasing. Most traditional ethylene oligomerization processes used for the manufacture of these olefins results in a wide range of products with a total yield of hexene and octene no more than 50%. In this connection, active development of processes that will yield hexene-1 from ethylene with a selectivity higher than 90% or octene-1 with a selectivity of more than 70% is under way. In the latter case, hexene-1 prevails in the byproducts.

The first of these processes—selective oligomerization (trimerization) of ethylene to form hexene-1—was implemented by Chevron Phillips in 2004 in Qatar. Used in this process were the Phillips chromium-based homogeneous catalysts, which are described mainly in patent literature [1–3]. The catalytic system activated by alkylaluminum compounds is obtained by mixing, for example, chromium(III) ethylhexanoate ($Cr(EH)_3$), a pyrrole ligand (e.g., 2,5-dimethylpyrrole, DMP), an organoaluminum activator (preferably triethylaluminum, TEA) and a halogen-containing cocatalyst (e.g,, diethylaluminum chloride (DEAC) or hexachloroethane). The typical ratio of components in the Phillips catalyst is $Cr(EH)_3$: DMP : TEA : DEAC = 1 : 3 : 11 : 8. The activity of the catalyst, according to patent data, is up to 157 kg of olefins/(gCr h) at 10 MPa of ethylene. At lower pressures, a second-order dependence of the catalyst activity on the pressure of ethylene is observed. Thus, at 4.6 MPa, the activity is about 68.6 kg of olefins/(gCr h) [1].

There is a large number of modifications to these catalytic systems, among which the developments of Mitsubishi Chemical can be distinguished [4–5]. It was found that the addition of Lewis acids that are not prone to coordination, such as $B(C_6F_5)_3$, makes it possible to increase the activity of the catalyst system. The Phillips and Mitsubishi catalytic systems are activated by readily available alkylaluminum compounds, whereas other designers use expensive methylaluminoxane (MAO) [6–8]. Of these, the ethylene trimerization system based on diphosphazane ligands (e.g., (o-methoxyphenyl)$_2$PN(Me)P(o-methoxyphenyl)$_2$), chromium salts, and MAO is the most active among the currently known relevant systems. Its activity reaches 1033 kg/(g Cr h) at 2 MPa of ethylene and a Cr : Al ratio of 1 : 300 [7]. Given the difference in pressure used, this system is 30–40 times more active than the Phillips catalyst per gram of chromium.

The role of the halogen-containing component in the catalytic trimerization system was discussed in a number of publications [9, 10]. In particular, it has been assumed that an increase in the activity of the catalyst system when using a halide co-catalyst can be due to a change in the structure (form) in which the activator occurs. It is known [11] that triethylaluminum (TEA) in the free state and solutions, except for very dilute solutions, occurs under normal conditions predominantly (>99%) as a dimer Al_2Et_6 with two bridging ethyl groups.

Kinetic studies show that the active species in the reactions of TEA is usually the monomeric form [12]. According to Yang et al. [9], the formation of an unstable complex of monomeric TEA with a halide can increase its reactivity. In the catalyst system, TEA plays the role of a deprotonating agent for the pyrrole compound to give the pyrrolide anion, destroys the organic acid radical in the chromium salt, and reduces chromium(III). An enhancement in the reactivity of TEA can lead to an increase in the yield of species that are active in the reaction of selective oligomerization. In particular, the increased activity of TEA as a reducing agent can facilitate an increase in the concentration of chromium(I) compounds, which appear to be responsible for the activity of the catalyst in the trimerization of ethylene [13].

As one of the ways to increase the activity of a catalyst, microwave irradiation can be used. Thus, microwave irradiation was used during a catalyst activation reaction to increase the activity of a silica-supported catalyst based on the cyclopentadienyl zirconium complex and MAO [14]. However, we have not been aware of any example of use of microwave treatment for the preparation of olefin oligomerization catalysts.

The purpose of this work was to study the feasibility of increasing the activity of an ethylene trimerization catalyst system by microwave irradiation during preparation of the catalyst. The basis for these studies was the assumption that microwave treatment can facilitate the monomerization of TEA, which would make it possible to increase the activity of the resulting catalyst and to reduce the required pressure of the reactant ethylene.

EXPERIMENTAL

All the solvents used in the study were dried by refluxing over metallic sodium followed by distillation from sodium hydride. A TEA solution in heptane was prepared from a 25% TEA solution in toluene by removing the solvent under vacuum (500–700 Pa), and diluting the residue with heptane to a required concentration. To prepare DEAC solutions, a 1.0 M DEAC solution in hexane was used. The reagent 2,5-dimethylpyrrole of 98% purity was used without further purification. Anhydrous chromium(III) ethylhexanoate was prepared according to a known procedure [15] with additional drying in a vacuum of 200 Pa at 200°C.

The microwave irradiation of OAC solutions of was conducted in a MARS-5 microwave oven, manufactured by CEM, in the continuous mode at a rated power of 400 W.

All catalyst samples prepared using microwave treatment were tested in the ethylene trimerization reaction run in a special setup designed for this purpose. The setup included a high-pressure reactor of 0.5 L capacity equipped with pressure and temperature sensors, an oil-filled cooling jacket connected to a thermostat, a 6-mL chamber for catalyst loading under pressure, and an ethylene feed line. The setup was equipped with a computer-run process control system, which made it possible to record sensor readings and to control the reactor temperature, the ethylene feed line, etc. The conditions of catalyst preparation and testing in different experiments are shown in Table 1. To study the possibility of increasing the catalyst activity and selectivity for ethylene trimerization by microwave irradiation, sets of experiments 1–3, 4–11, 12–14, 15–18, and 19–20 were carried out. The catalysts preparation and testing conditions were maintained to be identical within a set, except for the conditions of microwave treatment of OAC and/or the catalyst system as a whole.

Catalyst Preparation Procedure

A weighed sample of chromium(III) ethylhexanoate containing a required amount of chromium, dimethylpyrrole (3 mol with respect to chromium), and 5 mL of toluene were placed in a flask in which a nitrogen atmosphere was created then. A solution of TEA in heptane (154 mg/mL) with a required amount relative to chromium was mixed with a calculated amount of a cocatalyst. To this mixture, another 1 mL of toluene was added in runs 1–3, 0.5 mL of toluene was added in runs 4–7 and 9–11, and no toluene was used in runs 8 and 12–20. The resulting OAC solution was subjected to microwave irradiation within a specified time (Table 1), and then added to a mixture of $Cr(EH)_3$, DMP, and heptane. In control runs (1, 4, 12, 16), the microwave treatment of the OAC was not used, as well as in run 11.

After mixing all components, the catalyst in runs 3 and 11 was subjected to microwave irradiation for a given time. Fifteen minutes after mixing the reagents, the solvents were evaporated under vacuum at room temperature (residual vapor pressure of 600–800 Pa). The residue in the flask was diluted with *n*-heptane to 4 mL. The prepared catalyst solution was then tested in the ethylene trimerization reaction.

Catalyst Testing Procedure

The reactor was charged with 200 mL of a solvent (*n*-heptane in runs 1–18, cyclohexane in runs 19–20). In runs 1–11, TEA was also added to mixture in the reactor (Table 1). In runs 19–20, the solvent was saturated with hydrogen under a pressure of 100 kPa prior to the addition of the catalyst. Through a flow meter, the reactor was filled with a specified amount of ethylene, and the temperature was raised to 80°C. Then, the catalyst was introduced into the reactor at an excess pressure of argon (runs 1–18) or ethylene (runs 19–20) and the reaction was conducted; in the latter case, the pressure of 0.8 MPa during the course of the reaction was maintained by pumping-in ethylene as far as it was consumed. After a specified reaction time, 1 mL of isopropanol was added. The reactor was cooled to room temperature, and the pressure was released. The resulting polymer was separated and dried for 8 h at 100°C. The reaction mixture was analyzed by gas chromatography on an Agilent 7890A chromatograph with a FID. A sample (size, 1 mm^3) was injected with a model 7683B (G2913A) autosampler. The evaporator for use with capillary columns

Table 1. Conditions of the preparation and testing of ethylene trimerization catalysts

Run	Catalyst preparation conditions						Catalyst testing conditions		
	Cr, mg	MW irradiation time, min		delay after MW irradiation of OAC, min	cocatalyst, mol/mol Cr	TEA, mol/mol Cr	TEA, mol/mol Cr	charge C_2H_4, g	time, min
		OAC	catalyst						
1	6	0	0	–	–	12.8	4.2	32	30
2	6	3	0	<0.5	–	12.8	4.2	32	15
3	6	3	10	<0.5	–	12.8	4.2	32	30
4	4	0	0	–	DEAC (2.3)	15.5	8.5	37	16
5	4	1	0	<0.5	DEAC (2.3)	15.5	8.5	37	16
6	4	6	0	<0.5	DEAC (2.3)	15.5	8.5	37	16
7	4	6	0	<0.5	DEAC (2.3)	15.5	8.5	37	16
8	4	6	0	3	DEAC (2.3)	15.5	8.5	37	16
9	4	6	0	3	DEAC (2.3)	15.5	8.5	37	16
10	4	6	0	9	DEAC (2.3)	15.5	8.5	37	16
11	4	0	6	–	DEAC (2.3)	15.5	8.5	37	16
12[a]	3	0	0	–	$CHCl_3$ (2)	50	0	32	16
13[a]	3	6[b]	0	<0.5	$CHCl_3$ (2)	50	0	37	16
14[a]	3	6	0	<0.5	$CHCl_3$ (2)	50	0	37	16
15	4	3	0	<0.5	DEAC (3)	16	8	37	12
16	4	6	0	<0.5	DEAC (5.3)	21	0	37	15
17	1	6	0	<0.5	DEAC (12)	38	0	37	12
18	4	3	0	<0.5	DEAC (12)	16	0	37	30
19[c]	0.8	6	0	<0.5	DEAC (14)	36	0	0	30
20[c]	0.8	0	0	–	DEAC (14)	36	0	0	30

[a], heptane is used as a solvent in the catalyst preparation;
[b], irradiation of a TEA solution without $CHCl_3$ as a cocatalyst;
[c], 5 equiv. of DMP relative to Cr are used; a constant ethylene pressure of 0.8 MPa.

was a G3440A 113 injection port: temperature, 240°C; pressure, 111 kPa; septum airflow rate, 0.05 mL/s; split ratio, 200 : 1. The mixture of components was separated on an HP-5 capillary column coated with a nonpolar stationary phase (5% of diphenylpolysiloxane and 95% of dimethylpolysiloxane) of a 30 m length, a 0.32 mm inner diameter, and a film thickness of 0.25 μm. Analysis conditions: helium the carrier gas, column temperature programming from 50 to 120°C at a heating rate of 7°C/min and from 120 to 280°C at a rate of 30°C/min.

Measurement of the OAC Solution Temperature after Microwave Irradiation

A 3 : 1 TEA–DEAC mixture as 4 mL of solution in a 2 : 1 toluene–hexane blend with an aluminum concentration of 1.68 mol/L was placed in a plastic syringe with a wax-plugged hole in the wall for inserting an electronic thermometer. The mixture of the OACs was irradiated for 6 min. Then the temperature in the syringe was measured with an ETS-D5 thermometer (accuracy: 0.1°C) by forcing the plug into the syringe. The temperature of the solution 40 s after

Table 2. Results of testing for catalysts 1–11

Run	Irradiation time, min	Cr/DMP/TEA/DEAC	Activity[a], kg/(g Cr h)	Amount in product, wt %							Polymer, wt %
				1-C_6	1-C_6/C_6	C_4	C_6 without 1-C_6	C_8	C_{10}	C_{12+}	
1	0	1 : 3 : 17 : 0	3.6	66.3	85.0	1.2	11.7	2.5	13.6	4.6	0.55
2	2.5	1 : 3 : 17 : 0	7.8	63.2	86.7	1.9	9.8	2.3	14.8	8.0	0.20
3	2.5(+10)[b]	1 : 3 : 17 : 0	6.5	56.5	88.0	0.9	7.7	2.3	18.2	14.4	0.21
4	0	1 : 3 : 24 : 2.3	4.5	85.7	96.5	0.3	3.1	4.6	5.5	0.8	0.31
5	1	1 : 3 : 24 : 2.3	9.3	70.6	93.6	7.3	4.8	5.3	8.3	3.6	0.16
6	6	1 : 3 : 24 : 2.3	18.7	73.6	94.4	1.9	4.4	3.2	8.9	8.0	0.09
7[c]	6	1 : 3 : 24 : 2.3	21.6	76.7	94.4	1.3	4.5	2.1	8.9	6.5	0.04
8[d]	6	1 : 3 : 24 : 2.3	11.2	75.6	93.6	1.8	5.2	2.7	9.8	4.9	0.21
9[d]	6	1 : 3 : 24 : 2.3	13.8	73.8	93.0	2.7	5.6	3.1	10.3	4.5	0.10
10[e]	6	1 : 3 : 24 : 2.3	5.1	81.6	94.9	0.4	4.4	3.8	7.3	2.5	0.67
11	0(+6) [b]	1 : 3 : 24 : 2.3	9.0	70.0	92.0	5.5	6.1	5.8	10.9	1.7	0.10

[a], taking into account only liquid reaction products;
[b], microwave irradiation time for all components of the catalyst after mixing is given in the brackets;
[c], without toluene during irradiation of TEA/DEAC;
[d], delay 3 min between irradiation of TEA/DEAC and their mixing with $Cr(EH)_3$/DMP;
[e], delay 9 min between irradiation of TEA/DEAC and their mixing with $Cr(EH)_3$/DMP.

the end of irradiation was 32.4°C at an ambient temperature of 26.7°C.

RESULTS AND DISCUSSION

Experiments without Cocatalyst

Assuming that the catalyst activity and selectivity can be increased by microwave irradiation of TEA without the use of halogen-containing components, we carried out runs 1–3 without a cocatalyst. The component ratio of the $Cr(EH)_3$: DMP : TEA catalyst system was 1 : 3 : 12.8. To eliminate the influence of possible impurities on the catalyst, additional 4.2 mol TEA/mol Cr were added into the reactor prior to the introduction of the catalyst. The catalyst was prepared according to the general procedure, but TEA in runs 2 and 3 was subjected to microwave irradiation for 2.5 min and then was immediately mixed with $Cr(EH)_3$ and DMP in toluene. In run 3, in addition, the resulting catalyst system was irradiated for 10 min immediately after mixing the reagents in order to assess the effect of microwave irradiation on the formation of the catalyst. In this case, considerable warming of the catalytic system was noted. No appreciable warming was observed during the microwave irradiation of a TEA solution: the temperature rise did not exceed 6°C.

The testing results given in Table 2 for the obtained catalysts show that in runs 2 and 3, the activity of the catalysts prepared with the use of microwave irradiation is almost two times that in run 1. In this case, the reaction selectivity for hexene-1 remained at low levels. In run 3, the selectivity even decreased owing to the formation of a greater amount of heavier byproducts. It can be concluded that microwave irradiation of the TEA solution promotes the activity, rather than selectivity, of the catalyst whereas additional microwave irradiation of the entire catalyst system slightly reduces both the activity and selectivity of the catalyst.

Effect of Microwave Irradiation Time

In the subsequent experiments, a cocatalyst was used to increase the selectivity of the reaction for hex-

Table 3. Results of testing of catalysts containing $CHCl_3$

Run	MW irradiation time, min	Cr/DMP/ TEA/$CHCl_3$	Activity[a], kg/(g Cr h)	Amount in product, wt %							Polymer, wt %
				1-C_6	1-C_6/C_6	C_4	C_6 without 1-C_6	C_8	C_{10}	C_{12+}	
12	0	1 : 3 : 50 : 2	5.5	81.6	96.0	2.1	3.4	4.8	5.2	2.9	0.55
13	6[b]	1 : 3 : 50 : 2	12.4	86.9	96.1	1.7	3.5	2.3	4.5	1.1	0.20
14	6[c]	1 : 3 : 50 : 2	24.7	77.6	90.0	0.6	8.6	2.1	5.3	5.8	0.21

[a], taking into account liquid products alone;

[b], microwave irradiation of TEA in hexane, then mixing it with $CHCl_3$ and addition to $Cr(EH)_3$/DMP;

[c], microwave irradiation of TEA and $CHCl_3$ in hexane, then addition to $Cr(EH)_3$/DMP.

ene-1. In runs 4–11, the catalyst system consisted of $Cr(EH)_3$, DMP, TEA, and DEAC in the 1 : 3 : 15.5 : 2.3 ratio. In addition, 8.5 equivalents of TEA was introduced into the reactor prior to charging with the catalyst. The catalyst preparation procedure did not involve microwave irradiation in run 4, the mixture of TEA and DEAC was subjected to microwave irradiation for 1 min before mixing with $Cr(EH)_3$ and DMP in run 5, and the irradiation time was increased to 6 min in run 6. Run 7 was similar to run 6, but the OAC solutions to be irradiated did not contain toluene.

A comparison of runs 4–6 shows that microwave irradiation increases the activity of the catalyst. A longer microwave irradiation time in run 6 (6 min) compared with run 5 (1 min) provides a more active catalyst. The presence or absence of toluene in the OAC solution has no significant influence on the observed effect.

Relaxation Time of the Microwave Irradiation Effect

To elucidate the issue of relaxation time for the effect of alteration in the OAC properties by microwave irradiation, we performed. runs 8–10. For evaluating the change with time in the effect observed after microwave irradiation of OAC, a delay between the end of 6-minute microwave irradiation of a solution of TEA/DEAC and mixing it with $Cr(EH)_3$ and DMP was made during the preparation of the catalyst system. For runs 2, 3, and 5–7 the interval between the end of irradiation and mixing did not exceed 30 s. The delay was 3 min in runs 8 and 9, and it was increased to 9 min in run 10. The results of testing the catalysts in the trimerization reaction showed that the catalytic activity decreased with the increasing delay time. The conclusion is that the observed effect of microwave irradiation on the OAC is temporary and, as the time of delay between the end of irradiation and mixing with the chromium salt increases, it decreases until complete disappearance.

Note that in the case of the catalysts prepared with the use of microwave treatment, the proportion of the byproduct polymer decreases. Apparently, this is mainly due to an increased activity of the catalyst in the formation of liquid products, since the liquid : polymer product ratio increases in direct proportion to the total activity of the catalyst.

Chloroform as a Cocatalyst

To examine the effect of microwave irradiation when halogen-containing organic cocatalysts are involved, runs 12–14 have been carried out in which chloroform was used. The component ratio $Cr(EH)_3$: DMP : TEA : $CHCl_3$ was 1 : 3 : 50 : 2, In run 12, microwave irradiation was not used in the catalyst preparation, a mixture of a TEA solution and chloroform was added to $Cr(EH)_3$ and DMP in toluene. In run 13, a solution of TEA in heptane was subjected to microwave irradiation for 6 min before mixing with chloroform, and the resulting mixture was immediately mixed with the chromium salt and DMP. In run 14, a TEA solution and chloroform in heptane was subjected to microwave irradiation for 6 min before mixing with $Cr(EH)_3$ and DMP in toluene. The testing of catalysts 12–14 showed that microwave radiation in this case also has a positive effect (Table 3). However, there is a significant difference in product composition between runs 13 and 14. In the former case, the TEA alone was irradiated and an approximately twofold increase in catalytic activity compared to run 12 and a slight increase in the hexene-1 selectivity was observed. In run 14, in which the solution of TEA together with $CHCl_3$ was subjected to microwave irradiation, the activity increased by a factor of 4 (compared with run 12), but the reaction selectivity simultaneously decreased. It is also noteworthy that the formation of butenes in run 14 substantially decreased as compared with runs 12 and 13.

Microwave Irradiation after Mixing All Catalyst Components

In run 11, the microwave treatment of the TEA/DEAC mixture was not practiced. before mixing with the chromium salt and DMP Instead, the final mixture was subjected to microwave irradiation for 6 min immediately after mixing the components of the

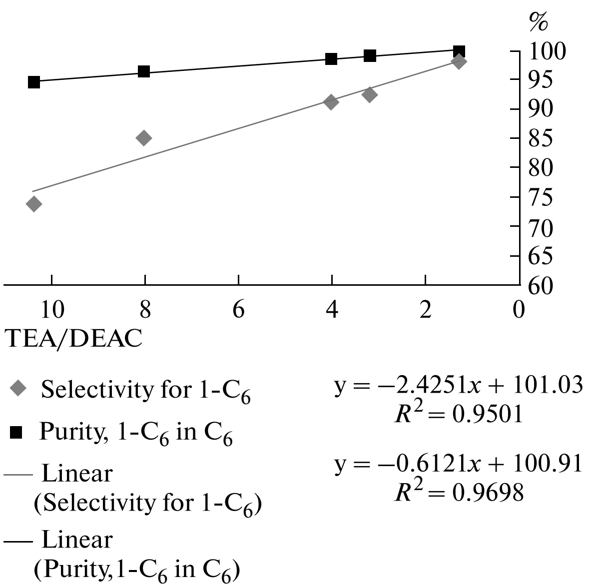

Fig. 1. Effect of the TEA/DEAC ratio on the activity and selectivity of the catalyst.

catalyst. The testing of the catalyst obtained in this manner also showed an approximately twofold improvement in activity compared with the control run 4. However, the activity of the catalyst in run 11 is almost twice lower than in run 6, in which the TEA/DEAC mixture only was subjected to microwave irradiation for 6 min and is comparable with the result of run 5 with a TEA/DEAC irradiation time of 1 min. Note that the composition of the products formed in runs 5 and 11 is similar.

It is known from the patent data that the formation of the Phillips catalytic system takes place within 5–15 min after mixing the components [3]. It can be assumed that in run 11, as well as in the experiments with the irradiation of OAC only, the impact of the microwave radiation on the OAC that has not yet reacted with the chromium salt plays the determining role. In the case of run 5, complete conversion of OAC to the activated form does not occur for 1 min of microwave irradiation. Thus, it may be assumed that $Cr(EH)_3$ and DMP interact with partially activated OACs in these cases and, consequently, the properties of the resulting catalytic systems turn out to be similar.

The selectivity in runs 4–14 with the use of DEAC and $CHCl_3$ as cocatalysts is significantly higher than in runs 1–3 in the absence of a co-catalyst, in agreement with published data. However, there is no unambiguous correlation between the microwave treatment and selectivity in these experiments. That is, it can be concluded that the TEA : cocatalyst ratio should be reduced for improving the selectivity of the reaction.

Optimization of Catalyst System Composition

Runs 15–18 on the optimization of the composition of the catalyst system to enhance its activity and selectivity have shown that in the case of microwave treatment of TEA and DEAC, the optimal TEA : DEAC ratio is 3.2 (Fig. 1). This is significantly higher than the typical ratio for the Phillips catalyst (1.3–1.4) [1]. At larger values of the ratio, the activity and selectivity of the reaction decreases; at lower values, the selectivity further increases, but the activity of the catalyst substantially decreases. The general character of the dependence of the activity and selectivity of the system upon the TEA/chlorine compound ratio is similar to published results for the system with 1,1,1-trichloroethane as a co-catalyst [9]. Table 4 shows the results of testing of catalysts 19 and 20 prepared with and without the use of microwave irradiation, respectively. In contrast to previous experiments, these tests were performed at a constant pressure of 0.8 MPa of ethylene maintained to compensate for its consumption. The TEA/DEAC ratio was close to the optimal value; in addition, to increase the activity of the catalyst, the solvent was saturated with hydrogen before the reaction. The plot of ethylene consumption during the reaction is shown in Fig. 2. The activity and selectivity in run 19 of the catalyst prepared using microwave irradiation of the OACs, was more than 1.5 times higher than the activity in run 20 for the catalyst prepared without microwave treatment.

Nature of Microwave Irradiation Effect

To study the nature of the action of microwave radiation on OACs, additional experiments were performed. At an ambient temperature of 26.7°C, the temperature of the 3 : 1 mixture of TEA and DEAC solutions was 32.4°C at 40 s after the end of microwave treatment. Since the OAC solution was added in an

Table 4. Results of testing of the optimized catalysts

Run	MW irradiation time, min	Cr/DMP/TEA/DEAC	Activity[a], kg/(g Cr h)	Amount in product, wt %							Polymer, wt %
				1-C_6	1-C_6/C_6	C_4	C_6 without 1-C_6	C_8	C_{10}	C_{12+}	
19	6	1 : 5 : 36 : 14	101.7	89.9	99.3	0.9	0.6	0.3	6.9	1.4	0.05
20	0	1 : 5 : 36 : 14	51.0	83.3	97.0	1.8	2.6	0.4	8.4	3.5	0.06

[a], taking into account only liquid reaction products.

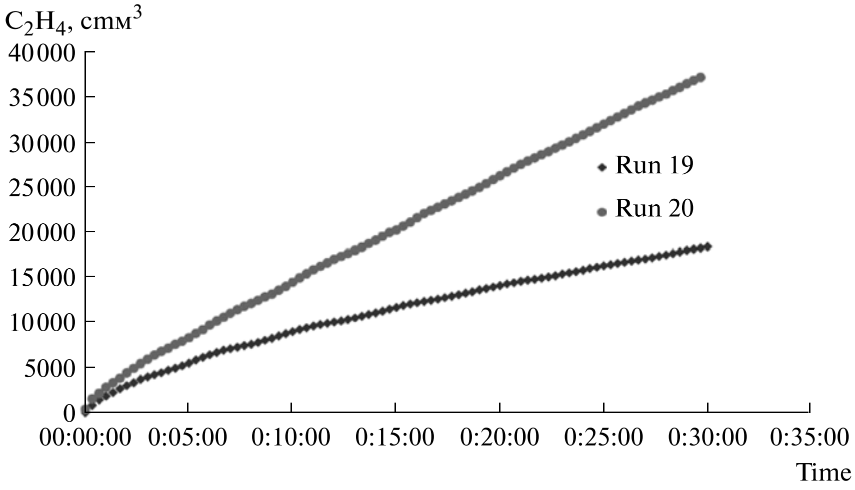

Fig. 2. Ethylene consumption during runs 19 and 20.

amount of 10–15% of the volume of the reaction mixture the fact that during the catalyst preparation, we may actually rule out that the observed effect is due to dielectric heating of the reactants by the action of microwave field.

To verify the hypothesis of possible monomerization of TEA under the action of microwave irradiation, the cryoscopic determination of the molar mass (MM) of TEA was performed 6 min after microwave irradiation of the TEA solution in toluene. The measured MM value was 160 ± 15 g/mol (temperature measurement 0.1°C) 1.5 min after irradiation. This value at 3 min after exposure was 202 ± 5 g/mol (temperature measurement with accuracy 0.01°C). The determination of the molar mass of TEA 15 min after irradiation for the same two solutions yielded results 240 ± 20 and 224 ± 5 g/mol, respectively. The latter values correspond to the MM of the TEA dimer (228.32 g/mol). The values of MM in the first minutes after irradiation are intermediate between the MM of the monomer (114.16 g/mol) and the dimer of TEA. Thus, the cryoscopic data indicate a partial monomerization of TEA by microwave irradiation. The difference in MM value at 1.5 and 3 min after exposure, as well as the return in 15 min to the value of the MM characteristic of the dimer, shows the temporary nature of the monomerization of TEA. This is consistent with the results of runs 8–10 demonstrating that the effect of increasing catalyst activity using irradiated OACs is observed within a few minutes after irradiation and rapidly decreases with the increasing time between the end of microwave irradiation and mixing OACs with the chromium salt.

Thus, it has been found that the activity of the ethylene trimerization catalyst can be substantially enhanced by microwave irradiation of organoaluminum compounds as components of the catalytic system, immediately before their mixing with the chromium salt. The observed effect is temporary in nature and weakens with the increasing time between microwave irradiation of the OACs and mixing them with the chromium salt. Very low heating of the OAC solution during the irradiation allows the thermal nature of the effect of microwave treatment to be disregarded. The cryoscopic data indicate a partial temporary monomerization of TEA by microwave irradiation.

It has been shown that an ethylene trimerization catalyst with a higher activity can be obtained by microwave irradiation of a TEA and cocatalyst solution and immediate mixing of the irradiated solution with a chromium salt and DMP. As prepared with the use of microwave irradiation of the TEA and DEAC solution, the Cr/DMP/TEA/DEAC catalyst with a component ratio of 1 : 5 : 36 : 14 optimized in activity and selectivity is characterized by an order of magnitude higher activity than the similar Phillips catalyst. This makes it possible to make the reaction conditions substantially milder in terms of ethylene pressure, namely, to lower it from 4.5–5.5 to 0.8–1.2 MPa. For industrial implementation, lowering the pressure leads to improvement in the economics of the process by substantially reducing capital expenditures. In addition, the use of the available alkylaluminum compounds instead of expensive MAO further improves the efficiency of the catalyst prepared by the method developed in this study.

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