



Review Article

Chromium catalysts for selective ethylene oligomerization to 1-hexene and 1-octene: Recent results

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ABSTRACT

The objective of this review is the analysis and comment of recent publication results (from July 2010 until February 2017) obtained for selective ethylene oligomerization toward 1-hexene and 1-octene catalyzed by chromium-based catalytic systems. Both the scientific and patent literature was taken into the consideration. The catalytic systems for ethylene oligomerization are classified on the basis of the ligand type employed. The activities and selectivities of the catalysts are provided throughout the text. Despite a big success in the field, there is still rather limited choice of catalysts affording simultaneously high activity, selectivity and low polymer proportion. This is especially true for ethylene to 1-octene tetramerization reaction. The results of the studies concerning oligomerization mechanisms obtained over the recent years are also included in this review.

1. Introduction

Linear α -olefins are important products of petrochemical industry. At the present time, they are produced mainly via full-range processes giving broad distributions of olefins [1]. Linear α -olefins are used for the production of polyethylene, synthetic lubricants, plasticizer alcohols, surfactants, etc. In 2014 about one half of linear α -olefins, mainly 1-butene, 1-hexene, and 1-octene, was consumed by ethylene copolymer producers [2]. The latter two comonomers are becoming more and more attractive because of superior copolymer properties as compared to the characteristics of ethylene/1-butene copolymers [1]. Consequently, an important goal is to selectively oligomerize ethylene to 1-hexene and 1-octene. This idea is also supported by the fact that many companies (e.g. Chevron Phillips Chemical Company, Sasol, Dow Global Technologies, LG Chem, Axens, Linde AG, SABIC, Mitsui, Nova Chemicals) are interested in the topic, and a few commercial processes for selective ethylene oligomerization are currently on stream.

In this paper, we review recent results published in English or Russian on the chromium-based catalytic systems able to perform the tri- and/or tetramerization of ethylene. The chromium catalysts promoting such processes are much more abundant than catalysts containing other transition metals (for example, titanium). Also they are very “flexible”, i.e. allow one to control the 1-octene/1-hexene ratio in a broad range and to use different complexes to obtain a certain ratio of the products. Results for *some* systems promoting ethylene polymeriza-

tion and non-selective oligomerization processes are also included to show the influence of different variables (complex structure, solvent and activator nature, reaction conditions and etc.) on the reaction outcome.

Several reviews of catalysts for selective ethylene tri- and tetramerization and mechanisms of their operation were published previously [3–8]. Therefore the reader is referred to those works, which comprehensively covered previously published results from different points of view. In addition, many review papers concerning various issues of this topic appeared [1,9–19]. The last review with the most complete bibliography containing the open and patent literature is a paper written by McGuinness D.S. [5]. Since then a lot of results on chromium catalyzed selective ethylene oligomerization have been published. The authors believe that there is no point to repeat the work which was done successfully by others before. Therefore the aim of our review is the analysis of the data appeared *recently* (from July 2010 until February 2017) to update the previously published reviews. As follows from the reference list, a lot of results appeared in the patent literature, being sometimes missed during the analysis of the state of the art.

The following notations are used in the present paper: 1-C₆, 1-C₈, C₁₀₊ are the contents of 1-hexene, 1-octene, and the products with ten and more carbon atoms respectively in the mixture of reaction products; α -C₆, α -C₈ are the contents of 1-hexene and 1-octene in the fraction containing products with six and eight carbons respectively

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(purity). The content of a product is expressed in weight percents where this is possible. When referring to product as a 1-hexene/1-octene mixture, we implied the mixture with the ratio $1/4 < 1-C_8/1-C_6 < 4/1$. When $1-C_8/1-C_6 > 4/1$ and $1-C_6 + 1-C_8 > 75\%$, we called this process tetramerization.

A quantity called activity [3,6,17,19] is used throughout this review. It is calculated as follows:

$$\text{Activity} = m(\text{RP}) \cdot 60 / [m(\text{Cr}) \cdot t],$$

where $m(\text{RP})$ is the mass of the reaction products, kg; $m(\text{Cr})$ is the mass of chromium used in a catalytic system to obtain the products, g; t is reaction time, min.

The activity cannot be used to precisely describe catalyst ability to accelerate reaction. However, taking into account that data on reaction kinetics and catalyst lifetime are often absent, this quantity is useful to estimate catalyst performance. Usually, runs to test the catalysts for selective ethylene oligomerization are terminated after 30–60 min. In the cases of shorter reaction times, we inform the reader about it.

2. Catalytic systems based on different ligands for ethylene oligomerization to 1-hexene

2.1. Phillips system and related catalysts based on pyrrole containing ligands

The main results concerning such catalytic systems and published before the period considered by us were analyzed in the previous reviews [3–5,17].

The Phillips ethylene oligomerization catalyst is the first catalytic system which showed a 1-hexene selectivity exceeding 80% [20]. It is used to commercially produce the trimer [3]. The catalyst consists of a chromium compound, pyrrole containing ligand, AlEt_3 and modifier. For example, the following combination of components allows one to carry out the process with high activity and selectivity: chromium(III) 2-ethylhexanoate ($\text{Cr}(\text{EH})_3$)/2,5-dimethylpyrrole (2,5-DMP)/ AlEt_3 / AlEt_2Cl (entry 1, Table 9). The Phillips system was discovered more than 20 years ago, and the investigations of this catalyst and its modifications are still being pursued.

Several papers describe the results of the influence of different modifiers on the activity and selectivity of catalytic systems $\text{CrX}_3/2,5\text{-DMP}/\text{AlEt}_3$ [21–23].

THF and CCl_4 were used to modify the performance of $\text{Cr}(\text{acac})_3/2,5\text{-DMP}/\text{AlEt}_3$ in *n*-heptane [21]. The best results were obtained using THF and CCl_4 in combination: $0.7 \text{ kg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $1-C_6 = 87.4\%$, $\text{PE} = 12.6\%$. It was found that the maximum values of activity and 1-hexene selectivity for the catalyst $\text{Cr}(\text{EH})_3/2,5\text{-DMP}/\text{AlEt}_3/\text{CCl}_4$ (*n*-heptane medium) could be obtained at $\text{CCl}_4/\text{Cr} = 2\text{-}3$ [22].

Tang et al. explored the influence of halogen containing compounds (CH_2Cl_2 , $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, $\text{CHCl}_2-\text{CH}_2\text{Cl}$, CCl_3-CH_3 , $\text{CHCl}_2-\text{CHCl}_2$, $\text{CCl}_2 = \text{CCl}_2$, $\text{CCl}_3-\text{CCl}_3$, CCl_4 , $\text{CHBr}_2-\text{CHBr}_2$) on the activity and selectivity of catalysts based on $\text{Cr}(\text{EH})_3/2,5\text{-DMP}/\text{AlEt}_3$ in *n*-heptane [23]. The highest activity values were observed when using $\text{CHCl}_2-\text{CHCl}_2$ ($214 \text{ kg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $1-C_6 = 88.9\%$, $\alpha-C_6 = 98.1\%$) and CCl_4 ($278 \text{ kg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $1-C_6 = 86.6\%$, $\alpha-C_6 = 96.9\%$).

The influence of haloalkenes (*trans*- $\text{CHCl} = \text{CHCl}$, $\text{CCl}_2 = \text{CHCl}$, $\text{CCl}_2 = \text{CCl}_2$) on the performance of catalysts based on $\text{Cr}(\text{EH})_3/2,5\text{-DMP}/\text{AlEt}_3$ or $\text{Cr}(\text{EH})_3/2,5\text{-DMP}/\text{AlEt}_3/\text{CH}_{(3-n)}\text{Cl}_n-\text{CH}_{(3-n)}\text{Cl}_n$ ($n = 2; 3$) in *n*-heptane medium at relatively high temperatures (120–140 °C) and pressures (6–7 MPa) was demonstrated [24]. The selectivities toward 1-hexene and, in several cases, activities of the systems can be increased by variation of the haloalkene to chromium molar ratio. Examples demonstrating the performance of the catalysts are in entries 2, 3 of Table 9. If a haloalkane with two or more carbon atoms is used, a haloalkene can form via the decomposition of the haloalkane during ethylene oligomerization. Consequently, the unsaturated compound

can be returned to an oligomerization reactor in a continuous process.

It follows from most of publications related to pyrrole-based systems that halogen-containing compounds are necessary to achieve high activity and selectivity. Halogen atoms may coordinate to chromium centers modulating their steric environment and electronic properties. In addition, organochloro-compounds may facilitate dissociation of AlEt_3 -dimers [3] and oxidize chromium species inactive with respect to ethylene trimerization to active ones. The oxidation function was proved for vanadium and titanium ethylene polymerization catalysts [25,26 and references therein].

It was published recently that the activity of the system $\text{Cr}(\text{acac})_3/2,5\text{-DMP}/\text{AlEt}_3$ ($2,5\text{-DMP}/\text{Cr} = 4/1$) in CyH (cyclohexane, Cy is cyclohexyl) can be increased by 25% (up to $298 \text{ kg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) upon the introduction of *N,N*-bis(diphenylphosphanyl)cyclopentanamine (L) into the system ($2,5\text{-DMP}/\text{Cr}/\text{L} = 4/1/1$) [27]. Selectivity remained almost unchanged ($1-C_6 = 92.1\text{--}93.3\%$). The best results in terms of activity and selectivity are presented in Table 9 (entry 4).

The activity and selectivity of ethylene oligomerization catalysts strongly depend on the nature of an activator used. Among the systems $\text{Cr}(\text{EH})_3/2,5\text{-DMP}/\text{activator}/\text{CHCl}_2-\text{CHCl}_2$ (activator: AlEt_3 , $\text{Al}(\text{Bu}^i)_3$, $\text{AlEt}_2\text{Cl}/\text{AlEt}_2\text{Cl}$, ZnEt_2) tested in *n*-heptane medium, the best results were obtained for that containing AlEt_3 [23]. Similar outcome was observed when the following organoaluminum compounds were tested as the activators (CyH medium): AlEt_3 , AlMe_3 , $\text{Al}(\text{Bu}^i)_3$, $\text{Al}(\text{n-C}_6\text{H}_{13})_3$, MAO [28].

The catalysts containing $\text{Cr}(\text{acac})_3/2,5\text{-DMP}$ in the presence of MAO or DMAO (product prepared by drying toluene solution of MAO in vacuo to remove AlMe_3 and toluene) in MeCy (methylcyclohexane) promoted only concurrent ethylene oligomerization/polymerization processes ($\text{PE} = 31.1\text{--}75.0\%$) [29,30]. However, selective ethylene trimerization to 1-hexene took place when $\text{DMAO}/\text{Al}(\text{Bu}^i)_3$ or $\text{DMAO}/\text{AlEt}_3$ was used as the activator. This was related to insufficient reduction of Cr(III) species to Cr(I) complexes in the presence of only DMAO. The highest activity and $\text{PE} = 0\%$ were obtained for the system with $\text{DMAO}/\text{Al}(\text{Bu}^i)_3$ (entry 5, Table 9). It is interesting that this system had very high efficiency without any added halogen sources.

Authors of [31,32] studied the effect of microwave irradiation of catalytic system components on the performance of $\text{Cr}(\text{EH})_3/2,5\text{-DMP}/\text{AlEt}_3/\text{modifier}$ (modifier: AlEt_2Cl or CHCl_3) in ethylene oligomerization. Generally, microwave irradiation of all the components after their mixing or of the solutions of organoaluminum compounds before adding to $\text{Cr}(\text{EH})_3/2,5\text{-DMP}$ led to increase in catalytic activity and to decrease in PE content in the oligomerization product. Variation of 1-hexene selectivity was dependent on catalyst composition and on the method of catalyst preparation. The influence of microwave irradiation is temporary in nature. As followed from the results of cryoscopic molecular weight determination, AlEt_3 partially monomerized after the irradiation [31]. Except for very dilute solutions AlEt_3 exists as a dimer. Therefore the irradiation of this component may increase the concentration of the monomeric form, probably more active. The following values were published for the optimized catalyst $\text{Cr}(\text{EH})_3/2,5\text{-DMP}/\text{AlEt}_3/\text{AlEt}_2\text{Cl}/\text{H}_2$ in CyH: $102 \text{ kg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $1-C_6 = 89.9\%$, $\alpha-C_6 = 99.3\%$, $\text{PE} = 0.05\%$.

The influence of ZnEt_2 on the purity of 1-hexene fraction and the activity of the catalyst $\text{Cr}(\text{EH})_3/2,5\text{-DMP}/\text{AlEt}_3/\text{AlEt}_2\text{Cl}$ was reported in [33]. Ethylene oligomerization was done in the presence of hydrogen in *n*-undecane or CyH. When a microwave irradiated $\text{AlEt}_3/\text{AlEt}_2\text{Cl}$ mixture was used, the introduction of ZnEt_2 increased catalyst activity and 1-hexene purity. On the contrary, without the application of the microwave treatment, negative influence of the dialkyl zinc on catalyst activity was observed. 1-Hexene purity remained the same or decreased depending on the ZnEt_2/Cr ratio. It was also found for the same system without ZnEt_2 that the application of *n*-undecane or a 4-ethyloctane/5-methylnonane/*n*-decane mixture as a reaction solvent leads to lower melting polymer by-products and lower reactor contamination compared to results obtained in CyH or 2,2,4-trimethylpentane (TMP) [34].

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