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Ethylene Oligomerization over Catalyst Systems Based on Chromium(III) and Aluminum Coordination Compounds

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Abstract—The influence of the nature of a cocatalyst, a stabilizing ligand, and an introduced modifier on the behavior of the ethylene oligo- and polymerization reaction in the presence of the $Cr(acac)_3$–AlR_3–L–M catalyst system, where AlR_3 is triethylaluminum ($AlEt_3$), dichloroethylaluminum ($AlEtCl_2$), or methylalumoxane (MAO); L is pyrrole (PyH) or bis(diphenylphosphino)cyclohexylamine ($(Ph_2P)_2NCy$); and M is tetrachloromethane (CCl_4), has been studied. The maximal selectivity for hexene-1 has been found to be 86 wt %.

Keywords: ethylene, chromium acetylacetonate, hexene-1, oligomerization, polymerization
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Selective oligomerization of ethylene is known as an effective process for the manufacturing of higher α-olefins with a higher molecular mass, which are in high demand due to their use in large-scale industrial processes of copolymerization with ethylene and propylene (production of medium-, low-, and ultralow-density polyethylene and modified grades of polypropylene); linear α-olefins are also used as feedstock for the synthesis of low-molecular-mass products, such as higher alcohols, acids, detergents, and synthetic base oils for the aircraft and automotive industries. Among higher α-olefins, butene-1, hexene-1, and octene-1 are currently of the greatest commercial interest.

Of all the currently existing processes for the manufacturing of higher (C_4–C_8) α-olefins, the selective oligomerization of ethylene using metal complex catalysts is the most promising. Typically, these catalysts are complexes of the "early" (Groups IV and V) or "late" (Groups VI and VIII) transition metals, which are further modified to increase their activity and selectivity for higher α-olefins.

The demand for butene-1 is presently covered by an industrial process for selective dimerization of ethylene to butene-1 [1, 2], but the scale of production of hexene-1 and octene-1 is insufficient. Of these two products, hexene-1 has received greater attention because it forms the basis for production of polyhexene, medium- and low-density polyethylenes, and other chemicals.

The formation of hexene-1 in a small amount was first observed during the preparation of PE in the presence of chromium catalysts [3]. Later, multicomponent homogeneous and heterogeneous catalyst systems (KS) based on chromium(III) compounds, stabilized by various mono-, bi-, or tridentate organic ligands, and organic aluminum compounds were found for the selective oligomerization of ethylene to hexene-1 [4–6]. These catalyst systems may also contain various modifiers that improve the selectivity for linear higher α-olefins [7–9].

The selectivity and catalytic activity of different chromium catalysts for ethylene oligomerization to higher α-olefins have been studied in detail, but there are almost no data on the kinetic characteristics of these reactions. Few rate curves have been reported in the literature to describe the oligomerization of ethylene in the presence of the catalyst systems $CrCl_3 \cdot 3THF$–MAO at 20°C and 0.1 MPa [10], $Cr(acac)_3$–PNP–MAO (PNP is bis(diphenylphosphino)isopropylamine) at 30–45°C and 3–4.5 MPa [11], $CrCl_3 \cdot 3THF$–PNP–$Al(C_6F_5)_3$ at 45°C and 4.0 MPa [12], and bis(2-dodecylsulfanilethyl)amine–CrC_3–MAO at 70°C and 0.1 MPa [13]. A kinetic model for the selective reaction of ethylene oligomerization predominantly to hexane-1 in the presence of the $CrCl_3 \cdot 3THF$–PNP–$AlEt_3$ system was also proposed in the literature [14].

In this work, we studied the catalytic features of the conversion of ethylene on the $Cr(acac)_3$–AlR_3–L–M catalyst system, where AlR_3 is triethylaluminum ($AlEt_3$), dichloroethylaluminum ($AlEtCl_2$), or methylalumoxane (MAO) and L is pyrrole (PyH) or bis(diphenylphosphino)cyclohexylamine ($(Ph_2P)_2NCy$), in the absence and presence of the modifier (M) tetrachloromethane

CCl_4 over the temperature range of 40–80°C at a pressure of 3.1 MPa and examined the activity and selectivity of the catalysts.

EXPERIMENTAL

Manipulations with solvents and components of the catalyst system were carried out in standard Schlenk flasks under argon. Toluene was purified and dried according to standard procedures [15]. PyH, $(Ph_2P)_2NCy$, $Cr(acac)_3$, $AlEt_3$, $AlEtCl_2$, MAO, and CCl_4 purchased from Aldrich were used without further purification. To make a catalyst, a toluene solution of a Cr(III) coordination compound and the ligand with a total volume of 20 mL was prepared in one Schlenk flask, using the components in the stoichiometric molar ratio. The color of the solution did not change. A cocatalyst solution was prepared in another flask, and toluene was added to bring the volume to 20 mL.

When the modifier was used, a solution of the Cr(III) coordination compound in 10 mL of toluene was prepared in one Schlenk flask, and 10 mL of a solution containing the ligand and the modifier in given molar ratios, in another flask. The color of the solution did not change. A toluene solution of the cocatalyst with a total volume of 20 mL was prepared in the third Schlenk flask.

The ethylene conversion process was run in a temperature-controlled 0.1-L stainless steel reactor. The reaction temperature was maintained with a thermostat feeding the heat transfer fluid to the reactor jacket. Before each experimental run, the reactor was evacuated for 30 min at the reaction temperature and filled with ethylene to 0.6 MPa; then, 20 mL of toluene, 20 mL of the complex and ligand solution (in the case of using the modifier, 10 mL of the complex solution first and 10 mL of the ligand and modifier solution next), and 20 mL of cocatalyst solution were successively injected with a special syringe. The pressure was adjusted to the working level. Ethylene was fed continuously to the reaction zone. After 30 min, the reactor was cooled and excess pressure was released to the atmosphere. The resulting products consisting of the liquid and solid phases were sampled for analysis. Quantitative analysis of the liquid phase for α-olefins was carried out on a Shimadzu GC-2010 Plus high-performance gas chromatograph with a mass detector and a HP5 column of 50 m length. Polyethylene was washed, dried, and weighed.

RESULTS AND DISCUSSION

In this study we investigated the catalytic features of ethylene conversion on the $Cr(acac)_3$–AlR_3–L–M system, where AlR_3 is triethylaluminum ($AlEt_3$), dichloroethylaluminum ($AlEtCl_2$), or methylalumoxane (MAO); L is pyrrole (PyH) or bis(diphenylphosphino)cyclohexylamine ($(Ph_2P)_2NCy$); and M is tetrachloromethane (CCl_4), in the absence and presence of the modifier M over the range of 40–80°C at a pressure of 1.3 MPa.

Since the primary aim of the research concerns the feasibility of obtaining α-olefins, we set about finding optimal conditions for ethylene oligomerization.

There are two reports in the literature on the feasibility of ethylene conversion in the presence of the $Cr(acac)_3$–$AlEt_2Cl$ [16] and $Cr(acac)_3$–MAO [17] catalyst systems. In the latter case, it was shown that the polymerization of ethylene at 50°C, an ethylene pressure of 0.1 MPa, and an Al : Cr molar ratio of 50 proceeds at a low rate (279 g_{PE} $(g_{Cr}\ h)^{-1}$) to give polyethylene with a broad bimodal molecular weight distribution (MWD). When$AlEt_3$ or $AliBu_3$ (triisobutylaluminum) was used instead of MAO with an Al : Cr molar ratio of 10, neither oligo- nor polymerization of ethylene was observed to any extent.

This fact noted in the literature seems rather surprising, and we have decided to conduct research using the $Cr(acac)_3$–$AlEt_3$ system at higher pressures and temperatures. Even the first experiments showed that pressure elevation in the range of 1–3 MPa activates the $Cr(acac)_3$–$AlEt_3$ catalyst at an Al : Cr ratio of 10 and causes the formation of PE. It was found that at an optimal molar ratio of Al : Cr = 20, the reaction product mixture contains a significant amount (up to 70 wt %) of the higher α-olefins butane-1, hexene-1, and octene-1 along with polyethylene (table).

Based on the published data for the $Cr(acac)_3$–$AlEt_3$–2,5-DMP catalyst system [18] and taking into account that the basicity and geometrical dimensions of the ligands can affect the selectivity of catalyst systems, we decided to use PyH as a ligand that has a lower basicity and a smaller geometric size.

Unlike the case of the two-component catalyst system CS1, 4 wt % polymer and 96 wt % higher α-olefins (of which hexene-1 makes 86 wt %) are produced in the presence of PyH (CS2) as the temperature is lowered to 40°C. Lowering the molar ratio to Al : Cr = 2 at 80°C led to an increase in the proportion of the polymer (to 25 wt %) and a decrease in the proportion of hexene-1 (to 66 wt %). The attempt to modify CS2 by introducing the modifier CCl_4 (CS3) resulted in an increase in the polymer yield (above 91 wt %).

Taking into consideration that ethylene absorption and the formation of various polymerization and oligomerization products take place in $Cr(acac)_3$–$AlEt_3$ catalyst system under the selected conditions, as well as the published data [16] on the transformation of ethylene on the $Cr(acac)_3$–$AlEt_2Cl$ catalyst, we decided to use $AlEtCl_2$ as a cocatalyst, which is a milder reducing agent in comparison with $AlEt_3$.

The replacement of the cocatalyst $AlEt_3$ in CS1 by less severe $AlEtCl_2$ (CS4) leads to the formation of exclusively PE; no oligomerization products were found in the liquid phase. In the case of PyH as a ligand (CS5), a decrease in the polymer yield (to 93 wt %) and the formation of butene-1 in trace amounts and about 5 wt % hexene-1 were observed.

Activity and selectivity of catalyst systems based on the $Cr(acac)_3$ coordination compound

Run	Cr : Al : L : CCl_4 molar ratio	T, °C	P, MPa	PE		Butene-1	Hexene-1	Octene-1	Catalyst activity, $g_{hexene\text{-}1}\ (g_{Cr} \cdot 0.5\ h)^{-1}$
				g	wt %	wt %			
$Cr(acac)_3/AlEt_3$ (CS1)									
1	1 : 20	80	3	0.77	30	17	40	13	136
$Cr(acac)_3/AlEt_3/PyH$ (CS2)									
2	1 : 20 : 3	80	3	0.69	54	Tr.	43	3	75
3	1 : 20 : 3	40	3	0.23	4	5	86	5	629
4	1 : 2 : 3	80	3	0.4	25	4	66	5	135
$Cr(acac)_3/AlEt_3/PyH/CCl_4$ (CS3)									
5	1 : 20 : 3 : 2	80	3	3.57	91	–	8	Tr.	45
$Cr(acac)_3/AlEtCl_2$ (CS4)									
6	1: 20	80	3	2.75	100	–	–	–	–
$Cr(acac)_3/AlEtCl_2/PyH$ (CS5)									
7	1 : 20 : 3	80	3	2.28	93	Tr.	5	–	17
$Cr(acac)_3/MAO$ (CS6)*									
8	1 : 300	60	3	0.48	15	–	45	40	268
$Cr(acac)_3/MAO/(Ph_2P)_2NCy$ (CS7)*									
9	1 : 300 : 1.5	60	3	0.24	100	–	–	–	–

The experimental conditions were as follows: [Cr] = 1.44×10^{-4} mol/L (for systems marked with asterisk *, [Cr] = 10^{-4} mol/L); solvent, toluene (57 mL); reaction time, 30 min.

The results obtained in the experiment are consistent with the previous results for CS3 and CS5 (table). This allows us to assume that the use of CCl_4 as a modifier or cocatalysts containing chloride ions ($AlEtCl_2$ in this case) leads to the early decay of the oligomerization-mediating active sites and to a shift in the direction of the reaction in the catalyst system towards the formation of PE.

On the basis of published data [17], the cocatalyst in CS1 was changed for MAO, the milder one. According to the experimental results, the formation of 15 wt % PE and almost equal amounts of hexene-1 and octene-1 (~85 wt % in total) takes place in CS7.

In view of the published data [11], the organophosphorus ligand PNP was introduced in CS6 (to get CS7), which ligand led to the complete disappearance of oligomerization products.

This result obtained with CS7 is presumably due to the fact the milder cocatalyst MAO displaces the acetylacetonate ligand from the parent complex and the coordination of the stabilizing tridentate ligand gives rise only to active sites responsible for the polymerization of ethylene. It is for this reason that the oligomerization products are absent from the reaction mixture.

Influence of N-Donor Ligand Nature on the Behavior of Catalyst System

As already noted, based on the previously reported experimental data [18], we used the less basic and more geometrically compact ligand PyH in this study. However, since both 2,5-DMP and PyH are ligands of the N-donor type, it is permissible to compare the results between them.

Considering the results for CS2, we see that the change of the ligand, other conditions being the same (run 2), leads to an increase in the yield of polymerization products, disappearance of butene-1, and a decrease in the selectivity for hexene-1. In activity, this system is also inferior to the previously tested one.

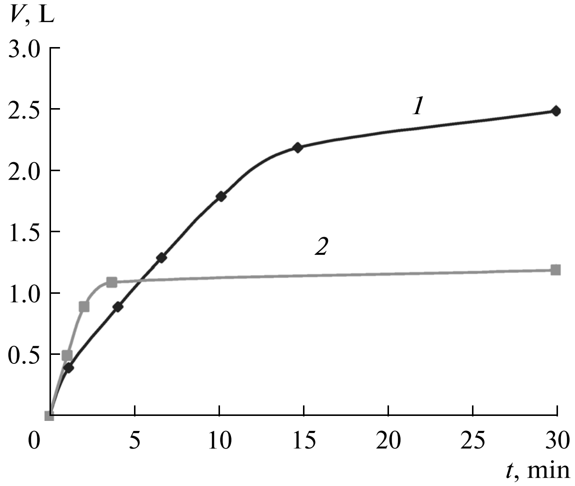
However, variation of the temperature (run 3) or the Al : Cr molar ratio (run 4) can result in a catalyst with a high hexene-1 selectivity (more than 86 wt %) and quite a good activity on the order of 629 $g_{hexene\text{-}1} \times (g_{Cr}\,0.5\ h)^{-1}$.

Comparison of the results for CS3 and CS4 [18] shows again that the change of the ligand leads to an increase in the amount of the product polyethylene and to almost complete disappearance of the oligomerization products (as low as 8 wt % hexene-1 and a trace amount of octene-1).

From these results of the comparison of the catalysts, it can be concluded that the change of the N-donor ligand affects the charge of the central ion, thereby leading to the preferred formation of active sites responsible for polymerization.

Influence of Chlorinated Cocatalyst on the Behavior of Catalyst System

As seen from the table, the replacement of triethylaluminum by the chlorine-containing organoaluminum compound for the binary system (CS4) leads to the formation of exclusively polymerization-mediating active sites, since no oligomers, even in trace amounts, were detected in the reaction mixture. At the same time, intro-



Ethylene uptake curves *1* and *2*. Experimental conditions: solvent, toluene; Al : Cr = 300; L : Cr = 1.5 (by mole); *P* = 3 MPa; 60°C; and reaction time, 30 min.

ducing an N-donor ligand into this system leads to results that are almost identical to those for CS3.

Influence of the PNP Ligand on the Behavior of Catalyst Systems

As shown by the experimental data, the introduction of an organophosphorus ligand of the PNP type into the test catalyst system can lead to quite unexpected results. The data in the table show that the introduction of PNP decreases the activity of the system and leads to the formation of active centers responsible for the polymerization reaction.

The figure shows rate curves for the catalyst system stabilized by the PNP ligand. No curves are presented for the system stabilized by the N-donor ligand PyH because they have a pattern similar to that reported in the literature [18] for the $Cr(acac)_3$–$AlEt_3$–2,5-DMP catalyst system. As can be seen, there are no induction periods for the binary $Cr(acac)_3/MAO$ (curve *1*) and the ternary $Cr(acac)_3/MAO/(Ph_2P)_2NCy$ (curve *2*) catalyst systems; the reaction starts immediately after introducing the cocatalyst into the reactor. During the first minute, the rates of both reactions are almost equal (slopes are the same), but then curve *1* shows that the rate is reduced and the system operates more stably and for a longer time (almost 15 min) Curve *2* shows that the reaction rate remains unchanged, with the deactivation of the system taking place as early as after the fourth minute.

It is not possible to compare CS6 and CS7 in the activity for hexene-1 because of its absence as a product for CS7; however, of all the catalysts tested, CS6 actually exhibits the highest activity for hexene-1, although its selectivity is on the same level with that of CS1 and CS2 (run 2).

Thus, the kinetic features of ethylene oligomerization has been first studied in the presence of the $Cr(acac)_3/AlEt_3/PyH$, $Cr(acac)_3/AlEt_3/PyH/CCl_4$, $Cr(acac)_3/AlEtCl_2$, $Cr(acac)_3/AlEtCl_2/PyH$, $Cr(acac)_3/MAO/(Ph_2P)_2NCy$, $Cr(acac)_3/MAO$, and $Cr(acac)_3/AlEt_3$ catalyst systems. It has been found that the $Cr(acac)_3/AlEt_3/PyH$ (molar ratio 1 : 20 : 3) system exhibits the highest selectivity and activity at 40°C and an ethylene pressure of 3MPa. The yield of hexene-1 was 86 wt % on an ethylene basis and the catalyst activity approached a value of 629 $g_{hexene\text{-}1}$ $(g_{Cr}\ 0.5h)^{-1}$.

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