ISSN 1813-1107, eISSN 2710-1185 *№ 3, 2025*

Chemical Journal of Kazakhstan
Volume 3, Number 91(2025), 171-193 https://doi.org/10.51580/2025-3.2710-1185.45
по заказу редакции

УДК 541.128:542.97:547.21

OLEFIN OLIGOMERIZATION CATALYSTS

S.R. Konuspayev*, K.A. Kadirbekov, O.K. Yugay

A.B. Bekturov Institute of Chemical Scineces JSC, Almaty, Kazakhstan

**E-mail: srkonuspayev@mail.ru*

Abstract: The article presents an analysis of literature and patent data concerning olefin oligomerization catalysts used for the production of long-chain linear α-olefins, which are of significant importance in the manufacture of consumer goods such as base lubricating oils, detergents, and various other products. Olefin oligomerization catalysts are typically coordination compounds of transition metals in combination with organoaluminum compounds. A key factor influencing catalytic performance is the nature of the central metal in the coordination complex: the greater the variety of oxidation states the metal can adopt, the more diverse the resulting complexes. In this context, chromium stands out, as evidenced by the large volume of patent literature dedicated to it. Olefin oligomerization catalytic systems generally comprise transition metal complexes and organoaluminum co-catalysts, and the reactions are typically carried out in solution under elevated temperatures and pressures. For each metal, the catalytic properties are determined by the nature of the ligands: their composition, structure, geometry, and acid-base characteristics. However, no clear patterns have been established for ligand selection, and the optimization remains largely empirical. Zeolites and ionic liquids may also serve as olefin oligomerization catalysts. Zeolite-based oligomerization is applied to butene-1 or butane-butylene fractions derived from petroleum refining to produce gasoline, with reactions conducted at temperatures above 300°C, where the zeolite acidic sites are activated. Of particular interest is using of ionic liquids as catalysts, on which oligomerization can be carried out at atmospheric pressure and below 100 °C, although there is little information on this.

Key words: oligomerization, α-olefin, catalyst, transition metals, zeolite, ionic liquid.

Konuspayev Saparkaly Retaevich	*Doctor of Chemical Sciences, Professor;* *E-mail: srkonuspayev@mail.ru*
Kadirbekov Kairat Adyrbekovich	*Doctor of Chemical Sciences, Professor;* *E-mail: kkairati@mail.ru*
Yugay Olga Konstantinovna	*Candidate of Chemical Sciences, Associate Professor;* *E-mail: yu.ok@mail.ru*

Citation: Konuspayev S.R., Kadirbekov K.A., Yugay O.K. Olefin Oligomerization Catalysts. *Chem. J. Kaz.*, **2025**, 3*(91)*, 171-193. DOI: https://doi.org/10.51580/2025-3.2710-1185.45

1. Introduction

Reactions in the field of hydrocarbon conversion are well known, yet the demands of modern industry require that such processes be conducted in more selective and energy-efficient forms. To achieve these objectives, catalysts are needed that are capable of lowering temperature and pressure while simultaneously increasing the yield of target products.

One of the key reactions in the processing of hydrocarbon feedstocks is oligomerization. Oligomerization is a chemical process in which monomeric compounds combine to form dimers, trimers, tetramers, or longer-chain molecules (oligomers). Oligomers of simple olefins, such as ethylene and propylene, are referred to as long-chain or linear α-olefins (LAOs). The importance of LAOs in petrochemical synthesis is difficult to overestimate, as they serve as intermediates in virtually all petrochemical processes. The production of polyolefin base oils, in which the double bond of the oligomer is subjected to hydrogenation, is carried out on a large scale. Approximately one third of synthetic base oils consist of polyalphaolefin lubricants (PAOLs) [1, 2].

Review articles [3–6] provide information on ethylene tetramerization [3], technologies for the production of higher linear α-olefins [4], as well as oligomerization catalysts for alkenes known up to 2015 [5]. In addition, study [6] summarizes results on dimerization and oligomerization of alkenes using transition-metal complexes. Other authors have focused their reviews on more specific reactions: [7] discusses the formation of cyclic hydrocarbons, whereas [8] is devoted to selective ethylene tetramerization.

Ethylene is the simplest alkene for oligomerization, and articles [3, 4, 6] describe both the mechanism of ethylene oligomerization and its industrial-scale implementation. Based on the analysis and generalization of the literature, authors [1, 3] proposed the following mechanism for ethylene tetramerization on chromium complexes. In chromium complexes, the ligands are organic molecules similar to those used in Ziegler–Natta catalysts. Initially, two ethylene molecules are adsorbed on the chromium center, and through oxidative coupling (oxidation of chromium) a cycle involving chromium is formed. Subsequent insertion of an ethylene molecule produces a six-membered ring with chromium, which upon elimination may yield 1-hexene. Further insertion of another ethylene molecule into this six-membered cycle results in an eight-membered ring with chromium, the elimination of which produces 1-octene. Ethylene oligomerization requires redox cycling of the complex-forming agent $Cr^n \leftrightarrow C^{n+2}$. During adsorption and complex formation, chromium is oxidized, whereas during the reductive elimination of the formed cycle, chromium is reduced. Reference [3] also discusses the formation of 1-octene via a binuclear complex at the active site, as well as the possible formation of methylcyclopentane and methylenecyclopentane as byproducts. Review [6] further elaborates on the intricacies of the mechanism of metal–complex catalysts, which depend on the nature of the central metal and the structure of the resulting α-olefins.

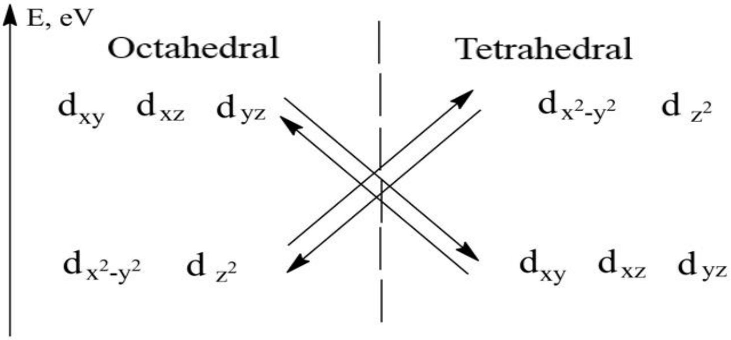
For a systematic analysis of the literature on alkene oligomerization, we have grouped the available data according to the nature of the central metal in complexes with various ligands. Ligands may include both organic and inorganic molecules, as well as ions. For oligomerization, organic ligands are generally preferred, in analogy with Ziegler–Natta catalysts.

2. Discussion

A series of studies [9–26] is devoted to oligomerization catalysts in which nickel acts as the central metal. Another sequence of works [27–63] examines chromium catalysts. References [64–67] provide data on oligomerization over iron complexes, whereas publications [68–76] report titanium-based catalysts. In addition, oligomerization on zeolites [77–82] and ionic liquids [83–87] has also been investigated.

A characteristic feature of metal–complex oligomerization catalysts is that all transition metals are multivalent, and catalytic activity is directly related to the redox state of the central metal, as demonstrated above for the mechanism of ethylene oligomerization. The development of ligand field theory, together with the interpretation of chemisorption of reactants as the formation of coordination bonds, and the combined consideration of coordination and catalysis, has expanded the understanding of catalytic mechanisms. Ligand field theory assumes interaction between ligands when their fields come into contact or overlap. Ligands located on opposite sides of the central atom cannot interact, as their fields do not overlap. Chemisorption on heterogeneous catalysts is interpreted as the formation of donor–acceptor (dative) bonds.

Catalysts are d-elements, which may have up to ten electrons in their d-orbitals or vacant orbitals available for donor–acceptor bonding with molecules or atoms possessing a free electron pair. The electronic states of transition d-metals in octahedral and tetrahedral coordination are presented in Scheme 1 below.



Scheme 1 – Energy state of the d-level of transition metals depending on the coordination factor.

Transition metals, depending on the charge of the ion, may exist in various coordination states. The scheme presents two configurations, tetrahedral and octahedral, in which d-electrons are distributed differently. The presence of these energetic oscillations determines the catalytic properties of transition metals. The behavior of such metal-complex catalysts is defined by the nature of the central metal ion. Therefore, as demonstrated above, the primary criterion for analysis was the nature of the central metal ion.

Studies [9–26] report results on catalysts in which nickel acted as the central metal ion. For ethylene oligomerization in a homogeneous medium, Ni^{2+} was coordinated with 1,10-phenanthroline (phen) [9]. The selectivity toward linear α-olefins was 43%. Introduction of carbonyl groups into positions 5 and 6 of 1,10-phenanthroline increased catalytic activity, whereas hydroxyl groups at the same positions decreased activity but enhanced selectivity toward butenes to 80–96%. Use of the activated σ-complex {[NiBr(Mes)(phen)], where Mes = 2,4,6-methylphenyl}, increased the activity of ethylene dimerization into butenes. At the same time, the σ-complex in combination with $Et_3Al_2Cl_3$ and $EtAlCl_2$, serving as activators, exhibited higher oligomerization activity but lower selectivity toward butenes, at 58–61%. The choice of 1,10-phenanthroline as ligand was justified by the authors [9] on the basis of literature analysis. To enhance the selectivity of ethylene dimerization into butene-1 on heterogeneous catalysts, in a manner analogous to homogeneous metal-complex catalysts, the authors [10] proposed anchoring a metal–organic framework {$Zn_5Cl_4(BTDD)_3$, where BTDD = bis(1H-1,2,3-triazolo[4,5-b] or [4′,5′-b])dibenzodioxane} that selectively catalyzes ethylene dimerization onto the surface of a heterogeneous catalyst. Ni^{2+} on the surface was further coordinated with tris-pyrazolylborate ligands. In the presence of ethylene and methylaluminoxane, ethylene dimerization proceeded at a rate of 41,500 mol per mol Ni per hour with selectivity toward butene-1 of up to 96.2%, which exceeds the selectivity of industrially used catalysts.

In their review, the authors [11], dedicated to the oligomerization and dimerization of ethylene on nickel metal-complex catalysts, divided the available data into two categories, homogeneous and heterogeneous, and attempted to identify correlations between ligand type and structural features. They concluded that the methodology remained largely empirical, based on trial and error. At the same time, they emphasized the potential of nickel-based metal-complex catalysts both for fundamental research and industrial applications. In [12], ethylene oligomerization was conducted over a heterogeneous Ni–Hβ catalyst in a flow regime, and optimal conditions of ethylene feed rate and reaction temperature were established with respect to conversion and yield of target products. For instance, at 120 °C, 25.6 bar, and an ethylene feed rate of 5.50 h^{-1}, conversion reached 44–47% with a selectivity toward butene-1 of 74.9%. After 8 h of operation, only minor coke deposition was observed, while conversion remained stable, suggesting that Ni–Hβ catalysts are suitable for ethylene oligomerization. In [13], nickel supported on SiO_2–Al_2O_3 with various Si/Al ratios, prepared by hydrolytic sol–gel and gel–sol methods, was tested for ethylene oligomerization at 150 °C, although product distributions were not reported. Catalysts prepared via ether-based synthesis demonstrated higher activity compared with those synthesized in alcoholic media.

LAOs were obtained both on homogeneous and heterogeneous catalysts in [14]. It was shown that the decisive factor is the nature of the central metal ion. For heterogeneous catalysts, anchoring a metal–organic framework on the surface is required. Ni–MOF-5 heterogeneous catalysts [15], obtained by co-precipitation of Ni^{2+} on MOF-5 (a zeolitic structure), demonstrated ultrahigh activity in ethylene dimerization: at 35 °C and 50 bar, 1 g of catalyst produced 9.040 g of oligomers, substantially exceeding the activity of known catalysts in this reaction. A similar catalyst was proposed in [16].

Ethylene oligomerization on Ni–H-β (H-β, acidic form of zeolite) was studied in [17, 25], where the role of nickel and Brønsted acid sites was discussed. A mechanism for the formation of $[Ni^{2+}–H]^{+}$ centers was proposed, involving adsorption of ethylene on Ni^{2+} and the Brønsted site. This interaction was shown to surpass the performance of all known heterogeneous nickel catalysts. Ni–H-Beta catalysts were prepared by ion exchange of NH_4-β and H-β zeolites with aqueous $Ni(NO_3)_2$ solution and subsequently characterized by hydrogen and ammonia temperature-programmed desorption and FTIR spectroscopy [25]. A comparative study of Ni2+ ion exchange with NH_4-β and H-β, followed by catalyst calcination at 500 °C in helium flow, revealed that the exchange capacity of Ni^{2+} with H-Beta was approximately 20% lower than with NH_4-β.

The authors [18] proposed a process for producing gasoline from renewable feedstocks: ethanol was dehydrated to ethylene, which was subsequently tetramerized to 1-octene (gasoline). A nickel catalyst supported on aluminosilicate was employed, demonstrating stable performance in a flow reactor at 120 °C, 50 bar ethylene pressure, and a feed rate of 8 h^{-1} over 170 h, with 99% ethylene conversion. Product composition was as follows: C_6 – 15%; C_8 – 25%; C_{10} – 18%; C_{12} – 10%. Alongside linear olefins, iso-olefins were also formed. To obtain gasoline, the C_5–C_{12} fraction was subjected to hydrogenation, and the resulting properties were consistent with commercial gasoline [18].

Further, [19] reported propylene dimerization on in-situ generated nickel hydride complexes, formed via reaction of Ni complexes with phosphorus-containing ligands, e.g., $Ni[P(OC_6H_4CH_3\text{-}o)_2]_2(C_2H_4)–CF_3COOH$. It was demonstrated that the reaction produced a nickel hydride complex in the cis-position relative to the phosphite ligands. The highest yield of n-hexene-1 87.5%, was obtained with the catalytic system $Ni[P(OEt)_3]_4–CF_3COOH$ in chlorobenzene medium. The mechanism was described in terms of nickel complex structure and ligand effects, showing how catalytically active hydride complexes influenced selectivity in propylene dimerization.

Nickel catalysts with various ligands were investigated in [20–23]. In [21], ethylene oligomerization was studied on nickel complexes with 2,9-disubstituted-1,10-phenanthrolines, characterized by FTIR spectroscopy and confirmed by X-ray crystallography. In [20, 22], formasans (azohydrazones) were employed as ligands for nickel complexes. Sixteen formasan complexes were synthesized and tested, yielding maximum values of ΣC_4 = 88.4%, ΣC_6 = 58.3%, and ΣC_8 = 71.0% [22]. In [23], nickel was supported on aluminosilicates with varying Si/Al ratios. Using temperature-programmed adsorption–desorption of nitrogen and ammonia, and XRF analysis, the authors evaluated catalyst aging, likely associated with particle agglomeration, oxidation, or carbon deposition. They noted that low Si/Al ratios, high temperatures, and balanced distribution of nickel and acid sites favored higher selectivity toward C10 oligomers. Octahedral coordination of Ni^{2+} reduced byproduct formation at elevated temperatures. Conditions such as temperature, ethylene feed rate, and nickel loading were optimized [23].

Reviews provide summaries of nickel complex catalyst applications in olefin oligomerization up to 2014 [26] and up to 2021 [24]. The article [24] provides a comprehensive mechanism of ethylene oligomerization on nickel catalysts, emphasizing bifunctional effects of nickel and acid sites. Based on experimental data, calculations, and kinetic modeling, it was shown that Ni^{2+} selectively oligomerizes ethylene into light linear alkenes via the Cossee–Arlman mechanism, whereas Brønsted acid sites catalyze subsequent alkylation, cracking, and isomerization reactions. The influence of reaction conditions on oligomerization selectivity and activity was also discussed. The Cossee–Arlman mechanism involves formation of an intermediate coordination complex containing both the growing polymer chain and the monomer (alkene). Within the coordination sphere of the metal, the ligands interact, elongating the polymer chain by two carbon atoms. Adjustment of the relative proportions of nickel, acid sites, and support framework enables rational catalyst design for targeted product yields. The authors [26] also highlighted not only the advantages of nickel catalysts but also their major limitation, namely sensitivity to poisoning by water, carbon monoxide, acetylene, butadiene, oxygen, and sulfur compounds, which restricts their industrial applicability.

The next series of studies [27–61] focused primarily on chromium as the central metal ion, along with other transition metals. A distinctive feature of chromium compared with other transition metals is its multivalency, with oxidation states ranging from +3 to +6.

In [27], ethylene oligomerization was conducted on a catalytic system comprising chromium ethylhexanoate, $Al(C_2H_5)_3$, and 2,5-dimethylpyrrole in the presence of CCl4. Preparation of the catalyst and experimental conditions for ethylene oligomerization were described. Optimal conditions for achieving a maximum 1-hexene yield of 96.8% were established: $CCl_4/Cr=2$, temperature 60 °C, ethylene pressure 2 MPa, and catalyst operation time of four hours. Kinetic aspects and the influence of component ratios on process activity were analyzed, although ligand effects were not separately addressed.

The authors [28] investigated the kinetics of ethylene trimerization on a homogeneous chromium–pyrrole catalyst under conditions similar to [27], varying temperature between 30 and 70 °C and ethylene pressure 0.4–1.6 MPa. Reaction orders with respect to ethylene were determined, and kinetic equations were derived, with calculations satisfactorily matching experimental results. In

[29], data were presented on the oligomerization of propylene, propane–propylene, and butane–butylene fractions over aluminum chloride in a carbon tetrachloride medium, modified with magnesium, nickel, and copper. At 30 °C, propylene conversion on $Al+CCl_4$ was 50%, on $Al+CCl_4+Mg$ 72%, on $Al+CCl_4+MgCl_2$ 76%, on $Al+CCl_4+NiCl_2$ 54%, and on $Al+CCl_4+CuCl_2$ 58%.

To obtain synthetic lubricants, study [30] presented the results of PAO synthesis through ethylene oligomerization on Lewis acids, such as $AlCl_3/BF_3$ systems, transition metal complexes, and ionic liquids. It was noted that active and selective catalysts are required for PAO production, and pathways for the development of efficient catalysts were recommended.

Studies [31–38] are devoted to the investigation of ethylene oligomerization using chromium complex catalysts. In [31], the authors employed N-arylphosphinamine ligands forming Cr^{3+} complexes for ethylene tetramerization: $C_6H_4(m\text{-}CF_3)N(PPh_2)_2$ (1); $C_6H_4(p\text{-}CF_3)N(PPh_2)_2$ (2); $C_6H_4(o\text{-}CF_3)N(PPh_2)_2$ (3); $C_6H_3(3,5\text{-bis}(CF_3))N(PPh_2)_2$ (4). Upon activation with MMAO-3A (co-catalyst), the novel catalytic system with the m-functional PNP ligand (1) exhibited high selectivity (90%) toward 1-octene at a rate of 2000 kg/g Cr·h. In contrast, ligands with para- and ortho-substitutions demonstrated significantly lower activity and selectivity. In [32], a PNP ligand incorporating an N-triptycene scaffold was employed. After activation with MMAO-3A, the catalytic mixture containing the Cr^{3+}/ligand complex effectively promoted ethylene tetramerization with high productivity (1733 kg/g Cr·h) and selectivity toward 1-octene (74.1%). PNP ligands bridging at the 1- or 1,4-positions of the triptycene moiety achieved high selectivity toward 1-hexene and 1-octene, exceeding 90% [32]. Comparative catalytic studies with various PNP ligands, with and without the N-triptycene framework, showed that rational design of PNP ligands with an optimal steric profile around the nitrogen center enables controlled and highly selective ethylene oligomerization involving C6 cyclic intermediates.

Study [33] presented a review of chromium catalysts for selective ethylene oligomerization into 1-hexene and 1-octene, where catalytic systems were classified according to ligand type. Despite significant advances in the field, the range of catalysts capable of combining high activity, selectivity, and low polymer formation remains limited, which is particularly relevant for ethylene tetramerization to 1-octene. The work also addressed recent issues regarding oligomerization mechanisms.

In [34], a series of Cr^{3+} complexes was synthesized: $[Cr\{1\text{-}(3\text{-phenoxypropyl})\text{-}1H\text{-pyrrole}\}Cl_3]_2$ (Cr1), [Cr{1-(3-phenoxypropyl)-3,5-dimethyl-1H-pyrrole}Cl3]2 (Cr2), and [Cr{1-(3-phenoxypropyl)-3-phenyl-1H-pyrrole}Cl3]2 (Cr3). These were characterized by elemental analysis, HRMS and IR spectroscopy. Upon activation with MAO, complexes Cr^2 and Cr^3 demonstrated moderate activity in ethylene oligomerization. In contrast, Cr1/MAO catalyzed ethylene polymerization (63.7 wt.%). Catalytic activity and selectivity were found to be highly sensitive to the R-group at the 3- and 5-positions of the pyrazolyl ring. Based on electronic and steric effects of R-substituents, the trend in ethylene oligomerization activity was established as Cr2(PzMe2) > Cr3(PzPh) > Cr1(Pz).

Study [35] reported highly active chromium catalysts for ethylene tri- and tetramerization using iminophosphine ligands. The influence of electronic and steric modifications of these ligands on activity and selectivity was examined by varying P- and/or N-substituents. After activation with MMAO, the ligand bearing a P-cyclohexyl group showed high activity (307 kg/g Cr·h) with 92.6% selectivity toward trimerization. Reduction of steric hindrance at the N-aryl group decreased selectivity toward 1-hexene to 74.5% and resulted in the formation of 10.3% 1-octene. X-ray structural analysis confirmed that ligands coordinated to the chromium center in a κ2-P,N binding mode.

In [36], bidentate PN ligands were applied for ethylene tri- and tetramerization. Steric restoration principles were used in the design of N-phosphinoamidinate ligands for chromium catalysts. The most effective system, Cr/PN/MMAO, producing 1-octene, differed from the reference Cr/PNP/MMAO system in that 1-octene selectivity was proportional to the ligand bite angle within a narrow range. Acyclic phosphine catalysts yielded lower amounts of 1-octene due to smaller bite angles. The relationship between ligand bite angle and 1-octene selectivity was disrupted when the Cr/PN/MMAO structure was modified [36].

In [37], ligands L1–L3 of the type $Ph_2PN(cyclopentyl)P(NR_2)_2$ were employed in chromium complexes, where R = methyl (L1), ethyl (L2), and isopropyl (L3), for selective ethylene tri-/tetramerization. It was established that the length of the radical affects both activity and oligomer selectivity. Maximum selectivity toward 1-octene was 67.98%, while catalysts with ethyl and isopropyl radicals demonstrated 97.76% selectivity toward 1-hexene. Aluminum complexes were used as precatalysts. Catalysts with higher Al/Cr ratios and under elevated ethylene pressure showed high activity and selectivity in ethylene oligomerization [37].

In [38], ethylene tetramerization was carried out using the complex $[2\text{-}CrCl_2]+[B(C_6F_5)_4]$ in combination with iBu_3Al, which achieved high tetramer yield at temperatures up to 90 °C with minimal polyethylene byproduct formation (0.03%). Screening of a series of $iPrN[P(C_6H_4\text{-}p\text{-}SiR_3)_2]_2$ ligands further confirmed that bulky R3Si substituents enhanced catalytic activity while reducing polyethylene formation. The authors of [39] proposed the chromium complex $[1\text{-}CrCl_2][B(C_6F_5)_4]$, where 1 = $iPrN[P(C_6H_4Si(Octyl)_3)_2]_2$, for ethylene tetramerization with minimal polyethylene byproduct. Experiments showed that polyethylene formation can be reduced by adjusting synthesis conditions for $[1\text{-}CrCl_2][B(C_6F_5)_4]$.

Many companies, such as Sasol, which produce polyolefin oils or long-chain α-olefins, use expensive MAO as a co-catalyst with transition metal complexes. In [40], the search for MAO-free ethylene oligomerization pathways was investigated. A chromium complex of the composition $[1\text{-}CrAl(acac)Cl_3(THF)]_2+[B(C_6F_5)_4]_{-2}$ was synthesized, which, in combination with iBu3Al, showed four times higher activity than the original Sasol system composed of $Cr(acac)_3$, $iPrN(PPh_2)2$, and MAO. This effect was achieved by introducing bulky trialkylsilyl substituents into the para-positions of phenyl groups, which reduced polyethylene formation even at elevated temperatures (<0.2%). The authors [40] discussed the intricacies of complex synthesis, paying particular attention to the steric effects of ligands, supported by NMR results and DFT calculations.

In [41], silicon-bridged N,P ligands (PNSiP) with Cr^{3+} were used for ethylene tri-/tetramerization, with various fluorinated hydrocarbons as modifiers. Modifiers such as perfluorohexane, hexafluorobenzene, and perfluorobiphenol significantly influenced ethylene oligomerization into 1-hexene and 1-octene. The best results were obtained with perfluorohexane at 90 °C. Detailed NMR, UV, and IR studies led the authors [41] to conclude that perfluorohexane can react with trimethylaluminum present in modified methylaluminoxane (MMAO). The solubility of Cr^{3+} in the solvent increased after the addition of perfluorohexane, and possible pathways of its interaction with trimethylaluminum and MMAO were proposed.

For ethylene tri-/tetramerization, the authors of [42] used the complex $[CrCl_3(THF)_3$ + MMAO]. Binuclear ligand frameworks were linked via alkyl spacers, the length of which affected catalyst activity and selectivity. Longer linkers inhibited catalytic activity, while the chromium complex with shorter linkers and stronger σ-donor P-isopropyl substituents exhibited high activity and selectivity of 93.1% for the sum of C_6 and C_8, with 53.0% attributed to 1-octene, along with a low yield of polyethylene byproduct.

In [43], Cr^{3+} complexes with ligands of the type Ph2C(R)=CHPPh(alkyl) were synthesized and tested in ethylene tri-/tetramerization. It was established that not only steric properties of the main chain substituents and P-substituents, but also electronic properties of the main chain, influenced catalytic activity. At 100 °C and 40 atm ethylene pressure, selectivity of 84.8% for C6+C8 and 56.1% for 1-octene was achieved. The synthesized complex combined with MMAO in ethylene oligomerization yielded productivity up to 2213 g Cr–1 h–1 with minimal polyethylene formation. The influence of ligand structure on activity and selectivity was discussed, demonstrating that electron-withdrawing phenyl groups in the main chain decrease chromium activity in ethylene tri-/tetramerization [43].

In [44], Cr^{3+} complexes with phenylene-bridged diphosphine ligands bearing P-alkyl substituents were employed for ethylene tri-/tetramerization. Selectivity was shown to depend on the steric properties of ligands. Reduction of ligand steric bulk favored trimerization, yielding 82.5% 1-hexene, while the introduction of a bulky PPhCy group increased 1-octene content to 43.3%, with productivity of 1874 kg/g Cr·h at 40 °C and negligible polyethylene byproduct formation.

In [45], Cr^{3+} was coordinated with bidentate nitrogen-containing ligands. Catalytic systems Cr(III)/TEA/L, where Cr(III) represented chromium tris(2-ethylhexanoate) ($Cr(EH)_3$) and chromium tris(acetylacetonate) ($Cr(acac)_3$), TEA was triethylaluminum, and L corresponded to 2,2’-bipyridine (bipy), 1,10-

phenanthroline (Phen), N,N’-bis(cyclohexyl)diazabutadiene-1,3 (DCy-DABD), and N,N’-bis(2,6-diisopropylphenyl)diazabutadiene-1,3 (Dipp-DABD), were applied for ethylene polymerization and oligomerization at 60–80 °C and 2–3 MPa. Their catalytic properties were evaluated, showing that increasing ligand basicity in the studied series promoted the formation of higher oligomers (ΣC_{8+}) and polyethylene. Selectivity toward 1-butene or 1-hexene decreased in all cases, with maximum selectivity of 98% for 1-butene and 92% for 1-hexene achieved on the DCy-DABD/TEA system, while the Dipp-DABD complex proved suitable for polymerization.

The authors [46] employed chromium(III) complexes with ligands of the type Ph2PC(R’’)=CHPRR’, containing a P-alkyl substituent, for the tri- and tetramerization of ethylene. These complexes exhibited high activity and a low polyethylene by-product yield of $\leq 0.1\%$. Dialkylphosphine ligands, being strong σ-donors, demonstrated higher activity than mixed alkyl/phenylphosphine analogues: the greater the electron-donor ability, the higher the catalytic activity. Reducing the steric volume of the ligand shifted the reaction pathway from trimerization toward tetramerization, yielding an octene-1 to hexene-1 ratio greater than 1, without compromising the high combined selectivity of hexene-1/octene-1 (> 90%). Furthermore, ligands with dialkylphosphine groups displayed high activity with high selectivity for octene-1 and complete suppression of polyethylene formation. In all cases, MMAO served as a cocatalyst. In [47], the use of chromium complexes with PNP ligands containing a condensed aryl fragment was reported, demonstrating 74.6% selectivity toward octene-1 and an octene-1/hexene-1 ratio of 3.4 when the nitrogen atom bearing the aromatic group was located at position 2.

The exceptional importance of long-chain or LAO for the production of base lubricating oils, surfactants (detergents), and other petrochemical syntheses has led to a vast body of patent literature, where chromium, along with other transition metals, serves as the principal complex-forming center [48–63]. In [48], a catalyst based on Cr(III) salts and diphosphine ligands was patented, with the structural design of the ligands described in detail. The catalyst was combined with a mixture of organoaluminum activators, namely methylaluminoxane–trimethylaluminum or a cocatalyst consisting of a pentafluorophenyl-substituted borate together with triisobutylaluminum.

In [49, 50], halogen-containing substituents in diphosphine ligands were employed for the tri-/tetramerization of ethylene. In [49], the invention described the structure of the halogen-substituted diphosphine ligand, including substituents on the phenyl rings of the phosphine complex and two ethylene substituents bridging the phosphorus atoms of the diphosphine framework. Similar results for diphosphine ligands in chromium(III) complexes were reported in [50].

Patent [51] disclosed a method of ethylene oligomerization to obtain hexene-1 and octene-1 in an organic solvent in the presence of a chromium catalyst and an organoaluminum compound. The ligand of the chromium complex was a derivative of 5,6-dihydrodibenzo[c,e]-1,2-azaphosphinine, whose structure significantly influenced the oligomerization pathway. In [52], a method for ethylene oligomerization into higher olefins C10–C30 using triazole-based ligands was patented. The general formula included substituents R=H, (4,5-bis(diphenylphosphanyl)-2H-1,2,3-triazole)-P,P)-trichlorochromium(III) – K1; R=$(CH_2)_5CH_3$, (4,5-bis(diphenylphosphanyl)-1-hexyl-1H-1,2,3-triazole)-P,P)-trichlorochromium(III) – K2; R=$(CH_2)_2S(CH_2)_7CH_3$, (4,5-bis(diphenylphosphanyl)-1-(2-octylthio)ethyl-1H-1,2,3-triazole)-P,P)-trichlorochromium(III) – K3; R=CH_3, (4,5-bis(diphenylphosphanyl)-2-methyl-2H-1,2,3-triazole)-P,P)-trichlorochromium(III) – K4; R=n-Bu, (4,5-bis(diphenylphosphanyl)-2-butyl-2H-1,2,3-triazole)-P,P)-trichlorochromium(III) – K5, among others.

In [53], ethylene oligomerization to hexene-1 or octene-1 employed a catalytic composition comprising a chromium complex with a diphosphineamine ligand (NPNPN) of the formula (R1)(R2)N-P(R3)-N(R4)-P(R5)-N(R6)(R7), where R1–R7 each independently represent hydrogen, linear or branched C1–C10 alkyl, phenyl, C6–C20 aryl, or C6–C20 alkyl-substituted phenyl, along with an activator or cocatalyst. The chromium center could be in oxidation state +2 or +3. The patent described 23 variations of the ligand structure. The activators or cocatalysts included trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, diethylaluminum chloride, ethylaluminum sesquichloride, ethylaluminum dichloride, methylaluminoxane, MMAO, or combinations thereof. In [54], a chromium complex for olefin oligomerization employed a diphosphinoaminyl ligand and an alkyl metal compound containing aluminoxane. The resulting mixture was prepared at metal-to-metal ratios of 100:1 to 3000:1, aged for 20 min at 10–130 °C in the substantial absence of olefin monomer, and then contacted with the monomer at 0–150 °C to afford an oligomeric product. The metal compound was chromium(III) chloride or chromium(III) acetylacetonate, with ligand structures and reaction conditions described across 15 claims.

The catalyst for ethylene oligomerization into higher olefins C_{10}–C_{30} patented in [55] comprised a series of triazole-based ligands: R=H, (4,5-bis(diphenylphosphanyl)-2H-1,2,3-triazole)-P,P)-trichlorochromium(III) – K1; R=$(CH_2)_5CH_3$, (4,5-bis(diphenylphosphanyl)-1-hexyl-1H-1,2,3-triazole)-P,P)-trichlorochromium(III) – K2, among others.

References [55–58] reported ethylene dimerization to butene-1. In [55], the process involved feeding ethylene into a reactor containing solvent and a catalyst/cocatalyst mixture, conducting oligomerization, and discharging the reactor effluent containing linear α-olefins including butene-1, unreacted ethylene dissolved in the effluent, and the catalytic composition, followed by separation of ethylene and butene-1. Fourteen claims detailed the process, with solvents including aromatic hydrocarbons, cyclic aliphatic hydrocarbons, and ethers, preferably toluene, benzene, ethylbenzene, cumene, xylenes, hexane, octane, and others. In [56], a single-pass reactor with an internal partition, separation system, and external drive was used to induce instabilities in the liquid flow. The authors of [58] noted that chromium, molybdenum, or tungsten could act as complex-forming centers, with ligand structures described in general terms.

Reference [59] reported ethylene oligomerization using treated solid oxides. Such catalytic systems could include a heteroatomic ligand complex of a transition metal, a chemically treated solid oxide, and an organoaluminum compound. The ligand complexes involved diphosphine derivatives, such as N_2-phosphinylamidinate, N_2-phosphinylformamidine, and N_2-phosphinylguanidine transition metal complexes, with synthesis methods provided. In [60], a catalytic system based on a heterocyclic transition metal complex with a [(phosphinyl)aminyl]imine ligand was proposed, with the structure and substituents detailed, combined with an organoaluminum compound. Ethylene oligomerization included contact of ethylene with the catalytic system and organoaluminum compound, optionally in the presence of hydrogen. A similar system with 2-[(phosphinyl)aminyl] cyclic imine ligands was described in [61]. In [62], a multistage activation method for ethylene oligomerization catalysts was introduced: formation of a first mixture of ethylene, chromium heteroatom ligand complex, and organoaluminum compound in an activation vessel, residence time control, subsequent introduction into the reaction zone with ethylene and a second organic medium, and product recovery. The process could be conducted under hydrogen or inert gas, with variations in stage sequencing and residence times considered.

Patent [63] disclosed a modified PNP ligand, its synthesis, and an ethylene oligomerization catalyst. The patent described seven variations of substituents in the diphosphine ligand and conditions for ligand formation. Cocatalysts included MAO, MMAO, alkyllithium compounds (methyl-, ethyl-, propyl-, isopropyl-, n-butyl-, sec-butyl-, tert-butyl-, amyl-, hexyl-, cyclohexyl-, tert-octyl-lithium), and triethylaluminum, with specified ratios relative to chromium. The catalyst selectively oligomerized ethylene in the presence of hydrogen.

Analysis of the patent data [48–63] highlights their applied orientation: the production of long-chain linear α-olefins, which are in high demand across numerous petrochemical syntheses. The most large-scale applications include the manufacture of polyolefin base oils and synthetic detergents. No consistent patterns have been identified regarding the influence of ligand structure in the transition metal complexes on catalytic performance, with only isolated empirical observations reported [48–63].

In studies [64–66], iron was employed as the transition-metal complex-forming center. The authors of [64] reported data on the oligomerization of ethylene catalyzed by iron formazanates and organoaluminum compounds. Complex synthesis involved $Fe(ClO_4)_2 \cdot H_2O$, while substituents in the nitrogen-containing backbone and two substituents in the benzene ring of the formazanate ligand were varied. Using a range of modern physical techniques, the properties of the synthesized complexes were determined and subsequently tested in oligomerization. The maximum content of hexene-1 (99%) was observed with complex 1.7Fe + MAO, and 95% with complex 1.5Fe + MAO; the maximum octene-1 content (60%) with complex 1.6Fe + MAO; and the maximum decene-1 content (64%) with complex 1.2Fe + $Al(C_2H_5)_2Cl$. These results indicate that iron complexes based on benzothiazolylformazan ligands combined with organoaluminum compounds exhibit selective catalytic activity in ethylene oligomerization to hexene-1, with lower efficiency for octene-1 and decene-1.

Patents [66, 67] provide data on ethylene oligomerization methods. In the invention described in [67], the catalytic system consists of a heteroatomic ligand–iron salt complex combined with an organoaluminum compound. Fourteen claims specify the composition and structure of the heteroatomic ligand. Reported outcomes include conversion to hexene-1 with 98.5% selectivity in the first catalytic system, octene-1 with 98% selectivity in the second, decene-1 with 97.5% selectivity in the third, and dodecene-1 with 96.5% selectivity in the fourth system, forming a C12 oligomeric product. Study [65] describes a technological scheme for continuous ethylene oligomerization using a bis(imino)pyridine–iron salt complex. The ligand was 2,6-bis[(arylimino)hydrocarbyl]pyridine, where the substituted aryl groups could be identical or different, or [(arylimino)hydrocarbyl][(substituted arylimino)hydrocarbyl]pyridine. The iron salt complex had the formula FeXn, where n = 2 and X represented a monoanionic species. The cocatalyst was an organoaluminum compound (alumoxane).

In the next series of studies [67–75], other transition metals were employed as complex-forming centers. The authors of [67] investigated selective ethylene trimerization using the system phenoxy–imine–ether(F1)$TiCl_3$/MAO. The results demonstrated that the system either trimerizes or polymerizes ethylene depending on the reaction temperature. At 30–40 °C, hexene-1 selectivity reached 85%. At temperatures above 60 °C, polyethylene was produced with 70–80% selectivity. The catalytic mechanism was discussed as being similar to that of Ziegler–Natta catalysts.

In [68], the authors described selective ethylene trimerization with titanium complexes containing phenoxy–imine ligands with side groups. Catalytic systems of the type (F1)$TiCl_3$/MAO, where F1 was a phenoxy–imine ligand with an additional aryl–O–CH_3 donor group, demonstrated high activity in selective trimerization. NMR and EPR spectroscopy were used to study titanium species formed in the catalytic systems (F1)$TiCl_3$/MAO, (F1)$TiCl_3$/MMAO, and (F1)$TiCl_3$/AlR3/$[Ph_3Cl]+[B(C_6F_5)_4]-$, where R = Me, Et, or iBu. It was shown that at the initial stage of the reaction, (F1)$TiCl_3$ with MAO, MMAO, or $AlMe_3/[Ph_3Cl]+[B(C_6F_5)_4]$ formed outer-sphere ion pairs, which partially converted into Ti^{3+} and Ti^{2+} species. The system (F1)$TiCl_3$/MMAO exhibited lower hexene-1 activity compared to (F1)$TiCl_3$/MAO due to undesired polyethylene formation. It was suggested that Ti^{2+} and Ti^{4+} ionic species participate in ethylene trimerization.

In [69], zirconium was used as the complex-forming center. Ethylene oligomerization was conducted on zirconium carboxylates derived from individual carboxylic acids $CH_3(CH_2)_2COOH$ and $CH_3(CH_2)_8COOH$. Catalyst activity depended on the composition of the zirconium complex and the nature of the solvent. The oligomers consisted of C_4–C_{10} fractions, and pathways to increase the C_{12}–C_{18} fraction were discussed. In [70], heterogeneous zirconium-containing catalytic systems activated with organoaluminum compounds in heptane, toluene, and chlorobenzene were employed. Activity was higher in the presence of diethylaluminum chloride compared to ethylaluminum dichloride. Oligomerization products consisted of C_4–C_{18} oligomers, while in the presence of ethylaluminum dichloride an oil fraction with boiling point > 350 °C was obtained in > 75% yield. The products were easily separated from the catalysts by simple decantation, and zirconium complexes could be reused for subsequent ethylene oligomerization.

Study [71] reported butene oligomerization over boron-containing alumina. The highest activity was observed with a catalyst containing 4.5% boron oxide, achieving butene conversions of 77.8–86.8% with 90% selectivity to liquid products at 150 °C, 8.0 MPa, and feed rates of 0.5–1.0 h−1. The catalyst was regenerable, with activity restored after regeneration.

Patent [73] disclosed a method and device for α-olefin production. The catalyst was based on alumina with a surface area of 450–460 m^2/g, modified with χ- and γ-dialuminum trioxide. Various fractions containing low-molecular-weight olefins were oligomerized. The technology involved multiple parallel–sequential stages in continuous operation, resulting in PAOs. Reactions proceeded at 60–100 °C and 1.0–4.0 MPa, with feed rates specified for different stages. However, no data were provided on the yield or composition of PAOs.

The authors of [73] also synthesized nine complexes based on oxovanadium(IV) and cobalt(II) ions combined with organic ligands such as dipicolinic acid, 2,2′-bipyridine, iminodiacetic acid, diglycolic acid, thiodiacetic acid, and 1,10-phenanthroline. Compound $[VO(tda)\cdot 0.5H_2O]$ was a novel complex, with its synthesis and structure described for the first time in [73]. These complexes were tested in ethylene oligomerization. The most effective catalyst was a cobalt(II) complex containing an iminodiacetate anion and 2,2′-bipyridine. Other polycarboxylate complexes also showed significant activity in ethylene oligomerization.

Study [74] described the preparation of a zirconium amide complex catalyst for ethylene oligomerization. The catalyst composition included a zirconium amide of general formula $ZrX_m\cdot{}_n(RCONR'R'')$, where X is a halogen atom (preferably chlorine), m = 4, n = 2, and R, R′, R″ are saturated or unsaturated aliphatic $C_{1\text{–}10}$ hydrocarbons, combined with an organoaluminum compound and an additive. Eleven claims specified zirconium ligand structures and types of organoaluminum compounds.

Review [75] emphasized the importance of producing LAO using metal–organic framework (MOF) catalysts. Various MOF-based methods for selective ethylene oligomerization were discussed. The process proceeds through a metallacyclic mechanism, with linear chain growth recognized as the accepted pathway for ethylene oligomerization and polymerization. The potential of MOFs for future studies in α-olefin oligomerization and polymerization was highlighted.

In the subsequent series of publications [76–81], zeolite catalysts were used for olefin oligomerization. Zeolites, being solid acids, exhibit their acidity at elevated temperatures, making them suitable for industrially important oligomerization processes such as gasoline production from butane–butylene fractions. Studies [76–79] focused on butene-1 oligomerization. In [76], synthetic zeolite ZSM-5 in its acidic H-ZSM-5 form was employed in a differential reactor under atmospheric pressure and varying temperatures. As the temperature increased from 150 to 200 °C, selectivity toward liquid hydrocarbons rose, but above 200 °C selectivity declined due to competing cracking reactions. The highest selectivity (86%) was obtained with H-ZSM-5 at 200 °C, 50 kPa partial pressure, and a feed rate of 12.5 × 10−3 h−1. In [77, 79], butene-1 oligomerization was carried out over H-ZSM-5 with SiO_2/Al_2O_3 ratios of 30–280 in fixed-bed reactors at 175–325 °C, 1.5–40 bar, and feed rates of 2–6 h−1. Catalyst regeneration was achieved by coke combustion in a steam–air mixture at 500 °C. In [78], olefin oligomerization was studied in a light gasoline FCC matrix in the presence of zeolites. Under optimal conditions (dual-layer bed, 270 °C, 40 bar, 1.0 h−1 feed rate), iso-olefin mixtures were obtained, which after hydrogenation could be converted into environmentally clean gasoline and diesel fuel components.

In [81], styrene oligomerization was performed over zeolites ZSM-12 both in solvent (chlorobenzene) and solvent-free systems, achieving high conversion (98–100%) and 82% selectivity toward linear dimers. The main oligomerization products on zeolite β were dimers (70–80%), predominantly the linear isomer trans-1,3-diphenylbutene-1. In contrast, the less active zeolite Y produced mixtures of oligomers, with dimers dominating (53–60% in chlorobenzene) or dimers and trimers (60–80% in bulk). Study [80] reported oligomerization of higher α-olefins using catalysts containing a perfluorinated copolymer F-4SF. Mesoporous catalysts demonstrated high activity in decene-1 oligomerization under both batch and continuous-flow conditions, achieving 95–99% conversion with 90–95% dimer yield in batch operation, and approximately 70% conversion in continuous mode.

Studies [82–86] present results on the oligomerization of olefins using ionic liquid catalysts. Ionic liquids are substances composed solely of ions, practically salts dissolved in water with melting points below 100 °C. The authors of [82] reported the oligomerization of olefins using novel and efficient catalytic systems based on Brønsted acidic ionic liquids. The main catalyst was a Brønsted ionic liquid, with tricaprylmethylammonium chloride employed as a cocatalyst. The synthesized ionic liquids with acid groups were characterized by Fourier-transform infrared spectroscopy, UV–visible spectroscopy, ^{1}H and ^{13}C NMR for structural and acidity analysis. The effects of different ionic liquids, catalyst loading, cocatalysts, molar ratios of ionic liquid to cocatalyst, reaction time, pressure, temperature, solvents, feedstock sources, and recycling of the catalytic systems were studied. Among the synthesized ionic liquids, 1-(4-sulfoacid)butyl-3-hexylimidazolium hydrogensulfate ([HIMBs]HSO_4) exhibited the highest activity. Under optimal reaction conditions, the conversion of isobutane reached 83.21 % with a trimer selectivity of 35.80 %. The catalytic system was reusable, and a plausible reaction mechanism was proposed. Ethylene, propylene, and isobutene were tested on the optimized catalytic system. It was demonstrated that ethylene produced linear α-olefins up to C_{15}, whereas isobutene and propylene yielded various branched olefins, with schematic pathways of oligomer formation provided.

In [83], ionic liquids were employed as oligomerization modifiers of α-olefins with conventional $AlCl_3$ catalysts in the reaction of 1-decene oligomerization into polyolefin oils. Various ionic liquids with identical anionic moieties but different cationic fragments were used, based on triethanolamine (TEA), tributylamine (TBA), and pyridine (Py) precursors. The results showed that ionic liquids derived from Py and TBA suppressed the molecular weight of PAO compared with neat aluminum chloride, whereas TEA-based ionic liquids enhanced it. According to ^{13}C NMR, oligomers obtained with TEA exhibited a higher degree of long-chain branching, which is favorable for improving viscosity indices. Schemes of 1-decene oligomerization on four catalytic systems with the percentage composition of the main oligomers were provided. Possible mechanisms of the reaction were discussed using ^{13}C and ^{1}H NMR results.

Article [84] reported the production of lubricants based on PAOs using (poly)ionic liquid/$AlCl_3$ catalysts as environmentally friendly alternatives to the conventional $AlCl_3$ route. To reduce the dosage of corrosive $AlCl_3$ in PAO production, two new (poly)ionic liquid/$AlCl_3$ catalysts were synthesized: first, ionic liquid (IL) was obtained by reacting 1-vinylimidazole with benzyl chloride, and subsequently, the vinyl group was polymerized via radical polymerization to yield polyionic liquid (PIL). The cationic oligomerization of three α-olefin monomers (1-hexene, 1-octene, 1-decene) was conducted with IL/AlCl3 and PIL/AlCl3 at a 50:50 ratio to minimize AlCl3 usage. A comparison of these catalysts with neat $AlCl_3$ showed that PIL/AlCl3 is a promising alternative to corrosive $AlCl_3$, achieving similar molecular weights while exhibiting superior viscosity properties.

The authors of [85] reported the oligomerization of 1-octene and 1-decene on chloroaluminate ionic liquids, which were characterized by high selectivity, low consumption, and recyclability. Viscosity–temperature dependence, lubricity, oxidation resistance, and volatility of the resulting oils were studied. Work [86] described the oligomerization of 1-hexene on recyclable chloroaluminate ionic liquid catalysts in combination with titanium complexes containing “grafted ionic liquid” ligands. It was shown that selective production of oligomers with oligoalkylnaphthene structures and narrow molecular weight distributions, free from double bonds, was achievable. The possibility of regulating the molecular weight of oligomeric products by varying the molar ratio of catalytic system components was established.

3. Conclusion

The principal catalysts for olefin oligomerization are coordination compounds of transition d-metals, where the nature of the central metal plays a decisive role: the greater the number of oxidation states, the broader the range of complexes formed. Chromium is particularly notable in this respect, as evidenced by a substantial body of patent data.

A review of the literature indicates that the catalytic performance in olefin oligomerization depends on the composition, structure, and acidity of ligands. However, no systematic correlations have been identified, and outcomes are determined primarily by experiment, that is, trial-and-error and empirical approaches.

Zeolite catalysts constitute a distinct class employed in the oligomerization of 1-butene and the butane–butene fractions of petroleum refining. Their catalytic activity is associated with acidic sites of the zeolite framework, which require elevated temperatures for activation and may be accompanied by competing cracking reactions.

Particular interest lies in the use of ionic liquids as olefin oligomerization catalysts, although data on their catalytic properties remain scarce.

Catalysis with transition-metal complexes is carried out in the presence of organoaluminum compounds (MAO, MMAO), often referred to by authors as cocatalysts. Numerous unresolved issues remain, the most significant being which complexes determine selectivity and which are responsible for activity in the catalytic system.

Research into the development of novel olefin oligomerization catalysts must therefore be continued, since experimental validation remains the decisive factor.

Funding: This work was supported by the targeted research funding program implemented by the Science Committee of the Ministry of Health, Higher Education and Science of the Republic of Kazakhstan, under program BR27101179 (2025–2026).

Conflict of interest: The authors declare no conflicts of interest.

ОЛЕФИНДЕРДІ ОЛИГОМЕРЛЕУ КАТАЛИЗАТОРЛАРЫ

С.Р.Қонысбаев*, К.А. Кадирбеков, О.К. Югай

Ә.Б. Бектуров атындағы химия ғылымдары институты, Алматы, Қазақстан
**E-mail: srkonuspayev@mail.ru*

Түйіндеме. Бұл мақалада олефиндерді олигомерлеу катализаторларына әдеби және патентті мәліметтерге талдау жасалған. Олефиндерді олигомерлеу арқылы ұзынтізбек сызықты α-олефиндерді алады, олардан елге керек базалық жағар майлар, жуғыш заттар тағы басқа керек нәрселер алынады. Олигомерлеу катализаторлары ретінде өтпелі металдарының комплексті мен қосылған алюминийорганикалық қосылыстары қолданылады, шешуші зат ретінде комплекс құраушы металдың табиғаты саналады, оның зарядталған саны неғұрлым көп болса соғұрлым пайда болатын комплекстердін саны көп болады, олардың ішінде хромның орны бөлек, оған арналған патент саны да көп. Олефиндерді олигомерлеу каталитикалық жүйелер өтпелі металдар комплекстері мен қосылған алюминийорганикалық қосылыстардан тұрады, реакцияларын еріткіш ортада жоғары температура мен жоғары қысымда жүргізіледі. Ал әр металда каталитикалық қасиеттерді анықтайтын лигандтардың табиғаты: құрамы, құрылысы, структурасы мен қышқыл-негіздік қасиеттері; бірак оларды таңдау заңдылықтары анықталмаған, оның жақсы-жаманын эксперимент анықтайды. Олефиндерді олигомерлеу катализаторлары ретінде цеолиттер және ионды сұйықтар болуы мүмкін. Цеолитте бутен-1 және мұнайөңдеудегі бутан-бутилен фракцияларын олигемерлеп бензин алады, процесте 300°С жоғары температурада цеолиттің қышқыл орталары белсенді болғанда жүргізеді. Ерекше қызықшылық танытатын катализатор ретінде қолданылатын иондық сұйықтар, оларда олигомерлеу реакциясы атмосфералық қысыммен 100°С төмен температурада өтеді, бірақ олар туралы мәлімет аздау.

Түйінді сөздер: олигомеризация, α-олефин, катализатор, ауысу металдары, цеолит, иондық сұйықтық.

Конуспаев Сапаркали Ретаевич	*химия ғылымдарының докторы, профессор*
Кадирбеов Кайрат Адырбекович	*химия ғылымдарының докторы, профессор*
Югай Ольга Константиновна	*химия ғылымдарының кандидаты, доцент*

КАТАЛИЗАТОРЫ ОЛИГОМЕРИЗАЦИИ ОЛЕФИНОВ

С.Р Конуспаев**, К.А. Кадирбеков, О.К. Югай

Институт химических наук имени А.Б. Бектурова, Алматы, Казахстан
**E-mail: srkonuspayev@mail.ru*

Резюме. В статье проведён анализ литературных и патентных данных по катализаторам олигомеризации олефинов для получения длинноцепных линейных α-олефинов, которые имеют важное значение для получения товаров народного потребления, как базовые смазочные масла, моющие средства и многое другое. Катализаторами олигомеризации олефинов являются комплексные соединения переходных металлов и их сочетание с алюминийорганическими соединениями, где решающим фактором является природа металла комплексообразователя, чем больше зарядовых состояний металла, тем разнообразнее образуемые ими комплексы и особо в этом отношении выделяется хром, которому посвящены большое количество патентных данных. Каталитические системы олигомеризации олефинов состоят из комплексов переходных металлов плюс алюминийорганические соединения, которых называют со катализаторами, реакции проводят в растворителе при повышенных температурах и давлениях. На каждом металле каталитические свойства определяются природой лиганда: состав, строение, структура, кислотно-основные характеристики, однако каких-то закономерностей по их подбору не обнаружено и все определяется экспериментом. В качестве катализаторов олигомеризации олефинов могут выступать цеолиты и ионные жидкости. На цеолитах олигомеризуют бутен-1 или бутан-бутиленовую фракцию нефтепереработки для получения бензина, процесс проводят при температурах выше 300°С, когда активируются его кислотные центры. Особый интерес вызывает использование в качестве катализаторов ионных жидкостей, на которых олигомеризацию можно проводить при атмосферном давлении и ниже 100°С, хотя информации по нему немного.

Ключевые слова: олигомеризация, α-олефин, катализатор, переходные металлы, цеолит, ионная жидкость.

Конуспаев Сапаркали Ретаевич	*доктор химических наук, профессор*
Кадирбеов Кайрат Адырбекович	*доктор химических наук, профессор*
Югай Ольга Константиновна	*кандидат химических наук, ассоциированный профессор*

References

1. Serebrjakov B.R., Plaskunov T.K., Ansheles V.R. i dr. *Vysshie olefiny. Proizvodstvo i primenenie*. L., Himija, **1984**, 264. (In Russ.)

2. Cvetkov O.N. *Poli-α-olefinovye masla: himija, tehnologija i primenenie*. M., Tehnika, **2006**, 197. (In Russ.)

3. Belov G.P. Tetramerizacija jetilena v okten-1 (obzor). *Neftehimija*, **2012**, *52,* 163–178. (In Russ.)

4. Belov G.P., Matkovskij P.E. Tehnologii poluchenija vysshih linejnyh α-olefinov. *Neftehimija*, **2010**, *50*, 296–302. (In Russ.)

5. Konuspaev S.R., Nurbaeva R.K., Zhurtbaeva A.A. Katalizatory i tehnologii oligomerizacii olefinov v poluchenii poliolefinovyh smazochnyh masel (obzor-1). *Vestnik NAN RK*, **2016**, *4,* No 362, 54–66.

6. Parfenova L.V., Bikmeeva A.Kh., Kovyazin P.V., Khalilov L.M. The Dimerization and Oligomerization of Alkenes Catalyzed with Transition Metal Complexes: Catalytic Systems and Reaction Mechanisms. *Molecules,* **2024**, *29,* No 2, 502–549.

7. Petit J., Magna L., Mézailles N. Alkene Oligomerization via metallacycles: Recent Advances and Mechanistic Insights**.***Coordination Chemistry Reviews*, **2022**, *450*, 214227. ff10.1016/j.ccr.2021.214227ff. ffhal-03405630f

8. Hao B., Alam F., Jiang Y., Wang L., Fan H., Ma J., Chen Y.., Wang Y., Jiang T. Selective ethylene tetramerization: an overview. *Inorg. Chem. Front***.**, **2023**, *10,* 2860–2902. DOI:10.1039/D3QI00321C

9. Bekmukhamedov G.E., Sukhov A.V., Kuchkaev A.M., Kuchkaev A.M., Khayarov Kh.R., Dobrynin A.B., Babaev V.M., Yakhvarov D.G. Catalytic performance of nickel(II) complexes bearing 1,10-phenanthroline based ligands in homogeneous ethylene oligomerization. *Polyhedron*, **2022**, *223,* 115978. DOI:10.1016/j.poly.2022.115978

10. Metzger E.D., Brozek C.K**.,** Comito R.J**.,** Dincă M. Selective Dimerization of Ethylene to 1-Butene with a Porous Catalyst. *ACS Cent. Sci.*, **2016**, *2*(3), 148–153. DOI:10.1021/acscentsci.6b00012

11. Olivier-Bourbigou H., Breuil P.-A., Magna L., Michel T., Espada Pastor M.F., Delcroix D. Nickel catalyzed olefin oligomerization and dimerization // *Chem. Rev.*2020, 120, 15, 7919–7983. DOI:10.1021/acs.chemrev.0c00076

12. Jan O., Song K., Dichiara A., Resende F.L.P. Ethylene Oligomerization over Heterogeneous Catalysts. *Industrial & Engineering Chemistry Research Ind. Eng. Chem. Res.*, **2018**, *57,* No 31, 10241–10250. DOI:10.1021/acs.iecr.8b01902

13. Al Khudhair A., Bouchmella K. Andrei R.D., Hulea V., Mehdi A.A. Comparative Study of Ni-Based Catalysts Prepared by Various Sol–Gel Routes. *Molecules*, **2024**, *29*, No17, 4172. DOI:10.3390/molecules29174172

14. Peng A., Huang Zh., Li G. Ethylene Oligomerization Catalyzed by Different Homogeneous or Heterogeneous Catalysts. *Catalysts,* **2024**, *14*(4), 268. DOI:10.1021/acs.iecr.8b01902

15. Chen C., Meng L., Alalouni M.R., Dong X., Wu Zh.-P., Zuo Sh., Zhang H. Ultra-Highly Active Ni-Doped MOF-5 Heterogeneous Catalysts for Ethylene Dimerization // Nano, micro, small. **2023**, *19*, No 25,2301235. DOI:10.1002/smll.202301235

16. Forget S., Olivier-Bourbigou H., Delcroix D. Homogeneous and Heterogeneous Nickel-Catalyzed Olefin Oligomerization: Experimental Investigation for a Common Mechanistic Proposition and Catalyst Optimization. *ChemCatChem*, **2017**, No 12, p. 2408-2417. DOI:10.1002/cctc.201700348

17. Seufitelli G.V.S., Park J.J.W., Tran P.N., Dichiara A., Resende F.L.P., Gustafson R. The Role of Nickel and Brønsted Sites on Ethylene Oligomerization with Ni-H-Beta Catalysts. *Catalysts,* **2022**, *12*(5), No 5, 565. DOI:10.3390/catal12050565

18. Betz M., Fuchs C., Zevaco T.A., Arnold U., Sauer J. Production of hydrocarbon fuels by heterogeneously catalyzed oligomerization of ethylene: Tuning of the product distribution. Biomass and Bioenergy, **2022**, *166*, 106595. DOI:10.1016/j.biombioe.2022.106595

19. Shmidt F.K., Titova Ju.Ju., Belyh L.B., Gomboogijn M. Dimerizacija propilena v prisutstvii gidridnyh kompleksov nikelja, formiruemyh insitu. *Neftehimija,* **2010**, *50.* No 3, 217–225. (In Russ.)

20. Zajdman A.V., Kajumov R.R., Belov G.P., Pervova I.G., Lipunov I.N., Harlampidi H.Je. Oligomerizacija jetilena v prisutstvii kataliticheskih sistem na osnove formazanatov nikelja (II). *Neftehimija*, **2010**, *50,* 459–463. (In Russ.)

21. Song J., Zhang S., Dzhi S, Li L., Lu X., Sunn V.-H. 2,9-Dizameshhennye-1,10-fenantrolinovye kompleksy nikelja: poluchenie, svojstva i primenenie v reakcii oligomerizacii jetilena. *Kinetika i kataliz*, **2007**, *48*, No5, 710–714. (In Russ.)

22. Zajdman A.V., Hasbiullin I.I., Belov G.P., Pervova I.G., Lipunov I.N. Kataliticheskaja aktivnost' novyh formazanatov nikelja (II) v reakcii oligomerizacii jetilena. *Neftehimija*, **2012**, *52*, 31–38. (In Russ.)

23. Chen L., Li G., Wang Z., Li S., Zhang M., Li X. Ethylene Oligomerization over Nickel Supported Silica-Alumina Catalysts with High Selectivity for C_{10+} Products. *Catalysts*, **2020**, *10*, 180. DOI:10.3390/catal10020180

24. Koninckx E., Mendes P.S.F., Thybaut J.W., Broadbelt L.J. Ethylene oligomerization on nickel catalysts on a solid acid support: From New mechanistic insights to tunable bifunctionality. *Applied Catalysis A: General, 2021, 624*, 118296. DOI:10.1016/j.apcata.2021.118296

25. McCaig J., Lamb H.H. Ni-H-Beta Catalysts for Ethylene Oligomerization: Impact of Parent Cation on Ni Loading, Speciation, and Siting. *Catalysts*, **2022**, *12*, 824. DOI:10.3390/catal12080824

26. Finiels A., Fajula F., Hulea V. Nickel-based solid catalysts for ethylene oligomerization – a review. *Catal. Sci. Technol.*, **2014**, *4*, 2412–2426. DOI:10.1039/C4CY00305E

27. Hasbiullin I.I., Belov G.P., Harlampidi H.Je., Vil'me A.I. Oligomerizacija jetilena na kataliticheskoj sisteme jetilgeksanoat Cr–Al(C2H5)3–2,5-dimetilpirrol v prisutstvii CCl4. *Neftehimija*, **2011**, *51*, No 6, 450–455. (In Russ.)

28. Zil'bershtejn T.M., Korlash V.A. Lipskih M.V., Suvorova V.V., Golovko A.V. Kinetika reakcii trimerizacii jetilena na gomogennom hrom-pirrol'nom katalizatore. *Neftehimija*, **2012**, *52*, No 5**,** 371–376. (In Russ.)

29. Gusejnova G.A., Alieva N. Oligomerizacija olefinov na modificirovannyh aljumohloridnyh kataliticheskih sistemah. *Sciences of Europe*, **2022**, *89*, 53–58. (In Russ.)

30. Hanifpour A., Bahri-Laleh N., Mohebbi A. Oligomerization of higher α-olefins to poly(α-olefins). *Iran Polym J*, **2022**, *31*, 107–126. DOI:10.1007/s13726-021-01011-x

31. Jaseer E. A., Garcia N., Barman S., Khawaji M., Xu W., Alasiri H., Peedikakkal A.M.P., Akhtar M.N., Theravalappi R. Highly Efficient Ethylene Tetramerization Using Cr Catalysts Constructed with Trifluoromethyl-Substituted N-Aryl PNP Ligands. *ACS Omega*, **2022**, *7*, No19, 16333–16340. DOI:10.1021/acsomega.1c06657

32. Barman S., Jaseer E.A., Garcia N., Elanany M., Khawaji M., Xu W., Lin S., Alasiri H., Akhtar M.N., Theravalappil R. A rational approach towards selective ethylene oligomerization via PNP-ligand design with an N-triptycene functionality. *Chem.Commun.*, **2022**, *58*, 10044–10047. DOI:10.1039/D2CC02456J

33. Alferov K.A.**,** Belov G.P.**,** Meng Y. Chromium catalysts for selective ethylene oligomerization to 1-hexene and 1-octene: Recent results. *Applied Catalysis A General*, **2017,** *542*, 71–124. DOI:10.1016/j.apcata.2017.05.014

34. Milani J.L.S., Casagrande Jr O.L. Chromium Complexes Supported by Phenyl Ether-Pyrazolyl [N,O] Ligands as Catalysts for the Oligo- and Polymerization of Ethylene. *Applied Organometallic Chemistry*, **2020**, *34*(12). e5984. DOI:10.1002/aoc.5984

35. Zhao X., Wang J., Liu D., Kong W., Zhang J. Chromium Ethylene Tri-/Tetramerization Catalysts Supported by Iminophosphine Ligands. *ACS Omega,*2023, *8*(38), 34549–34556. DOI:10.1021/acsomega.3c03356

36. Ogawa T., Lindeperg F., Stradiotto M., Turculet L., Sydora O.L. Chromium N-phosphinoamidine ethylene tri-/tetramerization catalysts: Designing a step change in 1-octene selectivity. *Journal of Catalysis*, **2021**, *394*, 444–450. DOI:10.1016/j.jcat.2020.10.021

37. Zhang J., Alam F., Fan H., Ma J., Jiang T. Chromium catalysts based on PNP(NR2)2 ligands for selective ethylene oligomerization. *Appl Organomet Chem.*, **2022**, *36*(06), e6454. DOI:10.1002/aoc.6454

38. Park H.S.**,** Kim T.H.**,** Baek J.W.**,** Lee H.J.**,** Kim T.J.**,** Ryu J.Y.**,** Lee J.**,** Lee B.Y. Extremely Active Ethylene Tetramerization Catalyst Avoiding the Use of Methylaluminoxane: $[\mathrm{iPrN}\{\mathrm{P}(\mathrm{C_6H_4}\text{-}p\text{-}\mathrm{SiR_3})_2\}_2\mathrm{CrCl_2}]^+[\mathrm{B}(\mathrm{C_6F_5})_4]^-$. *ChemCatChem.*, **2019**, *11*(17), 4351–4359. DOI:10.1002/cctc.201900898

39. Park J.H., Park J.Y., Baek J.W., Seo Y.H., Lee M.R., Lee J., Lee B.Y. Preparation of chromium complexes for ethylene tetramerization catalyst. *BKCS*, **2024**, *45*, No4, 331-340. DOI:10.1002/bkcs.12826

40. Kim T.H., Lee H.M., Park H.S., Kim S.D., Kwon S.J., Tahara A., Nagashima H., Lee B.Y. MAO-free and extremely active catalytic system for ethylene tetramerization. *Appl. Organomet. Chem.*, **2019**, *33*(04), e64544829. DOI:10.1002/aoc.4829

41. Yang X., Shao H., Hao B., Fan H., Wang Y., Jiang T. 1H-Perfluorohexane. An efficient modifier for ethylene tri-/tetramerization. *Appl Organomet Chem.*, **2023**, *37*(12).e67244. DOI:10.1002/aoc.7244

42. Fan H., Hao B., Jiang Y., Yang X., Wang Y., Jiang T. Selective ethylene tri-/tetramerization chromium catalysts based on binuclear PCCP ligands.*Molecular Catalysis,* **2023**, *549,* 113545. DOI:10.1016/j.mcat.2023.113545

43. Wang J., Liu D., Zuo J., Zhao X., Zhang J. Use of PCCP Ligands with a *P*-Ph(alkyl) Group in Chromium-Catalyzed Ethylene Tri-/Tetramerization.*Organometallics,* **2024**, *43,* No17, 1852–1860. DOI:10.1021/acs.organomet.4c00217

44. Kong W., Ma X., Zuo J., Zhao X., Zhang J. Ethylene Tri-/Tetramerization Catalysts Supported by Phenylene-Bridged Mixed Alkyl/Aryl Diphosphine Ligands. *Organometallics,* **2023**, *42*, 8, 651–659. DOI:10.1021/acs.organomet.2c00644

45. Babenko I.A., Kondrashov E.V., Rozentsveig I.B. The Catalytic Transformation of Ethylene Using Chromium(III) Complexes with Bidentate Nitrogen-Containing Ligands. *Catal Lett,* **2020**, *150,* 2873–2878. DOI:10.1007/s10562-019-03080-3

46. Zhao X., Ma X., Kong W., Zhang J. Switchable ethylene tri-/tetramerization with high catalytic performance: Subtle effect presented by P-alkyl substituent of PCCP ligands. *Journal of Catalysis,* **2022**, *415,* 95–101. DOI:10.1016/j.jcat.2022.09.030

47. Barman S., Jaseer E.A., Garcia N., Elanany M., Khawaji M., Maity N., Musa A. Tuning a Cr-Catalyzed Ethylene Oligomerization Product Profile via a Rational Design of the N-aryl PNP Ligands. *Catalysts,* **2024**, *14*, 441. DOI:10.3390/ catal14070441

48. Nifant'ev I.Je., Ivchenko P.V., Vinogradov A.A. *Method of ethylene oligomerization*. Zajavka na izobretenie RF, No020130768A, **2022**. https://yandex.ru/patents/doc/RU2020130768A_20220317 (accessed on 15 July 2025) (In Russ.)

49. U H., Chzhen M., Hu S., Li T., Lju C., Sjuj K., Van S., Pan' F. *Galogensoderzhashhee soedinenie i ego primenenie, sostav katalizatora i sposoby oligomerizacii, trimerizacii i tetramerizacii jetilena*. Zajavka na izobretenie RF, No 2021 122 810, **2023.** https://yandex.ru/patents/doc/RU2021122810A_20230216 (accessed on 15 July 2025) (In Russ.)

50. U H., Chzhen M., Hu S., Li T., Lju C., Sjuj K., Van S., Pan' F. *Galogensoderzhashhee soedinenie i ego primenenie, sostav katalizatora i sposoby oligomerizacii, trimerizacii i tetramerizacii jetilena*. Zajavka na izobretenie RF, No2802019, **2023.** https://yandex.ru/patents/doc/RU2802019C2_20230822 (accessed on 15 July 2025) (In Russ.)

51. Nifant'ev I.Je., Ivchenko P.V., Vinogradov A.A., Vinogradov A.A., Bagrov V.V. *Sposob oligomerizacii jetilena v srede organicheskogo rastvoritelja v prisutstvii hromovogo katalizatora i aljuminijorganicheskogo aktivatora*. Zajavka na izobretenie RF, No 2717241, **2020**. https://yandex.ru/patents/doc/RU2717241C1_20200319 (accessed on 15 July 2025) (In Russ.)

52. Poljanskij K.B., Afanas'ev V.V., Bespalova N.N. *Sposob oligomerizacii jetilena v vysshie olefiny C10-C30*. Zajavka na izobretenie RF, No2610624 C1, **20**17. https://yandex.ru/patents/doc/RU2610524C1_20170213 (accessed on 15 July 2025) (In Russ.)

53. Al'-Hazmi M.H., Al'kahtani A., Rozental' U., Mjuller B.H., Peuleke N.N., Harff M., Vol' A., Majsvinkl A., Bolt H., Mjuller V. *Kataliticheskaja kompozicija i sposob oligomerizacii jetilena s obrazovaniem 1-geksena i/ili 1-oktena*. Patent RU, No2665551C1, **2018**. https://yandex.ru/patents/doc/RU2665551C1_20180831 (accessed on 15 July 2025) (In Russ.)

54. Sydora O.L. *Catalysts for oligomerisation of olefins and methods for production and use thereof.* Zajavka na izobretenie RF, No2593394C2, 2016. https://patents.google.com/patent/RU2593374C2/ru (accessed on 15 July 2025) (In Russ.)

55. Poljanskij K.B., Afanas'ev V.V., Bespalova N.N. *Sposob oligomerizacii jetilena v vysshie olefiny C10-C30*. Zajavka na izobretenie RF, No2596197 C1, **2016**. https://yandex.ru/patents/doc/RU2596197C1_20160827 (accessed on 15 July 2025) (In Russ.)

56. Vjol' A., Mjuller V., Bjolt H., Majsvinkel A., Harff M., Vjellenhofer A., Hofmann K.-H., Zander H.-J., Ilijas A., Hurram Sh., Azam Sh., Al-Kahtani A. *Method of ethylene oligomerization*. Zajavka na izobretenie RF, No2616602C2, **2017**.https://patents.google.com/patent/RU2616602C2/ru (accessed on 15 July 2025) (In Russ.)

57. Shaik K.M., Xu W. *Ethylene oligomerization process*. Application US, No10022698B2, **2018**. https://patents.google.com/patent/US10022698B2/en (accessed on 15 July 2025)

58. De Boer E.J.M., van der Heijden H., An On Q., Smit J., Von Zon A. *Catalyst systems for the catalytic oligomerization of olefinic monomers*. Application US, No9073809B2, **2015**. https://patents.google.com/patent/US9073809B2/en (accessed on 15 July 2025)

59. Kilgore U.J., Hutchison S.R., Sydora O.L., Bishof S.M., Fern J.T., McDaniel M.P. *Ethylene oligomerization catalyst systems using chemically-treated solid oxides*. Application US, No9707549B1, **2017**. https://patents.google.com/patent/US9707549B1/en (accessed on 15 July 2025)

60. Kilgore U.J., Bishof S.M.*Catalyst systems and ethylene oligomerization method*. Application US, No10807921B2**, 2020.**https://patents.google.com/patent/US10807921B2/en (accessed on 15 July 2025)

61. Kilgore U.J., Bishof S.M., Sydora O.L. *Catalyst systems and ethylene oligomerization method*. Application US, No11117845B2**, 2021.** https://patents.google.com/patent/US11117845B2/en (accessed on 15 July 2025)

62. Bishof S.M., Hillier J.L., Kilgore U.J., Hutchison S.R., Kreischer B.E., Sydora O.L. *Oligomerization catalyst system activation and related ethylene oligomerization processes and reaction systems*. Application US, No11267909B2, **2022**. https://patents.google.com/patent/US11267909B2/en (accessed on 15 July 2025)

63. Qilong F., Yingbo X., MengZh., Peng L., Xilin L., Xuguang W., RuiyingY, HongyeY., Weijie Y. *Modified PNP catalyst ligand, preparation method thereof and ethylene selective oligomerization catalyst*. Application CN, No114989341B, **2024.** https://patents.google.com/patent/CN114989341B/en (accessed on 15 July 2025)

64. Pavlova I.S., Pervova I.G., Belov G.P., Hasbiullin I.I., Slepuhin P.A.Oligomerizacija jetilena pod dejstviem formazanatov zheleza i aljuminijorganicheskih soedinenij. *Neftehimija*, **2013**, *53,* No2, 144–150. DOI:10.7868/S002824211302007X (In Russ.)

65. Bishof S.M., Smoll B.L. *Methods of oligomerisation of ethylene*. Zajavka na izobretenie RF, No2741600 C1, **2021**. https://yandex.ru/patents/doc/RU2741600C1_20210127 (доступ 5 июня 2025) (accessed on 15 July 2025) (In Russ.)

66. Bishof S.M., Smoll B.L. *Methods of oligomerisation of ethylene*. Zajavka na izobretenie RF, No2738392 C1, 2020.https://yandex.ru/patents/doc/RU2738392C1_20201211 (accessed on 15 July 2025) (In Russ.)

67. Cordier A., Breuil P.-A., Michel T., Magna L., Olivier-Bourbigou H., Raynaud J., Boisson C., Monteil V. Titanium-based phenoxy-imine catalyst for selective ethylene trimerization: effect of temperature on the activity, selectivity and properties of polymeric side products. *Catal. Sci. Technol.*, **2020**, *10,* 1602–1608. DOI:10.1039/C9CY02056J. https://pubs.rsc.org/en/content/articlelanding/2020/cy/c9cy02056j

68. Jing Ma, Ke-Qing Zhao, Semikolenova N.V., Zakharov V.A., Soshnikov I.E., Bryliakov K.P., Redshawa C., Talsi E.P. Selective ethylene trimerization by titanium complexes bearing phenoxy-imine ligands with a pendant arm: NMR− and EPR−spectroscopic studies of the reaction intermediates. *Organometallics,* **2014**, *33,* No 6, 1431–1439. DOI:10.1021/om500017r

69. Gadjieva-Etayi K.Sh., Khanmetov A.A., Khamiyev M.D., Bagirova Sh.R., Seidova Kh.G., Ibragimova M.D., Aliyeva R.V. Oligomerization of ethylene to linear α-olefins in the presence of complex catalytic systems based on zirconium carboxylates. *Kataliz v promyshlennosti*, **2021**, *21,* No4, 238-246. (In Russ.) DOI:10.18412/1816-0387-2021-4-238-246

70. Azizov A.H., Khamiyev M.J., Khanmetov A.A., Alieva R.V., Aliyev B.M., Ahmedbekova S.F. Oligomerization of the ethylene in the presence of new heterogenized Zr-containing complex catalytic systems. *Eur. Chem. Bull.*, **2015**, *4*(11), 503–511. http://epa.oszk.hu/02200/02286/00036/pdf/EPA02286_european_chemical_bulletin_2015_10-12_503-511.pdf

71. Lavrenov A.V., Dupljakin V.K. Oligomerizacija butenov na boratsoderzhashhem okside aljuminija. *Kinetika i kataliz,* **2009**, *50,* No 2, 249–255. (In Russ.)

72. Winkler F., Schneider R., Mündl F. *Method and device for manufacturing alpha olefins*. Application EP, No3686177A1, **2020**. https://patents.google.com/patent/EP3686177A1/en (accessed on 15 July 2025)

73. Jacewicz D., Pawlak M., Drzeżdżon J., Gawdzik B., Gołąbiewska A., Mielczarek P., Nowak A., Wzorek Z. A Comparison of the Catalytic Activities of Oxovanadium (IV) And Cobalt (II) Complex Compounds in the Oligomerization of Ethylene. *Polyhedron,* **2023**, *250,*116810. DOI:10.1016/j.poly.2023.116810

74. Singh G., Rani R., Kaur S., Singh D., Chopra A., Kapur G.C., Ramakumar Sh.Sh.V. *Sposob poluchenija katalizatora oligomerizacii jetilena i ego oligomerizacija.* Opisanie izobretenija k patentu RF, No2759004 C1, **2021**. https://patents.s3.yandex.net/RU2759004C1_20211108.pdf (accessed on 15 July 2025) (In Russ.)

75. Alzamly A., Bakiro M., Hussein Ahmed S., Siddig L.A., Nguyen H.L. Linear α-olefin oligomerization and polymerization catalyzed by metal-organic frameworks. *Coordination Chemistry Reviews*, **2022**, *462*, 214522. DOI:10.1016/j.ccr.2022.214522

76. Coelho A., Caeiro G., Lemos M., Lemos F., Ramôa Ribeiro F. 1-Butene oligomerization over ZSM-5 zeolite: Part 1 – Effect of reaction conditions. *Fuel*, **2013**, *111,* 449–460. DOI:10.1016/j.fuel.2013.03.066

77. Díaz M., Epelde E., Valecillos J., Izaddoust S., Aguayo A.T., Bilbao J. Coke deactivation and regeneration of HZSM-5 zeolite catalysts in the oligomerization of 1-butene . *Applied Catalysis B: Environmental*, **2021**, *291,* 120076. DOI:10.1016/j.apcatb.2021.120076

78. Kriván E., Tomasek S., Hancsók J. Application Possibilities of Zeolite Catalysts in Oligomerization of Light Olefins. *Periodica Polytechnica Chemical Engineering*, **2014**, *58*, No 2, 149–156. DOI:10.3311/PPch.7204

79. Díaz M., Epelde E., Tabernilla Z., Ateka A., Aguayo A., Bilbao J. Operating conditions to maximize clean liquid fuels yield by oligomerization of 1-butene on HZSM-5 zeolite catalysts. *Energy*, **2020,** *207***,** 118317. DOI:10.1016/j.energy.2020.118317

80. Maksimov A.L., Kulikov A.B., Pugacheva A.A., Vilesov A.S.,Smirnov M.B., Galkina E.V., Reshetnikov D.M., Zvinchuk A.A. Oligomerizacija vysshih α-olefinov na katalizatorah, soderzhashhih perftorirovannyj sopolimer F-4SF. *Neftehimija*, **2014**, *54*, No2, 122–130. DOI:10.7868/S0028242114020063 (In Russ.)

81. Grigor'eva N.G., Talipova R.R., Korzhova L.F., Bubennov S.V., Kutepov B.I., Dzhemilev U.M. Oligomerizacija stirola na ceolitah razlichnyh strukturnyh tipov. *Neftehimija*, **2010**, *50*, No2, 141–145. (In Russ.)

82. Wang G., Song H., Li R., Li Zh., Chen J. Olefin oligomerization via new and efficient Brönsted acidic ionic liquid catalyst systems. *Chinese Journal of Catalysis*, **2018**, *39*, No 6, 1110-1120. DOI:10.1016/S1872-2067(18)63071-2

83. Mashayekhi M., Moballegh L., Bahri-Laleh N., Sadjadi S., Poater A. Ionic liquids as modifier for the oligomerization of α-olefins to reactive poly (α-olefins) via traditional $AlCl_3$ catalyst. *Molecular Catalysis*, **2023**, *547*, 113403. https://doi.org/10.1016/j.mcat.2023.113403

84. Mashayekhi M., Talebi S., Sadjadi S., Bahri-Laleh N.Production of polyalfaolefin-based lubricants using new (poly)ionic liquid /$AlCl_3$ catalysts as environmentally friendly alternatives to commercial $AlCl_3$ route. *Applied Catalysis A: General*, **2021**, *623*, 118274. DOI:10.1016/j.apcata.2021.118274

85. Ibragimova M.D., Samedova F.I., Gasanova R.Z., Azmamedov N.G., Jejvazov Je.Z. Sintez oligooktenovyh i oligodecenovyh masel v prisutstvii hloraljuminatnyh ionnyh zhidkostej. Neftehimija, **2007**, *47*, No 1, 64–70. (In Russ.)

86. Azizov A.G., Kalbalieva Je.S., Alieva R.V., Bektashi N.R., Aliev B.M. Oligomerizacija geksena-1 v prisutstvii kataliticheskih sistem na osnove ionnyh zhidkostej. Neftehimija, **2010**, *50*, No 1, 57–65. (In Russ.)