



Editor Choice Paper

Reaction kinetics of the ethene tetramerization catalyst system $\text{CrCl}_3(\text{THF})_3$, $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ and MAO: The unexpected and unusual formation of odd-numbered 1-olefins

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ABSTRACT

This paper describes a kinetic investigation of the ethene tetramerization catalyst system comprising $\text{CrCl}_3(\text{THF})_3$, a bis(diphenylphosphino)isopropylamine $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ as ligand and MAO as catalyst activator. The main focus of the experimental study lied on the influence of the ligand to chromium molar ratio on the catalyst performance and the selectivity towards 1-octene. It was found that a sub-stoichiometric ligand/Cr ratio leads to a Schulz–Flory product distribution, while unusual odd-numbered 1-olefins as by-products were formed.

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1. Introduction

Linear alpha olefins (LAOs) are useful and versatile intermediates for many industrially important substances like co-monomers for HDPE or LLDPE, alcohols, aldehydes, carboxylic acids or sulfonates. Conventional full range producers of LAOs, which obtain a wide product distribution, have to meet a formidable challenge to match the market demand. The reason is that each market segment served exhibits a very different behavior in terms of market size and growth, geography, fragmentation etc. The conventional technologies, like the Shell Higher Olefin Process (SHOP) or the state-of-the-art α -Sablin process, are based on an ethene insertion/ β -elimination mechanism via chain growth (Scheme 1) resulting in a Schulz–Flory product distribution [1].

Thus, the on-purpose production of the most economically viable LAOs, i.e. comonomer-grade 1-hexene and more recently

1-octene, appears highly desirable [2]. For selective ethene oligomerization routes, a ring mechanism is generally accepted, instead of the chain-growth pathway. In this ring mechanism, two ethene units coordinate at the catalytically active site and form a metallacyclopentane via oxidative coupling. Insertions of further ethene units result in larger metallacycles. Through β -elimination/reductive elimination the desired LAOs are released (Scheme 2) [3].

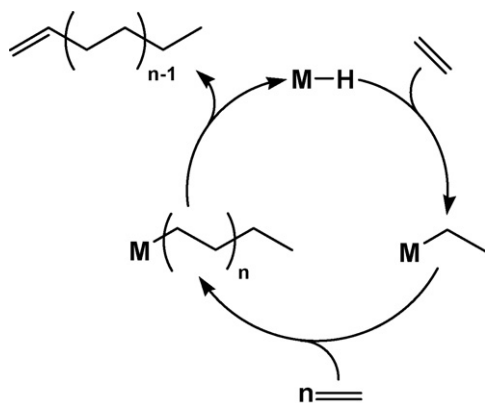
For the high selectivity to 1-hexene during ethene trimerization, the difference in the relative stability of the formed five- and seven-membered rings with respect to elimination is the determining factor of this mechanistic suggestion (Scheme 3) [2].

A mechanism for tetramerization of ethene to yield 1-octene, based on metallacycles as intermediates, requires discrimination between seven- and nine-membered rings. Some studies conclude that the generally accepted metallacyclic mechanism for the selective oligomerization cannot explain the selectivity to 1-octene (Scheme 4) [4,5].

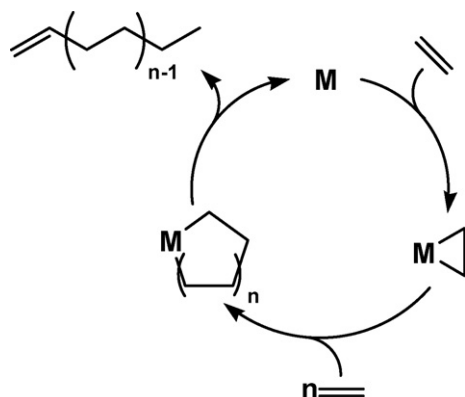
If the tetramerization is not explainable by the presented monometallic mechanism, alternatively a bimetallic mechanisms based on two chromium centers appears conceivable [6].

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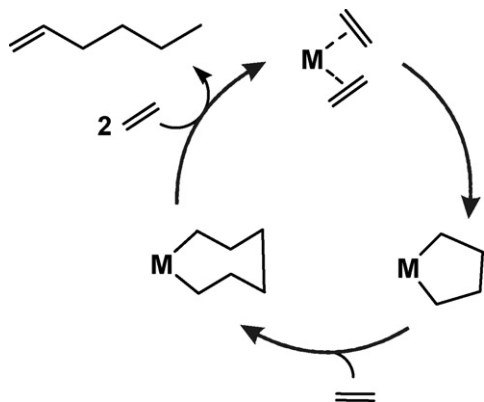
Scheme 1. Ethene oligomerization via a chain mechanism.



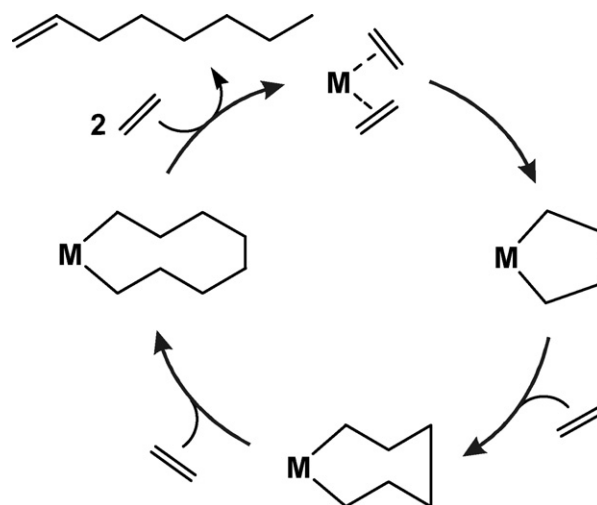
Scheme 2. Ethene oligomerization via a ring mechanism.

Nevertheless, in 2004 a catalyst system for selective ethene tetramerization was reported, using a modified bis(diarylphosphino)amine (PNP) chromium catalyst which gives up to 68 wt.% 1-octene along with 1-hexene as the main by-product [2k]. On the basis of these systems, ligand effects were investigated in detail. In general, more sterically hindered ligands favor trimerization over tetramerization. Methoxy substituents in ortho position of the aryl groups also have a strong effect of supporting trimerization. Nitrogen substituents exhibit a subtle influence which could not yet be fully rationalized [2].

Several publications [7] deal with kinetic investigations of these selective tri- and tetramerization catalysts, making an important contribution to the understanding of the catalytic mechanism with



Scheme 3. Ethene trimerization to 1-hexene.



Scheme 4. Ethene tetramerization to 1-octene.

the goal to optimize reactor design and process parameters, particularly with regard of an enhancement of activity and selectivity.

Walsh et al. [7b] investigated the reaction kinetics of the ethene tetramerization catalyst consisting of the pre-catalyst $\text{Cr}(\text{acac})_3$, $\text{Ph}_2\text{PN}(\text{tPr})\text{PPh}_2$ as ligand and MAO as activator. It was found that the initial reaction rate follows a typical Arrhenius behavior with an apparent activation energy of 64.6 kJ/(mol K) in the temperature range between 35 and 45 °C. However, the deactivation rate is strongly influenced by temperature.

A reaction rate model was developed to provide a good description of reaction performance and selectivity data, accounting for the effects of pressure, temperature and time on stream. Increased temperature and decreased pressure result in increased 1-hexene and decreased 1-octene selectivity, while time on stream-data indicate the occurrence of secondary incorporation reactions of 1-hexene and 1-octene. The typical ethene tetramerization reaction yields a complex mixture of olefins, such as predominantly 1-hexene and 1-octene and smaller quantities of C10 along with heavier alpha olefins. Additionally, small amounts of C6 cyclics such as methylene cyclopentane and methyl cyclopentane are formed as well as branched C10, C12 and C14 olefins which are produced by secondary co-oligomerization of 1-C6 and 1-C8. Odd numbered LAOs were not described as by-products.

Some discrepancies regarding the influence of ethene concentration are noteworthy.

For instance Manyik et al. [3b] and Yang et al. [7a] reported a second-order dependence on ethene concentration for two different chromium-based ethene trimerization catalyst systems. These results lead to the conclusion that the rate-determining step is the formation of a metallacyclopentane intermediate via two coordinated ethene molecules.

Contrary to these results, modeling studies carried out by van Rensburg et al. [5c] for a chromium-pyrrolyl catalyst support a first-order dependence with respect to ethene concentration. Blok et al. [5d] as well as Tobisch and Ziegler [5b] investigated theoretically the titanium-catalyzed trimerization mechanism and also identified the metallacycle growth as rate-determining step, consequently leading to a first-order dependency. Kuhlmann [7d] found in his studies on the Cr/PNP-system a first-order ethene dependency for the trimerization reaction and a second-order dependency for the tetramerization. This results in an overall reaction order of 1.71, which is in good agreement with the observed non-integer reaction order of 1.57 by Walsh et al. [7b], suggesting a competition of two different pathways for tri- and tetramerization.

To the best of our knowledge, in these and other publications in this field the effect of ligand/Cr molar ratios on catalytic performance was investigated only in one paper from Jiang et al. [7c]. It was described that the ligand/Cr molar ratio has significant effects on catalytic activity and selectivity in chromium-catalyzed ethene tetramerization to 1-octene. It was shown that an increase of the ligand/Cr molar ratio from 1 to 4 resulted in a decrease in catalytic activity. The highest selectivity towards 1-octene was achieved with a ligand/Cr molar ratio of 2. The authors explained this tentatively by the formation of active Cr species via the interaction with other catalytic components 'of proper ratios'. Lower ligand/Cr molar ratios than 1 were not investigated.

We here report the results of a kinetic study carried out on the bis(diphenylphosphino)isopropylamine $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2/\text{CrCl}_3(\text{THF})_3/\text{MAO}$ ethene tetramerization catalyst system. More specifically, the ligand to Cr-molar ratio was investigated in detail. It was found that this ratio has a remarkable influence on the product distribution.

2. Experimental

2.1. Materials

All chemicals were handled either in a glove box or under inert argon atmosphere by using standard Schlenk techniques. $\text{CrCl}_3(\text{THF})_3$ (97% purity) was obtained from Sigma-Aldrich and used without further purification. MAO solution (10 wt.% in toluene) was delivered by Sigma-Aldrich. The bis(diphenylphosphino)isopropylamine ligand was synthesized according to a published procedure [2k]. Toluene (>99.9% purity) was obtained by Merck Chemicals and was dried over sodium with benzophenone and was then distilled in inert gas atmosphere (N_2).

Argon 5.0 and ethene 3.0 were purchased from Linde Gas and used as received.

2.2. Reactor equipment and ethene oligomerization procedure

The syntheses were performed in a 0.3 l Parr autoclave equipped with a hollow shaft gas-entrainment stirrer. The ethene supply was maintained by an aluminum pressurized gas cylinder on a balance to monitor the ethene consumption over time by means of a computerized data acquisition system. The autoclave's temperature was measured by a thermocouple inside the reactor's liquid phase and controlled by an electrical heating jacket and a water cooling-coil, submerged in the liquid phase. The autoclave could be depressurized and evacuated by means of a rotary vane vacuum pump (10^{-1} mbar). For inertization, a low pressure argon supply (1.5 bar absolute) was used.

A complete P&ID-schematic of the experimental test rig is given in Fig. 1.

Before conducting an experiment, the reactor was heated to 100°C at reduced pressure for several hours to eliminate traces of water, oxygen and oxygenated impurities. The reactor was then allowed to cool down to ambient temperature and the prepared catalyst solution was transferred to the evacuated reactor by means of the pressure differential to the argon inert atmosphere. The speed of the gas entrainment stirrer was set to 1000 rpm to exclude gas-to-liquid mass transfer limitations. This was verified earlier by separate measurements of the volumetric mass transfer coefficients (ethene into toluene) as a function of agitation speed. In the next step, the reactor was pressurized with ethene to 30 bar (absolute pressure). All reactions were performed at a constant reaction temperature of 50°C .

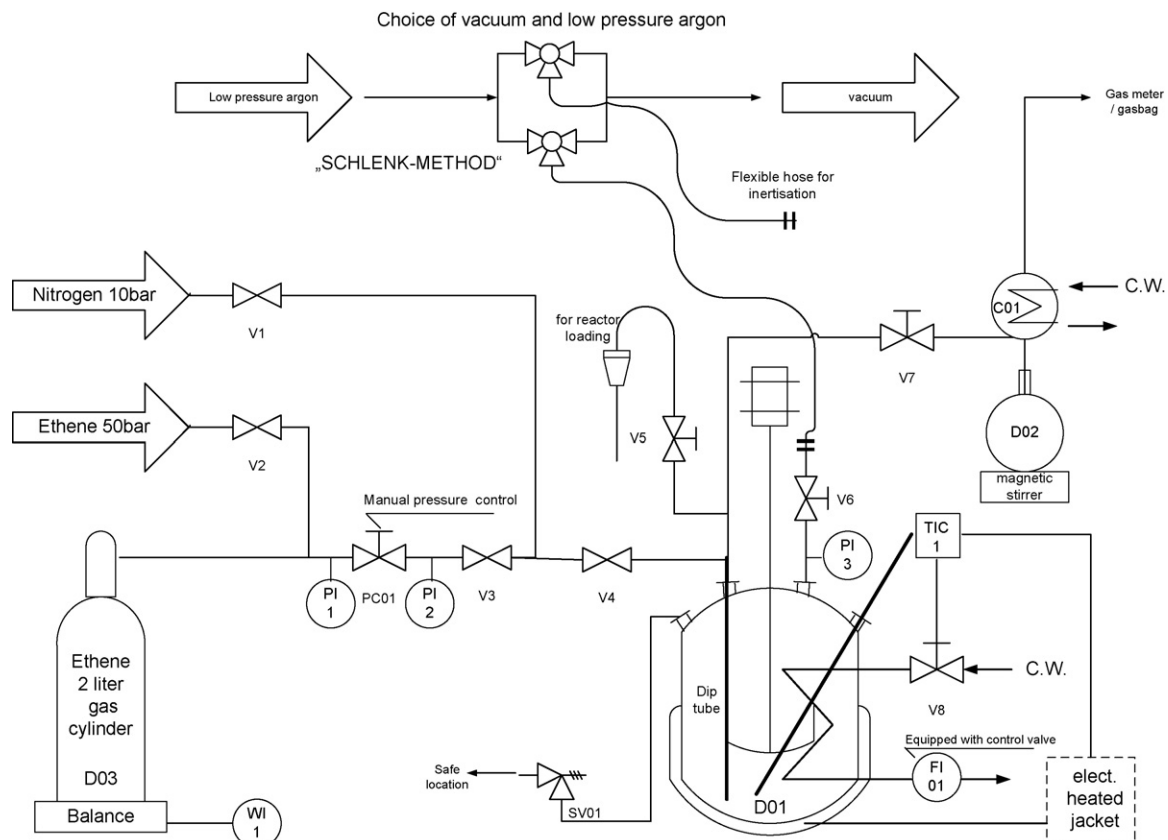


Fig. 1. Schematic of the 0.3l Parr kinetic test rig.

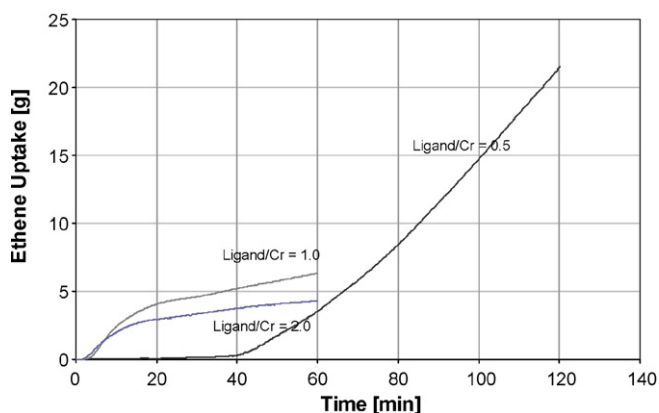


Fig. 2. Effect of ligand/Cr molar ratio on ethene uptake rate.

After the reaction, the reaction solution was discharged by transferring the liquid by means of the headspace pressure via the reactor's dip tube into a round-bottom flask with HCl-acidified water for catalyst quenching. The volume of the gaseous product phase was measured by a gas meter and collected completely in a gasbag.

The mass balance of the experiment was determined via quantification and GC–FID analysis of the gaseous and liquid products separately, followed by comparison to the ethene uptake data.

2.3. Catalyst preparation

All reactions were performed using 1 mmol/l Cr concentration and a MAO/Cr ratio of 150. In this investigation the ligand/Cr molar ratios were varied in the range from 0.25 to 2.0.

For the catalyst preparation, a suitable amount of the PNP ligand and $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, and $\text{CrCl}_3(\text{THF})_3$ was weighed in and charged to a Schlenk tube under inert atmosphere. A volume of 100 ml dried toluene was added and the solution was stirred by means of a magnetic stirrer. After dissolving Cr-compound and ligand, the required amount of MAO was added. The solution was immediately transferred to the reactor and the reaction was started by opening the ethene supply.

3. Results and discussion

3.1. Influence of the ligand/chromium ratio on reaction kinetics

In separate gas-to-liquid mass transfer experiments, the mass transfer coefficient of ethene to toluene was determined to be $k_{\text{La}} \geq 1100 \text{ h}^{-1}$ at 50 °C in the current experimental configuration, rendering the mass transport at least a factor of 100 faster than the characteristic time scale of the reaction. This was further supported by a kinetic model-based evaluation of the ethene

uptake curves in the absence of the reaction system, taking into account the temperature- and pressure-dependent equilibrium solubility of ethene in toluene. Clearly, the composition of the liquid phase changes with residence time as products are being formed. However, even if the phase transfer slowed down over time due to changing composition of the reaction mass, so does the tri-/tetramerization reaction itself, due to the observed catalyst deactivation. Therefore, the phase transfer is not expected to become competitive with the intrinsic kinetics of the chemical reaction.

Based on these considerations, the kinetic behavior of the chromium-catalyzed tetramerization reaction is reflected by the time characteristics of the ethene uptake curve.

This ethene uptake curve (Fig. 2), is not influenced by the ligand/Cr molar ratios above 1.0. In general, the time characteristics and the curvature of the obtained ethene uptake curves are qualitatively similar to the ones published by Walsh et al. [7b] at a ligand/Cr molar ratio of 1.35 and a temperature of 50 °C. Although other parameters, such as pressure, solvent, catalyst concentration or MAO/Cr ratio and a different catalyst preparation procedure (charging of the catalyst under ethene pressure) were applied, the measured curves show the typical induction period and the catalyst deactivation over time as described in [7b]. As shown in Table 1, the activity decreases significantly by doubling the ligand/Cr molar ratio from 1.0 to 2.0. Variations of activity values from published results [7b,c] can probably be traced back to the fact that different reaction conditions were chosen.

Using a sub-stoichiometric ligand/Cr molar ratio of 0.5, meaning that two chromium units form the active catalyst with one ligand, results in a dramatic change in the kinetic behavior (Fig. 2). After a long induction period of 40 min the reaction starts and then accelerates to a small extent, as indicated by the mild upward curvature.

3.2. Influence of the ligand/chromium ratio on product distribution

Contrary to the results of Jiang et al. [7c], we found that the selectivity towards 1-octene is not strongly affected by high ligand/Cr ratios and we see only a slight decrease while increasing the ligand/Cr ratio from 1.0 to 2.0. The selectivity towards 1-hexene also decreases in this regime. At a ligand/Cr ratio of 2.0, a higher amount of undesirable side-products, like branched decenes, are formed. However, in general the selectivity towards 1-hexene and 1-octene is considerable (Table 1).

Using the sub-stoichiometric ligand/Cr molar ratio, the high selectivity towards the main products vanishes gradually and the mechanism changes from the metallacycle to a typical insertion/ β -elimination. This results in a superposition of a Schulz–Flory distribution and a residual selective reaction, the latter leading particularly to a higher 1-octene peak than expected on the basis of a Schulz–Flory distribution only.

Table 1
Effects of ligand/Cr molar ratios on catalytic activity and product selectivity.

Ligand/Cr (mol/mol)	Activity (kg/(g cat h))	Product selectivity (wt.%)								Polymer (g)	
		1-C4 ^a	1-C6 ^a	1-C8 ^a	1-C10 ^a	1-C12 ^a	1-C14 ^a	1-C16 ^a	1-C18 ^a		Odd-numbered LAOs
0.25 ^a	1.4	10.0	17.9	29.6	8.7	5.9	3.4	1.7	0.8	6.9	0.61
0.5 ^a	3.1	8.3	17.1	24.2	9.5	7.7	5.9	4.5	3.5	5.7	0.52
0.75 ^a	1.4	1.7	18.7	61.7	1.1	0.5	0.4	0.3	0.2	1.6	0.45
1.0	1.9	0.6	25.2	62.5	0.7	0.3	0.3	0.1	0.2	0.7	0.09
2.0	1.3	0.7	21.2	61.6	0.7	0.4	0.3	0.1	0.5	0.0	0.05

Reaction conditions: solvent toluene; temperature = 50 °C; pressure = 30 bar; MAO/Cr = 150 mol/mol; reaction time = 60 min.

^a Reaction time = 120 min.

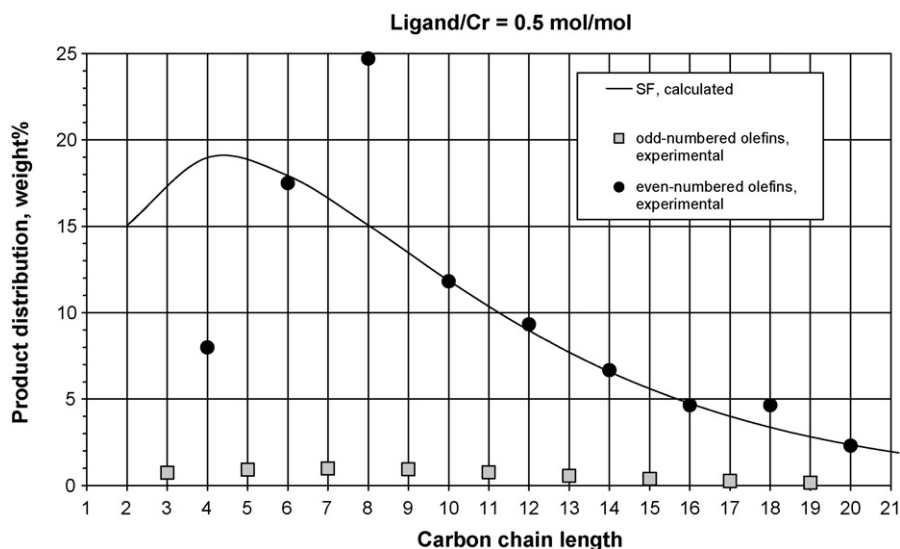


Fig. 3. Measured product distribution at ligand/Cr=0.5 mol/mol. Reaction conditions: solvent toluene; temperature=50 °C; pressure=30 bar; MAO/Cr=150 mol/mol; ligand/Cr=0.5 mol/mol; reaction time=120 min. The solid line indicates a Schulz-Flory (SF) weight-distribution (for comparison) with a chain propagation probability of $p=0.63 \pm 0.01$. Error limits were estimated on the basis of the precision of the analytical data and the quality of the fit to the SF-formalism.

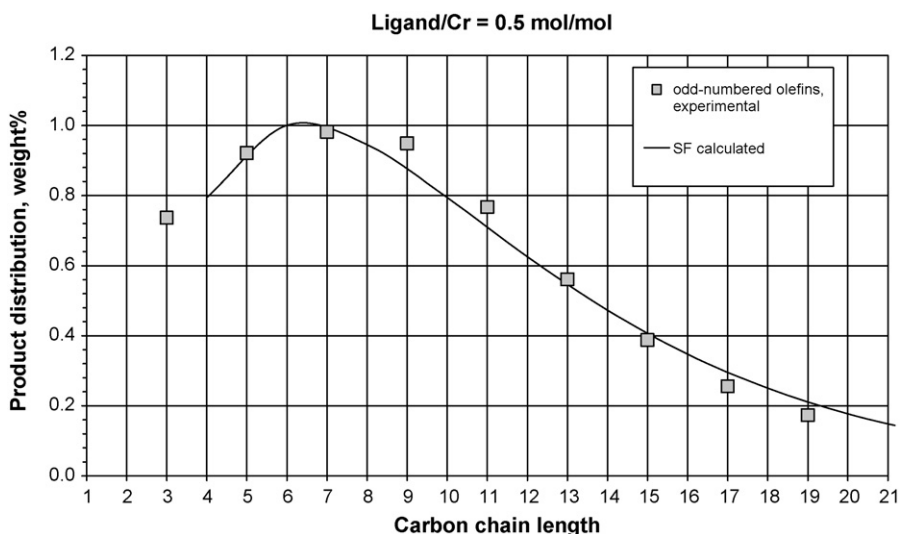


Fig. 4. Distribution of odd-numbered α -olefins at ligand/Cr=0.5 mol/mol. Reaction conditions as Fig. 3. The solid line indicates a Schulz-Flory (SF) weight-distribution (for comparison), shifted against the corresponding even-numbered distribution by about one C-unit. The chain propagation probability was determined as $p=0.63 \pm 0.015$.

While at a ligand to chromium ratio of 0.75 mol/mol the creation of higher alkenes is unincisive, a further reduction of the ligand/Cr ratio decreases the selectivity towards 1-hexene and 1-octene. The amount of formed polymer also increases with decreasing ligand/Cr ratio.

Surprisingly, at sub-stoichiometric ligand/Cr-ratios, also odd-numbered olefins are formed as by-products (Fig. 3), an observation that, to the best of our knowledge, was not reported anywhere before. As illustrated by Fig. 3, at ligand/Cr=0.5 mol/mol, the obtained product distribution of even-numbered (regarding the carbon-chain length) α -olefins widely follows a Schulz-Flory weight distribution,

$$fw(x) = x(1-p)^2 p^{(x-1)}$$

with a chain propagation probability of $p=0.63 \pm 0.01$ and x = number of monomer units (ethene) incorporated into the carbon chain. Only the 1-butene and the 1-octene yield does not follow this statistical distribution, the latter clearly owing to an underlying,

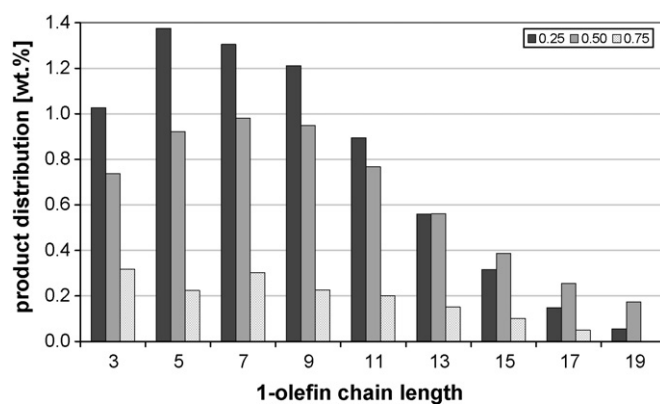


Fig. 5. Formation of odd-numbered 1-olefins at sub-stoichiometric ligand/Cr molar ratios. Reaction conditions: solvent toluene; temperature=50 °C; pressure=30 bar; MAO/Cr=150 mol/mol; ligand/Cr=0.25, 0.5 and 0.75 mol/mol; reaction time=120 min.

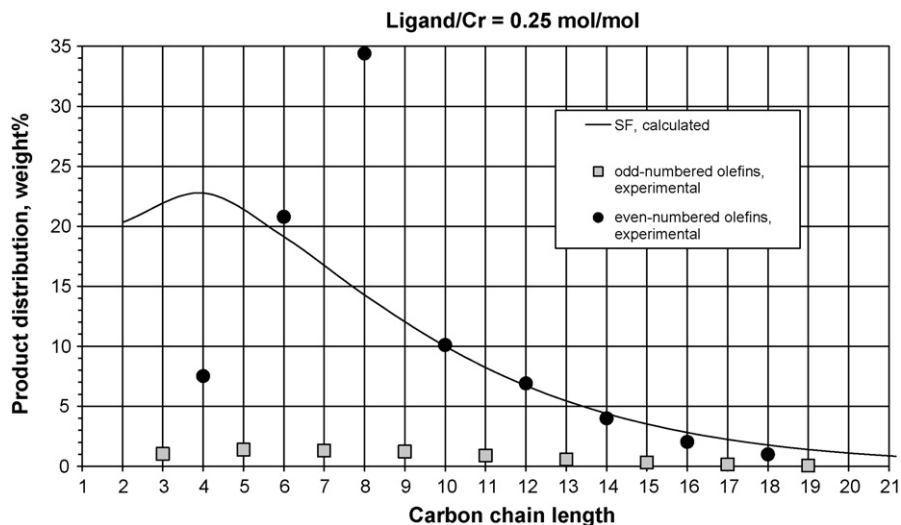


Fig. 6. As Fig. 3 but Ligand/Cr = 0.25 mol/mol. Reaction conditions as Fig. 3 but ligand/Cr = 0.25 mol/mol and chain propagation probability $p = 0.56 \pm 0.01$.

'residual', selective tetramerization mechanism. Also the 1-butene concentration is significantly lower than expected on the basis of the statistical product distribution and it can be speculated in how far this can be interpreted in terms of 1-octene formation via dimerization of two C₄-units.

Like the expected even-numbered 1-olefins, the odd-numbered 1-olefins follow a distribution which is slightly shifted by about one C-unit in the carbon chain with respect to the distribution of the corresponding even-numbered 1-olefins (Fig. 4). Remarkably, the chain propagation probability for this odd-numbered distribution was determined to be $p = 0.63 \pm 0.015$ as well. This suggests that the odd-numbered distribution is closely linked to the even-numbered product distribution, in fact, that it is even directly derived from the latter.

The total percentage of odd-numbered 1-olefins is a function of the ligand/Cr ratio and increases significantly with decreasing ratio (Fig. 5). This leads to the question, how the product distribution behavior changes at even lower ligand/Cr ratios than

0.5, e.g. at the lowest ratio investigated in this study, namely ligand/Cr = 0.25 mol/mol. As shown in Fig. 6 for the even-numbered products and Fig. 7 for the odd-numbered ones, respectively, one observes a totally equivalent behavior compared to the situation at ligand/Cr = 0.5 mol/mol: again, the even-numbered products can be described by a Schulz-Flory distribution if an underlying 'residual' selective tetramerization reaction channel is assumed to account for the high 1-octene figure. Again, far less 1-butene is observed than expected on the basis of a Schulz-Flory distribution alone and the odd-numbered distribution can be fitted reasonably well with a Schulz-Flory, shifted by about one C-unit (Fig. 7).

The important difference to the situation at ligand/Cr = 0.5 mol/mol is that both, even- and odd-numbered product distributions, indicate one single consistent figure for the chain propagation probability of $p = 0.56 \pm 0.02$. The lower value of p as compared to ligand/Cr = 0.5 mol/mol characterizes the gradual shift to narrower product distributions as the ligand/Cr ratio is being lowered.

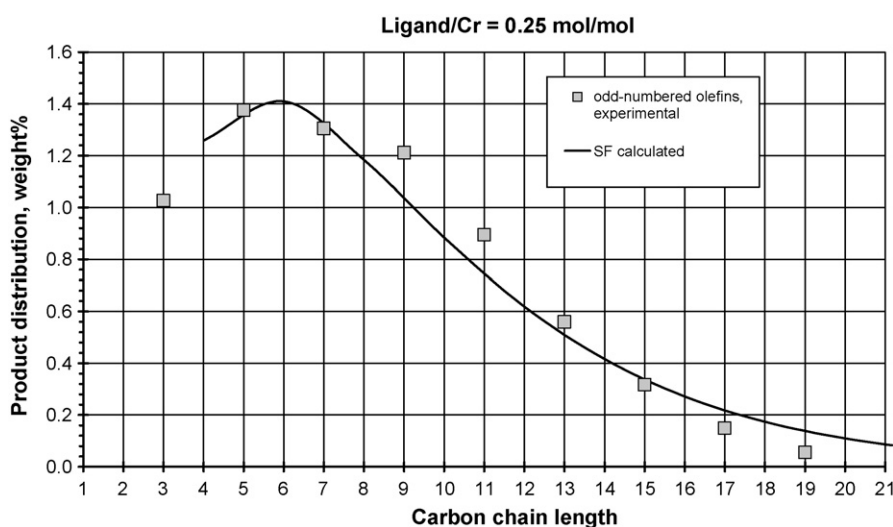
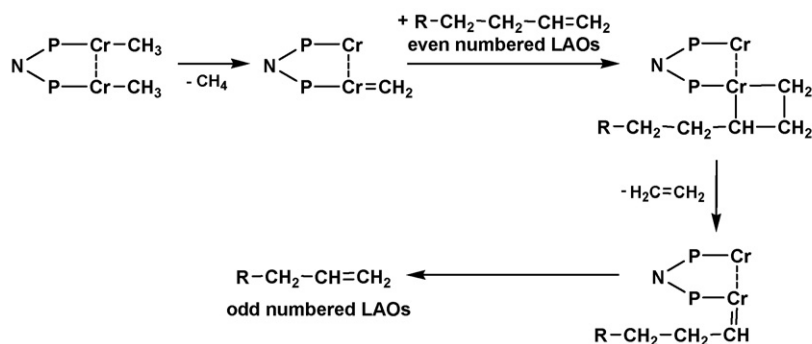


Fig. 7. Distribution of odd-numbered α -olefins at ligand/Cr = 0.25 mol/mol. Reaction conditions as Fig. 3 but ligand/Cr = 0.25 mol/mol and chain propagation probability $p = 0.56 \pm 0.02$. The solid line indicates a Schulz-Flory (SF) weight-distribution (for comparison), shifted against the corresponding even-numbered distribution (Fig. 6) by about one C-unit.



Scheme 5. Simplified principle for the formation of odd-numbered LAOs.

These results strongly suggest, that the unexpected formation of odd-numbered linear α -olefins in $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2/\text{CrCl}_3(\text{THF})_3/\text{MAO}$ systems at sub-stoichiometric ligand/Cr ratios (below about ligand/Cr = 0.5 mol/mol) proceeds via the initially formed 'regular' α -olefins with even-numbered carbon chain length.

4. Conclusion

The most important result of the investigation presented here is the fact that the ligand/Cr ratio influences remarkably the product distribution. At a ligand/chromium ratio of 0.5 the selective process towards 1-hexene and 1-octene changes into a Schulz–Flory-like distribution with some residual selective reaction to 1-C₈⁺ and possibly 1-C₆⁻. Moreover, odd numbered 1-olefins are formed at sub-stoichiometric ratios. This has two consequences for the understanding of the catalytic system.

The first conclusion is that with sub-stoichiometric ligand/Cr ratios a completely different active catalyst species is formed from chromium and the chelating PNP–ligand than the well known SASOL catalyst with a stoichiometric ligand/Cr ratio “(PNP)Cr” (1:1). Most likely, with the ratio of 0.5 binuclear complexes “(PNP)Cr₂” (0.5:1) or higher aggregates with bridging PNP ligands are formed, showing a completely different behavior regarding kinetics and selectivity.

Secondly, it is likely that after the alkylation with MAO such binuclear complexes result in methyl compounds “(PNP)Cr₂(Me)_n”. An elimination of methane favors the creation of chromium carbene “Cr=CH₂” groups. These carbene groups could react with recently formed even-numbered LAOs like R–CH₂–CH₂–CH=CH₂ in a metathesis reaction to ethene and to long-chain carbenes “Cr=CH–CH₂–CH₂–R”, resulting in the observed odd numbered LAOs like, e.g., H₂C=CH–CH₂–R (Scheme 5).

Clearly, a sharp discrimination between the different catalytic species is impossible and an equilibrium of differently acting centers always exists. Consequently, a smooth transition between the different ligand/Cr ratios and their respective behaviors is observed. For instance, the enhanced polymer formation, especially at very low ligand/Cr ratios, can be explained by an increasing number of “naked” Cr species (Ligand: Cr = 0:1) in the equilibria. We also conclude that binuclear complexes with one bridging PNP ligand and two chromium atoms such as “(PNP)Cr₂” (0.5:1) or higher aggregates are responsible for the Schulz–Flory product distribution and the formation of odd-numbered LAOs. The selectivity towards 1-hexene and 1-octene can only be reached by adjustment of a stoichiometric ratio of ligand to chromium, either by a monometallic

center like “(PNP)Cr” (1:1) or a bimetallic center as “(PNP)₂Cr₂” (1:1).

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