Accepted Manuscript

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PII:S0926-860X(14)00057-XDOI:http://dx.doi.org/doi:10.1016/j.apcata.2014.01.051Reference:APCATA 14689To appear in:Applied Catalysis A: GeneralReceived date:30-9-2013Received date:30-9-2014

 Revised date:
 22-1-2014

 Accepted date:
 29-1-2014

Please cite this article as: Decene formation in ethylene trimerization reaction catalyzed by Cr-pyrrole system, *Applied Catalysis A, General* (2014), http://dx.doi.org/10.1016/j.apcata.2014.01.051

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Decene formation in ethylene trimerization reaction catalyzed by Crpyrrole system

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Abstract

Decene formation in the ethylene trimerization reaction was studied using a chromium(III) 2-ethylhexanoate/2,5dimethylpyrrole/triethylaluminum/diethylaluminum chloride catalyst system. Kinetic investigations revealed that some decene formation reactions did not depend on 1-hexene concentration, because 1-hexene and catalyst may react with ethylene before dissociation of 1-hexene – catalyst complex after 1-hexene formation. The results demonstrated that decene formation is an intrinsic part of the trimerization reaction mechanism. It was also shown that a stepwise elimination mechanism for the decomposition of the chromacycloheptane intermediate cannot explain the observed product distribution. The dependencies found allow selection of appropriate conditions for low or high decene formation in the ethylene trimerization reaction.

Keywords: Ethylene trimerization, Cr-pyrrole catalyst, metallacyclic mechanism, co-trimerization

1. Introduction

The ethylene trimerization reaction predominantly produces 1-hexene, which is chiefly used as a comonomer in polyethylene production. The reaction, which has been applied industrially by Chevron Phillips since 2004, is catalyzed by transition metal complexes which are typically chromium-based and activated by organoaluminum compounds. Comprehensive reviews on trimerization catalysts and the mechanism of the reaction have been published [1-3].

It is generally accepted that the reaction mechanism includes the formation of metallacyclic intermediates. The basic mechanism proposed by Briggs [4] (Scheme 1) was later supported by experimental [5,6] and theoretical [7,8] findings. It involves the coordination of two ethylene

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molecules to the catalyst center, followed by metallacyclopentane formation. A metallacycloheptane is then formed by expansion of the ring with a third ethylene molecule. The metallacycloheptane presumably undergoes β -elimination and reductive elimination, which results in 1-hexene formation and regeneration of the catalyst. An alternative explanation suggests a concerted 3,7-hydrogen shift in the metallacycloheptane leading to the same product.

By-products of the reaction, usually about 10% in total, include 1-butene, 1-octene, internal hexenes, decenes, and higher olefins. 1-Butene may be formed due to non-selective oligomerization, or from the metallacyclopentane. 1-Octene is believed to be formed due to further metallacycle expansion to metallacyclononane, which also undergoes reactions analogous to the metallacycloheptane. Decene isomers are formed in a co-trimerization reaction of 1-hexene and two ethylene molecules [9,10]. Decenes are often the most significant by-products in the reaction, regardless of the catalyst used. [1,9–11]. Heavier olefins can be formed through other co-trimerization reactions [10].



Scheme 1. Ethylene trimerization mechanism.

Most kinetics studies of the ethylene trimerization reaction have considered the formation of the main product, 1-hexene, or studied the total ethylene consumption or the catalyst productivity [11-16]. Details of the decene formation kinetics in the ethylene trimerization reaction remain unknown. We have not found studies devoted to the topic, although there are papers that consider the formation of co-trimerization products using various conditions and catalysts [6,10,17]. This work was intended to investigate the key features of decene formation kinetics in the ethylene

trimerization reaction, as it affects the 1-hexene selectivity in the reaction. These data could also help to increase the understanding of the reaction mechanism.

2. Experimental

2.1. Materials

Chromium(III) 2-ethylhexanoate (Cr(EH)₃) was prepared by a known method from aqueous chromium(III) chloride and sodium 2-ethylhexanoate [18], but the final drying with ethylhexanoic acid was carried out at 200° C and 200 Pa, in order to maximize the associated water removal. A 25% solution of triethylaluminum (TEA) in toluene and 2,5-dimethylpyrrole (DMP) were purchased from Aldrich. 1-Hexene, 1-octene and 1-decene for standards and diethylaluminum chloride (DEAC) (1,0 M solution in hexanes) were purchased from Acros Organics. These reagents were used without further purification. Hydrocarbon solvents were refluxed over Na and NaH, and freshly distilled before use. The polymer-grade ethylene was further purified by passing it through a steel bottle filled with activated molecular sieves 5Å.

2.2. Instruments

A stainless steel jacketed reactor (0.5 l) equipped with an overhead stirrer, thermostat, pressure and temperature sensors, nitrogen line, hydrogen line, bottom needle valve, and ethylene dosing line with a flow meter was used for the study. A computer-based control system was used to control the stirrer speed, reactor and jacket temperatures, flow rate of ethylene, and other parameters.

Reaction products were analyzed using gas chromatography (Agilent 7890A with FIDdetector, Agilent 7890A with 5975C mass-selective detector) with HP-5 capillary column. NMR spectra were recorded in CDCl₃ using Bruker Avance III 400 (400 MHz) spectrometer.

2.3. Procedures

2.3.1. Catalyst preparation

The catalyst was prepared according to a previously described enhanced method [19] by using $Cr(EH)_3/DMP/TEA/DEAC$ in the ratio 1 : 5 : 36 : 14. $Cr(EH)_3$ (29 mg, 60 µmol) and DMP (29 mg, 305 µmol) were placed in a flask. Then 5 ml of ethylbenzene was added. The mixture of 1.15 ml of

1.9 M TEA solution in toluene (2.2 mmol) and 0.84 ml of 1 M heptane solution of DEAC (0.84 mmol) was microwave-irradiated in a polypropylene syringe using CEM MARS 5 microwave oven at rated power 400W for 6 minutes (with little heating). Then, within 30 seconds after the end of the irradiation, the TEA/DEAC solution was added to the mixture of $Cr(EH)_3$ and DMP in ethylbenzene. After 15 min since TEA/DEAC addition, solvents were removed in vacuo at 40 °C. The residue in the flask was diluted with 20 ml of cyclohexane to obtain the catalyst solution (0.003 M Cr).

2.3.2. Ethylene trimerization

The reactor was dried at 120 °C under nitrogen flow, and then evacuated and filled with hydrogen. Cyclohexane (200 ml) was added with a dosing pump under a hydrogen atmosphere. The solvent was saturated with hydrogen at atmospheric pressure and the desired reaction temperature. The catalyst solution in cyclohexane (2 ml, 6 μ mol Cr) was injected into the reactor via a syringe under hydrogen counter flow. Ethylene was swiftly added to build up the desired pressure, and then ethylene was dosed to maintain the pressure constant. Reactor temperature was maintained at the set value by an automated system. Sampling was performed from the bottom valve during the reaction. The pressure was reduced and the reaction mixture was unloaded after 60 min.

During each run, seven samples were collected for GC analysis at 2, 5, 10, 15, 30, 45 and 60 min after ethylene addition (sample volume 1-1.5 ml).

2.3.3. Distillation of decene fraction

The combined reaction mixtures were exposed to air for 2 h, which resulted in precipitation of small amount of brown solids. These were filtered off, and the filtrate was distilled using a laboratory distillation column to obtain a bottom residue containing about 50% cyclohexane and hexenes, 40% decenes, and 10% heavy products. The residue was additionally distilled using a laboratory column *in vacuo*, and a fraction with the boiling point $108-112^{\circ}C/18$ kPa was collected. GC/MS analysis confirmed a content of 94% C₁₀ olefins. The sample also contained about 2% of cyclohexane, 1.8% of ethylbenzene and 1.3% of 1-octene.

3. Results and discussion

3.1. The scope of the experiments

We performed a series of trimerization runs, varying the ethylene pressure and reaction temperature. Our measurements allowed us to determine the average reaction rate between sampling points for every product, including the decene isomers. The average reaction rates for 1-hexene and the decenes at 15–30 min intervals were calculated from GC data for all runs. The results are listed in Table 1.

Table 1

				Average	formation rate
		$P(C_2H_4),$	Activity at 30 min,	over 15-3	0 min interval,
Run	T, °C	MPa	$kg \cdot (g Cr \cdot h)^{-1}$	TOF, mo	$ol (mol Cr \cdot s)^{-1}$
				$1 - C_6$	C_{10}^{b}
1	25	0.8	72.0	10.9	0.32
2	40	0.8	132.7	15.8	0.32
3	50	0.4	79.4	11.1	0.42
4	50	0.8	131.8	20.0	0.51
5	50	1.2	170.9	25.9	0.93
6	50	1.5	216.2	33.0	0.76
7	50	2.0	277.7	40.1	1.35
8	65	0.4	25.7	3.73	0.13
9	65	0.6	56.2	8.65	0.33
10	65	0.8	84.4	16.2	0.50
11	65	1.0	166.7	28.2	1.18
12	65	1.2	156.0	25.9	1.11
13	65	1.45	156.0	25.3	1.00

Reaction rates at 15–30 min intervals.^a

^a General conditions: 6 μmol Cr (0.03 mmol/L), cyclohexane, Cr(EH)₃:DMP:TEA:DEAC 1:5:36:14.

Cr(EH)₃:DMP:TEA:DEAC 1:5:30 ^b Total decenes formation rate

The typical time course of product formation during the ethylene trimerization reaction is shown in Fig. 1.



Fig. 1. Product formation versus time during the ethylene trimerization reaction, run 6. In order to present a concise diagram, 1-hexene and decene/heavy olefin amounts were scaled down by a factor of 100 and 10, respectively.

3.2. Identification of the decenes

Scheme 2 illustrates pathways for decene formation in accordance with the metallacycle mechanism. Seven main decenes were formed, including 1-decene (6), 4-decene (7) and 5-decene (5). GC analysis could not distinguish 5 and 7, so only six major decene peaks were discerned by GC/MS.



Scheme 2. Mechanism of decenes formation.

The decenes were distilled from the reaction products for identification purposes. The fraction contained about 94% decenes, according to GC/MS analysis. The mixture also contained small amounts of 1-octene (1.3%) and ethylbenzene (1.8%) which had been used in the catalyst preparation. The remainder was mostly cyclohexane solvent. Decenes were identified by ¹³C NMR analysis of the decenes mixture. The Distortionless Enhancement by Polarization Transfer (DEPT) method was used to establish the signal positions of the vinyl CH₂ and CH carbons, as well as the aliphatic CH (branching points). 5-Methyl-1-nonene (1) and *cis*-4-decene (7) were synthesized by Bercaw et al [10], and ¹³C NMR data were given. It was found that *cis*-4-decene (7) was the major isomer among linear olefins **5**, **6** and **7**, and only small amount of **5** was found (Fig. 2). The *trans*-

isomer of **7** was not detected. 1-Decene (**6**) and 5-methylene-nonane (**2**) were also identified using the NIST mass spectral database. 1-Decene was additionally confirmed by comparison of the retention time with a standard solution. The vinyl signals of 1-octene were indistinguishable from the corresponding 1-decene signals, which was responsible for about 50% increase in the signal intensity of the vinyl carbons of **6**. The NMR-based identification was in agreement with the GC/MS data. The results are given in the Table 2. All expected isomers were found; there was no indication of other isomers in the NMR spectra. Only traces of other C_{10} olefin isomers were detected by GC/MS.

Table 2

Decene	Content in C_{10} , %	Signal 1			Signal 2		Signal 3			
	(GC)	Group	δ, ppm	rel. int.	Group	δ, ppm	rel. int.	Group	δ, ppm	rel. int.
1	33	<u>C</u> H ₂ =CH-	114.1 ^a	5.1	CH₂= <u>C</u> H-	139.5 ^a	3.8	CH2CH(CH3)CH2	32.5 ^a	5.7
2	11 ^b	<u>C</u> H ₂ =C(C ₄ H ₉) ₂	108.6 ^c	1.4	CH ₂ = <u>C</u> (C ₄ H ₉) ₂	150.2 ^c	0.6	-		
3	23	<u>C</u> H₂=CH-CH	114.0	3.1	СН ₂ = <u>С</u> Н-СН	143.8	2.7	CH₂=CH <u>C</u> H	44.2	2.1
4	18	<u>C</u> H₂=CH-CH₂CH	115.6	2.7	CH ₂ =CHCH ₂ CH	137.8	1.8	CH2=CHCH2CH	39.0	2.8
5	-	-			$CH_2CH=CHCH_2$	130.4 ^d	-	-		
6	3 ^b	<u>C</u> H ₂ =CH-	114.2 ^d	1.0	CH₂= <u>C</u> H-	139.3 ^d	0.5	-		
					CH.CH=CHCH.	130.0 ^a	1.1			
7	12 ^e				Ch <u>e</u> ne <u>c</u> hen <u>e</u>	130.5 ^a	1.1	-		

Identification of the decenes using ¹³C NMR and GC/MS data.

^a Confirmed by comparison with data for the pure compound in [10]

^bConfirmed by comparison with NIST mass spectra database

^c Confirmed by comparison with data from [20]

^d Confirmed by comparison with SDBS NMR database

^e Together with **5**; less than 1% of **5** in the mixture according to NMR data



Fig. 2. Fragment of the ¹³C NMR spectra of the decenes mixture.

3.3. 1-Hexene concentration dependence of decene formation rate

The GC data were obtained for every sample taken during the reaction, so content of every decene isomer was measured. The average formation rate between sampling in the form of TOF for every isomer was calculated as a change in the decene isomer molar content per molar amount of the catalyst and the time interval. It was previously shown that addition of 1-hexene to the reaction mixture results in elevated amount of decenes formed [9]. It was also demonstrated by Do and coworkers that adding 1-heptene leads to olefins C_{11} [10]. As decenes are formed from 1-hexene, it was assumed that the decene formation rate would be dependent on 1-hexene concentration. Indeed, during the reaction, it was found that the decene formation rate increased proportionally to the 1-hexene concentration, calculated as an average value for the same time intervals. Good linearity was observed in most cases after the initial period (5–10 min of the reaction). Examples are shown in Fig. 3. However, at low 1-hexene concentrations, the decene formation rate did not stay close to zero, but rather remained near a constant value. This was true for all decenes **1–7** under different reaction conditions. The constant component of the formation rate on 1-hexene concentration. The trend lines intercepted the vertical axis above zero.

We can conclude that there are two groups of reactions that lead to decene formation: one that is first-order dependent on 1-hexene concentration, and a second group that is independent of 1-hexene concentration.

The decenes formation rate dependence values shown in Fig. 3 allowed the determination of conditional constants for the hexene-dependent and hexene-independent formation reactions of every isomer. The hexene-dependent conditional constants were determined from the slopes of the trend lines. The hexene-independent constants were established as the vertical axis intercepts by the trend lines.

The following equations were used for hexene-dependent (1) and hexene-independent reactions (2):

 $d[C_{10}]/dt = k'[1-C_6][Cr]$ $d[C_{10}]/dt = k''[Cr]$



where $[C_{10}]$ is the concentration of decenes **1–7** (mol L⁻¹); [Cr] is the concentration of chromium (mol L⁻¹); and [1-C₆] is the 1-hexene concentration, (mol L⁻¹). The conditional constants k' (L mol⁻¹ s⁻¹) and k'' (s⁻¹) include the ethylene pressure, which was kept constant during the runs.



Fig. 3. Decenes **1–7** formation rates under various conditions: a) run 1, 25 °C, 0.8 MPa; b) run 6, 50 °C, 1.5 MPa; c) run 10, 65 °C, 0.8 MPa.

3.4. Ethylene pressure dependence of decenes formation rates

The conditional constants k' and k" were found to be dependent on the ethylene pressure. Plots of the ethylene pressure dependence at 50 and 65° C are shown in Figs. 4 and 5.



Fig. 4. Dependence of the conditional constants for decenes formation on ethylene pressure at 50°C:a) hexene-dependent reactions and b) hexene-independent reactions.



Fig. 5. Dependence of the conditional constants of decenes formation on ethylene pressure at 65°C:a) hexene-dependent reactions and b) hexene-independent reactions.

At 50°C, decenes formation in hexene-dependent reactions was negatively dependent on the ethylene pressure, which indicated inhibition by ethylene (Fig. 4, a). At 65°C, a similar dependence was observed (Fig.5, a) for ethylene pressure above 1.0 MPa (Table 1, entries 11–13), as 1-hexene formation occurred at almost the same rate. That is in accordance with the observations that 1-butene addition at the initial stage of the reaction results not only in the increased octenes formation due to 1-butene co-trimerization, but also causes decreased decenes formation [9]. At lower pressure, the 1-hexene formation rate showed approximately second-order dependence on ethylene pressure (Table 1, runs 8-11), and the hexene-dependent decene formation rate revealed nearly first-order dependence with respect to ethylene. We believe that the difference between **Fig. 5**, **a** and **Fig. 4**, **a** is

caused by different kinetics of trimerization reaction at 50 °C and 65 °C, because at 50 °C 1-hexene formation is nearly linear-dependent on ethylene pressure (Table 1, runs 3-7). The detailed investigation of the 1-hexene and 1-octene formation at different temperatures is under way.

Hexene-independent reactions were approximately first-order dependent with respect to ethylene at both studied temperatures (Fig. 4, b and Fig. 5, b). This indicated the absence of concurrent inhibition by ethylene for this group of reactions.

3.5. Mechanism of chromacycloheptane decomposition

Generally, the decene ratios under various reaction conditions for the hexene-dependent and the hexene-independent reactions were similar (Table 3). All six decenes were present in both cases, which meant that at least two of the routes I, II, and III (Scheme 2) were implemented in both groups of reactions.

Table 3

Decene	Share of total decenes,	Share of total decenes,		
	hexene-dependent reactions, %	hexene-independent reactions, %		
1	38.2–57.8	23.6–34.3		
2	8.2–12.5	9.3-12.9		
3	12.7–20.4	24.5-30.2		
4	12.3–16.9	17.8–23.5		
5+7	4.6–11.4	9.0–11.7		
6	3.4–7.2	0.6–2.3		

Decenes 1-7 formation ratios in the hexene-dependent and -independent reactions.

The formation of **1** and **2** was highly preferred for the diphosphinoamine (PNP) catalyst, which resulted in 95% total selectivity for these decenes [17]. With our catalyst, compound **1** also prevailed in both the hexene-dependent and hexene-independent reactions. However, its share did not exceed 60% under any of the conditions used.

The route III should have little impact on the distribution of the products. Otherwise, the subsequent insertion of ethylene would have resulted in higher share of olefins **5-7**, because in the route III they are formed after ethylene insertion from the less hindered unsubstituted side. The route II is unlikely to be hexene-independent, as 1-hexene insertion here should compete with ethylene insertion. Therefore, we may conclude that the route I is the major pathway, especially for the hexene-independent reactions, as the olefins **1-4** make up more than 85% of the products in that case. The isomers **5-7** are formed only via the route III in the case of hexene-independent reactions. The

presence of route II in the hexene-dependent reactions leads to higher amount of **6**, and much more pronounced increase of isomer **1** formation. This indicates that unsubstituted chromacyclopentane is preferably expanded by 1,2-insertion of 1-hexene rather 2,1-insertion. Both 1-hexene insertions are much slower than the competing ethylene insertion leading to 1-hexene formation. The same preference was observed in the case of Cr-PNP catalyst [10,17].

Two possible mechanisms for 1-hexene release from the chromacycloheptane intermediate have been suggested: a two-step process involving β -elimination followed by reductive elimination, and a one-step concerted 3,7-hydrogen shift [2] (Scheme 3). The computational studies [7,21] indicate that the concerted shift is more energetically favorable for chromium trimerization catalysts. However, no experimental evidence in favor of one of these mechanisms has been published yet.

Both of these proposed reaction pathways may be stereoselective, and therefore, the structure of the substituted chromacycloheptane can determine the structure of the product.



Scheme 3. Possible mechanisms of 1-hexene formation from the chromacycloheptane.





Our analysis of the decenes mixture allowed us identify and measure the ratio of the linear decenes **5**, **6** and **7**, which contribute about 15% of the decenes composition. In the previous work [10] only 3% of the linear decenes was found in the mixture, which made their identification and quantification difficult. The difference should be attributed to the different catalyst systems used in this work and by authors of [10]. We can use the known composition of these decenes in our mechanistic investigations. Scheme 4 illustrates the formation of decenes **5**, **6** and **7** according to the stepwise mechanism of β -elimination followed by reductive elimination. Structures **a** and **b** are possible isomers of chromacycloheptane, with yet unknown substituents on the chromium centre.

 β -Elimination can be either stereo- and regioselective (E2 mechanism), or regioselective only (E1 mechanism). In the latter case, the most substituted olefins should be formed. This was disproven by the experimental data, as α -olefins prevailed in the C₁₀ mixture.

During β-elimination according to the E2 mechanism, Cr should be in the same plane with the hydrogen in position 3 or 6 and carbons C(2) and C(3), or C(6) and C(7), respectively. In the case of the exocyclic elimination, Cr should be coplanar with hydrogen from the alpha-methylene group. For the 2-substituted chromacycloheptane (Scheme 4) β-elimination from position 6 is preferable or at least comparable with elimination from position 3, because there is no hindrance for elimination from position 6. Consequently, the proportion of **6** should be equal to or higher than that of **5**. This was in accordance with the experimental data, because ¹³C NMR showed very small signal for **5** (Fig. 2). The isomer **7** was formed due to the exocyclic hydrogen elimination (or the hydrogen transfer). The exocyclic reaction should have less structural limitations, so the product **7** should prevail among linear decenes. This was also in accordance with the experimental data. The exocyclic β-elimination should lead to a mixture of *cis* and *trans* isomers of **7**, with excess of the *trans*-olefin, which is typical for E2 reaction. However, we found that the only product of the exocyclic reaction was *cis*-4-decene. The corresponding *trans* isomer would have been easily distinguished in the ¹³C NMR spectra, but no such signals were found.

Such a high selectivity cannot be explained using β -elimination mechanism, especially for the structure **a** with pseudo-equatorial orientation of the butyl substituent. That is an experimental proof that the stepwise elimination is unlikely to be the mechanism for substituted chromacycloheptane decomposition. Other mechanisms, such as the concerted hydrogen shift, may better explain the observed selectivity, which is in accordance with the computational data [7,21]. However, the mechanism of chromacycloheptane decomposition requires further investigation.

The concerted hydrogen shift mechanism is an intramolecular reaction, unlike the stepwise elimination. One may suppose that if the reaction indeed proceeds via concerted hydrogen shift, then the nature of the catalyst center should affect this stage more than the chemical environment. It is not likely that this stage can be influenced by any additives, provided they do not alter the catalyst species.

3.6. Temperature dependence and decene formation pathways

The hexene-independent decene formation reactions, which were not inhibited by ethylene, should have a non-limiting stage of 1-hexene coordination to the catalyst. The experimental data demonstrated that this stage remained non-limiting even at very low 1-hexene concentration in the reaction mixture (see 3.3, Fig. 3). It is reasonable to consider that there is no difference in the following stages between the hexene-dependent and the hexene-independent reactions after the

formation of the butyl-substituted chromacyclopentane (see 3.2, Scheme 2). Consequently, the difference should be connected with the previous stage of 1-hexene and ethylene coordination to the catalyst.

The coordination of the 1-hexene double bond to the chromium center was predicted as the final stage of the catalytic cycle by the computational study of the chromium-pyrrole system [7]. Then formed 1-hexene should be then released from the catalyst, which concludes the catalytic cycle. We suggest that there is another way for the transformation of the catalyst – 1-hexene complex, where ethylene molecule coordinates to it before 1-hexene is released. This results in formation of substituted chromacyclopentanes, which in turn transform into decene isomers.

Taking into account the fact that 1-hexene release from the catalyst is very fast and usually non-limiting stage in the catalytic cycle, we can conclude that the catalyst – 1-hexene complex is quite unstable. Its decomposition should accelerate with an increase in temperature. Therefore, the shortened lifetime of the complex at a higher temperature will result in lower probability of ethylene coordination leading to decenes, and the hexene-independent reactions will be suppressed.

Indeed, we found that the hexene-independent reactions slowed when the temperature was increased (Fig. 6). In contrast, the hexene-dependent reactions accelerated as the temperature increased (Fig. 7). We can conclude that the pathways of the hexene-independent and hexene-dependent reactions are different. The competition between ethylene and hexene in the hexene-dependent decene formation reactions is in accordance with substitution of one of the ethylene molecules with 1-hexene in the metallacyclic mechanism (Schemes 1 and 2).



Fig. 6. Temperature dependence of the conditional constants for hexene-independent decenes formation at 0.8 MPa ethylene.



Fig. 7. Temperature dependence of the conditional constants for hexene-dependent decenes formation at 0.8 MPa ethylene.

The results discussed above allow us to suggest new details of the mechanism of by-product formation in the ethylene trimerization reaction (Scheme 5). It should be noted that hexeneindependent decene formation reactions cannot be fully avoided, because they presumably occur due to ethylene coordination to the complex of the newly formed 1-hexene and the catalyst. Therefore, these reactions are an intrinsic part of the ethylene trimerization mechanism.





Decenes formation during the ethylene trimerization reaction is a complex process. It is affected by the ethylene pressure, 1-hexene concentration, temperature, and other factors. Decenes formation can be inhibited by keeping the ethylene pressure high and minimizing the 1-hexene concentration. However, this will affect only the hexene-dependent reactions. The hexene-independent formation of decenes accelerates with increasing ethylene pressure, but slows at higher temperatures. In order to achieve higher 1-hexene selectivity, one should keep temperature high in order to minimize hexene-independent by-product formation, while maintaining low 1-hexene concentration and high ethylene pressure to suppress hexene-dependent decene formation. In contrast, if increased decenes formation is desired, one should provide high 1-hexene concentration and use low ethylene pressure during the reaction. In that case, the temperature should be kept high but not excessively to avoid suppression of hexene-independent decene formation reactions.

4. Conclusions

We investigated decenes formation in the ethylene trimerization reaction using a chromiumpyrrole catalyst. The reaction products were identified, and it was shown that all major decene isomers were formed in accordance with the metallacycle mechanism. Two groups of reactions leading to decenes were found: those with first-order dependence on 1-hexene concentration, and those which were independent of 1-hexene concentration. The hexene-dependent reactions accelerated with an increase in temperature, whereas the hexene-independent reactions slowed. The hexene-independent formation of decenes was explained as arising from coordination of ethylene to the catalyst still in complex with just formed 1-hexene. It was shown that the stepwise elimination mechanism of chromacycloheptane decomposition cannot explain the observed product distribution, so an alternative hydrogen shift mechanism should be considered. The results help identify the optimal conditions for low or high decene formation in ethylene trimerization reaction.

5. Acknowledgement

The authors thank Mr. Stanislav Kiselev for his help with NMR spectra, and Dr. Denis Lenev for his comments on the paper. The authors also thank SIBUR Holding, Ltd., for financing the research and approving the publication of this article.

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Highlights

- Isomeric decenes were formed in accordance with metallacyclic mechanism
- There are hexene-dependent and hexene-independent decene formation pathways
- Hexene-independent pathways seem to start before 1-hexene release from the catalyst
- The stepwise elimination mechanism is inconsistent with the product distribution

[22]

