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Oligomerization of α-Olefins to Higher Oligomers

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Contents

Jadwiga Skupińska was born in Poland and obtained a M.Sc. degree in chemistry from Warsaw University of Technology (Politechnika) in 1970, working on the reaction of organoaluminum compounds with benzonitrile for her diploma. The copolymerization of carbon dioxide with propylene oxide in the presence of organozinc catalysts was the subject of her Ph.D. work which she finished at 1975 also at Warsaw University of Technology. Since 1976 she has been working as a tutor at the Faculty of Chemistry of Warsaw University. Her current interests are chemical technology, homogeneous catalysis, and metaloorganic chemistry.

Abbreviations

Cy	cyclohexyl
Cp	cyclopentadienyl
COD	cyclooctadiene
acac	acetylacetonato (2,4-pentanedionato)
sacsac	2,4-pentanedithionato
P⌒O	bifunctional phosphine
PE	polyethylene
PP	polypropylene
EPR	electron paramagnetic resonance

I. Introduction

Olefins, particularly ethylene, propylene, and butenes, are the basic building block of the petrochemical industry. They are easily available, cheap, reactive, and readily transferable into a range of useful products. The last 20 years have witnessed increasing importance of higher linear C_{6-20} α-olefins which are today a source of biodegradable detergents, new kinds of polymers, lubricants, and many other industrially useful chemicals.

α-Olefins are obtained generally through the following processes: thermal and catalytical cracking of paraffins, oligomerization of ethylene, dehydrogenation of paraffins, dimerization and metathesis of olefins, dehydration of alcohols, and electrolysis of C_{3-30} straight-chain carboxylic acids. Of this group the first two are commonly used—first for C_{2-5} olefins and the second for higher C_{9-30} α-olefins manufactured in large scale. This last process has recently become an area of theoretical and technological investigations.[1-3]

In this review, based on the literature up to December 1989, an attempt has been made to present a comprehensive study of the catalyst and the process for ethylene, propylene, and higher olefins oligomerization. The literature data are divided into three parts: ethylene oligomerization, propylene oligomerization, and higher olefins oligomerization. In every part the following catalysts used in these reactions are described: transition-metal complexes, organoaluminum compounds, Lewis and Bröensted type compounds, and inorganic salts and oxides. Also, the olefin oligomerization mechanism in the presence of these catalysts is discussed. The most important oligomerization reactions involves the use of transition-metal complexes as catalysts and, therefore, form the main subject of this

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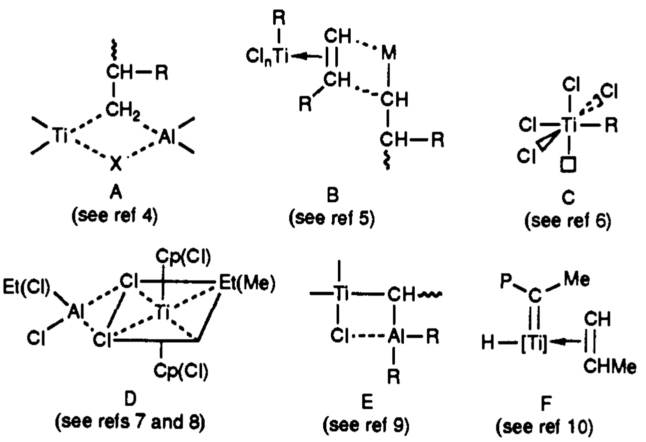
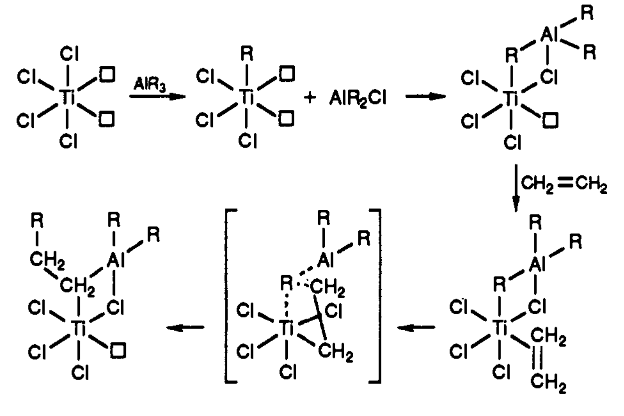
SCHEME I. Bi- and Monometallic Types of Active Centra Proposed for the Ziegler–Natta Catalysts[47]



SCHEME II. Bimetallic Mechanism of Ethylene Oligomerization According to Rodriguez and Looy[11]



paper. The industrial processes used in olefin oligomerization are also described at the end.

II. Principles of Oligomerization Reactions

Polyolefin chain formation depending on a number of *n* reacting molecules is named as follows:[1] dimerization when $n = 2$; oligomerization when $2 > n > 100$; and polymerization when $n > 100$.

The most desirable ethylene oligomerization products are those for which $n \leq 20$. This reaction occurs only in the presence of catalysts. Catalytic cycle of this reaction consists of two steps, the first, the chain growth (propagation) step:

$$\text{Cat—R} + \text{H}_2\text{C}{=}\text{CH}_2 \xrightarrow{r_p} \text{Cat—CH}_2\text{CH}_2\text{—R} \quad (1)$$

where Cat stands for catalyst; R, alkyl or hydrogen; r_p, propagation rate.

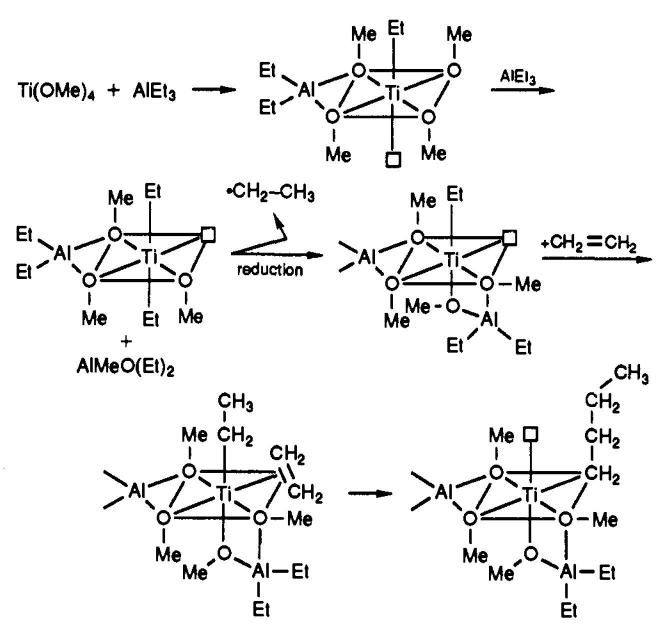
The second step is the hydrogen elimination from β-carbon to the catalytic center:[2]

$$\text{Cat—CH}_2\text{CH}_2\text{—R} \xrightarrow{r_t} \text{Cat—H} + \text{CH}_2{=}\text{CHR} \quad (2)$$

where r_t equals chain-transfer rate.

Depending on the catalyst, β-elimination of the hydride occurs when a metal–hydrogen bond is restored, or of a proton, when an acidic center is formed again. The relative reaction 1 and 2 rates, r_p and r_t, respectively, determines the molecular weight of the obtained product. If $r_p > r_t$, many propagation steps begin before the β-hydrogen transfer occurs and a high molecular weight polymer is formed, when $r_t > r_p$ dimers are obtained, and finally when $r_t \approx r_p$ oligomers are produced. Many factors determine the ratio of the propagation to the chain transfer rate and thereby the molecular weight of oligomerization products. These factors are kind of metal and its oxidation state; electronic properties and steric volume of the ligands attached to metal; reaction temperature and pressure; monomer concentration; and nature of solvent and molecular weight moderators. The influence of these factors on olefin oligomerization will be discussed in the following sections.

SCHEME III. Novaro–Chow–Magnouat Bimetallic Mechanism of Ethylene Oligomerization[12]



III. Ethylene Oligomerization

Depending on the mechanism of catalyst action the catalysts are divided into the following classifications: transition-metal complexes in homogenous and heterogeneous systems; organoaluminum compounds; and inorganic salts and oxides.

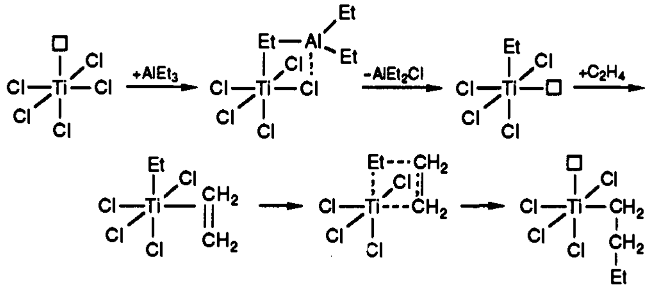
III.1. Transition-Metal Complexes as Catalysts for Ethylene Oligomerization

Complexes of titanium and nickel are the most often used catalysts for ethylene oligomerization. Zirconium complexes have also been found to be very active catalyst in this reaction.[1-3] The use of other transition-metal complexes in ethylene oligomerization is very rare. In catalytic reactions by transition-metal complexes obtained ethylene oligomers follow a Schulz–Flory type distribution.[24,17,55]

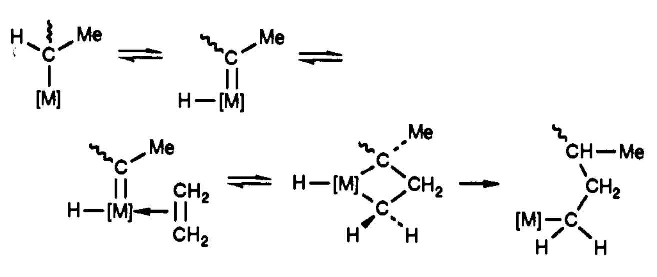
III.1.1. Titanium

Chloro and alkoxy derivatives of titanium modified with organoaluminum compounds—particularly with chloroalkylaluminum one—are active in ethylene oligomerization. This reaction takes place via the following steps: active center formation, olefin coordination

SCHEME IV. Cossee–Arlman Monometallic Mechanism of Ethylene Oligomer Chain Growth[6]



SCHEME V. Green Monometallic Mechanism of Ethylene Oligomer Chain Growth (Metathesis Type)[10]



on the titanium atom and chain propagation, and termination of the chain growth.

Formation of Titanium Catalytic Center. An unoccupied coordination site and titanium–alkyl bond in the titanium complex are fundamental requirements for its catalytic activity in olefin oligomerization reaction. The titanium–alkyl bond is formed in the reaction of a titanium compound with alkyl or alkylchloroaluminum compounds when e.g. halide atoms or alkoxy groups of titanium compounds are replaced by alkyl groups of aluminum derivatives. There are many proposals concerning the structure of the Ziegler–Natta catalyst active centers. They are presented on Scheme I. They consist of bimetallic systems in which titanium is bonded to aluminum through halide or halide–alkyl bridges or of monometallic systems where only a titanium ion is the catalytic center.

Oligomer Chain Growth. Oligomer chain growth occurs as the result of olefin coordination on a titanium atom and consecutive olefin insertion into a Ti–C bond. Olefin insertion into a titanium–alkyl bond is the fundamental step of the olefin oligomerization reaction in the Ziegler–Natta catalysts. Extensive studies of olefin insertion mechanism support the bimetallic or monometallic models of catalytic centers.

The olefin oligomerization mechanism on bimetallic center proposed by Rodriguez and Looy[11] is presented in Schemes II and III for ethylene oligomerization on the $(MeO)_4Ti/Et_3Al$ system.[12] In these two examples, the first step of the reaction is the alkylation of the titanium center. Next ethylene is coordinated to the titanium center. This is the cause of the weakness of Ti–C bond and it in turn helps ethylene to insert into the Ti–C bond. Simultaneously, according to Rodriguez and Looy[11] (Scheme II), the Al–C bond is cleaved and the new bridge Al–C–Ti is formed. This way the new active center is regenerated and the catalytic cycle continues.

For the catalytical complex $(MeO)_4Ti/Et_3Al$, presented in Scheme III part a, structure of a trigonal bipyrimid has been proposed. The organoaluminum compound plays a dual role. It exchanges the ligands with the titanium ion thereby forming a labile titanium-alkyl bond and forms, via the Al–O–Ti bridges, the adequately geometrical structure and reduces the titanium(IV) ion to a titanium(III) one. Ethylene complexation causes the change in the complex structure to an octahedra in which ethylene is coordinated and then inserted into the Ti–C bond.

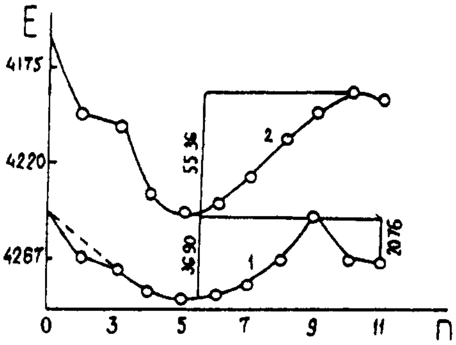
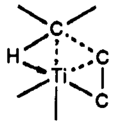


Figure 1. Variation in the energy (*E*, cal/mol) of the basic state in the course of polymerization ($TiCl_4/R_3Al$):[16] 1, via bimetallic mechanism; 2, via monometallic mechanism.

In the case of the monometallic active center three mechanisms are postulated. The first, where olefin insertion occurs via four-center intermediate proposed by Cossee and Arlman,[6] is presented on Scheme IV. The ethylene oligomerization is initiated here only with the titanium ion and its ligands. Organoaluminum compounds alkylate only the titanium ion. The resulting titanium complex has an octahedral structure with one unoccupied coordination site, which is the active center where ethylene is coordinated at the first step of catalytic cycle.

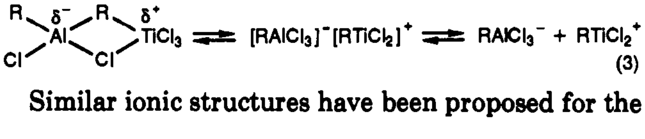
The metathesis type mechanism of olefin oligomerization proposed by Green and Rooney[10] is presented on Scheme V. A metal carbene Ti═CHR is the catalyst center here. This is formed as a result of α-hydrogen shift from the growing oligomer chain to the titanium ion.

Recently, Brookhart and Green[13,14] have proposed a mechanism which is a minor variation of the earlier example. In this mechanism the cleavage of the C–H bond does not occur exactly as in the above model. The "agostic" hydrogen structure is postulated as



Both the mono and bimetallic mechanism are supported by theoretical calculations, the results of which e.g. obtained by Minsker[16] are pictured in Figure 1. These calculations show that the bimetallic mechanism is energetically favorable but the Jolly and Marynick calculations for $Cp_2TiCH_3^+$ claim that olefin insertion into the titanium–alkyl bond should occur in the absence of organoaluminum compounds.[15]

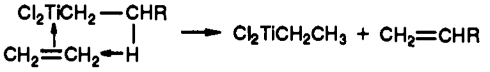
Langer[17] has proposed for the $TiCl_4$/alkylchloroaluminum system an ionic structure of three equivalent forms:



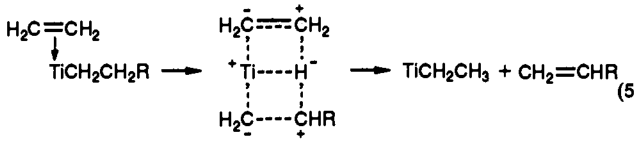
$$\mathrm{R(Cl)}\overset{\delta^-}{\mathrm{Al}}(\mu\text{-R})(\mu\text{-Cl})\overset{\delta^+}{\mathrm{TiCl_3}} \rightleftharpoons [\mathrm{RAlCl_3}]^-[\mathrm{RTiCl_2}]^+ \rightleftharpoons \mathrm{RAlCl_3}^- + \mathrm{RTiCl_2}^+ \qquad (3)$$

Similar ionic structures have been proposed for the following systems active in the ethylene oligomerization: CH_3TiCl_3/CH_3AlCl_2[18] and $TiCl_4/R_{3-n}AlCl_n$.[19] The influence of the solvents used in this reaction was investigated[19,20] and the following order of their effect was established: chlorohydrocarbons > toluene > heptane. This implies that the increase of solvent polarity enhances the ethylene oligomerization rate. This observation supports an ionic character of olefin oligomerization catalysts. More detailed investigations[25] showed that at relatively low temperatures, from 293 to 313 K, ethylene and propylene cooligomerization occurs according to anionic coordination mechanism, but at temperatures > 353 K, this reaction assumes a cationic character.

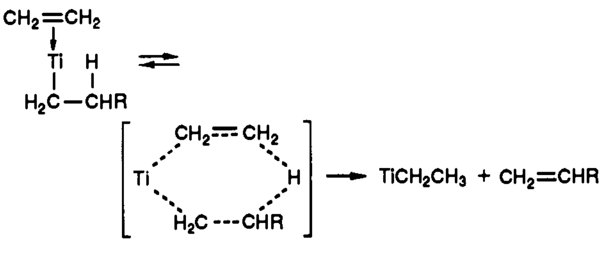
Chain-Transfer Reaction. As mentioned above, the relative rates of chain growth and chain transfer determine the molecular weight of obtained oligomers. This process on the titanium complex catalysts occurs as a result of the β-hydrogen elimination from the oligomer chain to the coordinated olefin[21] after which the α-olefin oligomer is liberated and the catalytic center, namely, the titanium–alkyl bond is restored.


(4)

Investigations of the temperature influence on ethylene oligomerization in presence of $(EtO)_4Ti/EtAlCl_2$ system[22] show that activation energy of the β-hydrogen elimination (28 kJ/mol) is lower than that of olefin insertion into a Ti–C bond (38.7 kJ/mol). This fact is explained by a six-center intermediate formation during the β-elimination step:


(5)

Novaro and co-workers,[12] on the basis of a theoretical analysis of the oligomer chain growth, β-hydrogen transfer, and kinetics of ethylene oligomerization on titanium catalysts, have proposed an alternate six-center intermediate without Ti–H bonds[2,12,21] for the β-hydrogen-elimination step:


(6)

Most data concerns ethylene oligomerization on the $TiCl_4/Et_nAlCl_{3-n}$ systems. The influence of reaction conditions on selectivity, Schulz–Flory molecular weight oligomers distribution and yields has been investigated. These factors are catalyst composition—Ti/Al ratio, catalyst concentration, pressure and temperature, kind of solvent, reaction time, and kind of the titanium and aluminum ligand.

Al/Ti Ratio.[17,19,23,24] When the ratio Al/Ti ≤ 1 the ethylene oligomerization does not occur. At ratios > 2, the catalyst efficiency improves.

Catalyst Concentration.[23,24] A decrease of catalyst concentration causes an increase of the oligomer chain transfer rate—more short chain olefins are obtained. Increasing the catalyst concentration gives more polymer; thus, decreasing the reaction selectivity. This polymer formation is a result of cooligomerization of ethylene with oligomers.

Pressure.[19,23,24] With increase of reaction pressure, the molecular weight of oligomers as well as conversion to linear α-olefins increases. An increase in the ethylene pressure also inhibits the ethylene cooligomerization with higher α-olefins.

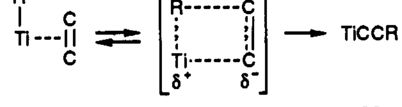
Temperature.[19,23,24] Increase in the ethylene oligomerization temperature increases the molecular weight of the oligomers and amount of nonlinear α-olefins in the products.

The rise of the molecular weight of the obtained oligomers is in this case a result of higher activation energy of the chain growth compared to the activation energy of the chain transfer to the monomer (β-hydrogen transfer). Under these conditions, ethylene cooligomerizes with the preformed α-olefins resulting in a significant amount of branched hydrocarbons. Also the reduction of Ti(IV) ions to Ti(III) with organoaluminum compounds is accelerated. This, in turn, gives more catalytically active polymerization centers (Ti(III) ions) and therefore more polyethylene in the products. At higher temperatures the ethylene alkylation of solvents is also accelerated.

Solvent.[20,26,29] Increasing solvent polarity activates titanium catalyst in the ethylene oligomerization and decreases the molecular weight of obtained oligomers.[17,20] More branched olefins exist in the product in view of the fact that in more polar solvents the cationic character of the catalyst increases.

Reaction Time.[17,27] Prolonged reaction time leads to an increase in oligomers' yield and an increase in the amount of branched olefins.

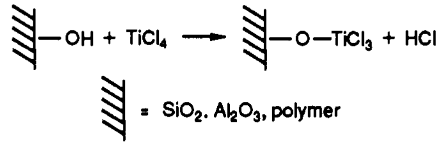
Ligands of Titanium and Aluminum. An increase of acidity of organoaluminum compounds causes a decrease of the oligomer molecular weight. When titanium halide (acceptor) ligands in the system $TiX_4/EtAlCl_2$ are changed for alkoxy (donor) more polyethylene is obtained in the products.[28] Halide ligands, having acceptor properties, polarize Ti–X bonds by giving a positive charge to the titanium ion. This helps the six-center intermediate formation (see reaction 6) and the termination of the oligomer chain, which is a result of strong polarization of neighboring bonds (including the polarization of C_β–H). Donor ligands, on the other hand, decreasing positive charge on a titanium ion, favor the four-center intermediate formation and the olefin insertion into the Ti–C bond according to the equation 7.[2]


(7)

Donor ligands added to the system $TiCl_4/Et_nAlCl_{3-n}$ (n = 1,2) increase the catalyst selectivity to linear α-olefins.[29] In Table I the catalysts, modified by an addition of ketones, amines, nitriles, phosphines, and sulfur compounds, are presented. With the use of these catalysts the 70–80% yields of C_{8-20} olefins, with selectivity to linear α-olefins equal to 90%, were obtained.

Very high yields have been also obtained for the system $[(C_6H_5O)_2PS_2]_2TiCl_2/EtAlCl_2$, 1875 g of oligomer (g of Ti)$^{-1}$ h^{-1} with a selectivity to α-olefins of 75–85%.[30] Donor ligands, here, increase electron density around the titanium ion, which in turn allows only ethylene to coordinate on the titanium and therefore inhibit the cooligomerization between higher α-olefins. Large steric effects of these ligands, in addition to electronic influences, are probably responsible for linear olefin formation.[2]

Heterogenized Titanium Catalysts. Reaction of titanium compounds with surface hydroxyls of inorganic gels and their strong adsorbtion on the inorganic salts or oxides and their reaction with active functional groups of polymers lead to heterogenized titanium catalysts, which after modification with alkyl metal derivatives, are active in the olefin oligomerization reactions (reaction 8).



(8)

In this reaction, the system (η^5-C_5H_5)$_2$TiCl$_2$/polybutadiene/EtAlCl$_2$ is highly active for more than 1000 h[31] with stable selectivity to linear α-olefins of 95–97%. This long activity is a result of isolation of active centers when titanium ions are bonded to the polymer chain in such distances that make the titanium ion aglomerization impossible which in homogeneous systems inhibits catalytic activity.[32] Since the long-chain olefins, unlike ethylene, cannot easily reach the catalytic centers located in the pores of the polymeric support, only a small amount of branched olefins is formed. In this case the molecular weight distribution does not follow the Schulz–Flory rule. Relatively, less high molecular weight product is obtained, what probably is connected with diffusion effect. In comparison to its homogeneous analogues, this system is less sensitive to air and moisture.

On the other hand, the catalyst, in which silica gel has the following ligands bound to its surface: $(CH_2)_2S(CH_2)_2OH$, $CH_2SC_{10}H_7$, and $(CH_2)_2C(NH_2)NOH$ and is the carrier of the system $TiCl_4/Et_3Al_2Cl_3$, shows less activity and selectivity compared to homogeneous catalysts.[33] In this case, blocking of centers by the formed polyethylene is observed. The system with the sulfur-containing ligands is more active than that one with nitrogen. This phenomena is explained by stronger catalyst stabilization effects caused by back-donation of 3d sulfur orbitals.

Heterogenous catalysts, namely $TiCl_4/EtAlCl_2$, supported on carriers with amine groups, (3-aminopropyl)triethoxysilane[34] or p-(diaminomethyl)styrene[35] on their surfaces, show low ethylene oligomerization activity. They give 15–218 g of oligomer (g of Ti)$^{-1}$ h^{-1} with linear olefin selectivity of about 70%.

III.1.2. Zirconium

The systems $ZrCl_4$, $Zr(OOCR)_4$, $Zr(C_5H_7O_2)_4$, and $Zr(CH_2C_6H_5)_4$ modified with alkylchloroaluminum derivatives are highly active in ethylene oligomerization to long-chain α-olefins.[36-38] Kinetic investigations of the ethylene oligomerization in presence of the catalyst $Zr[OOCCH(CH_3)_2]_4/Et_3Al_2Cl_3$ have shown that (1) the oligomerization does not occur when the ratio Al/Zr < 8; (2) the average oligomerization degree (p_n) decreases when the ratio Al/Zr increases; and (3) the p_n is not influenced by the kind of the solvent used.

Condition 1—the ratio Al/Zr = 8—is explained by the necessary presence of the four dimeric sesquichlorosesquiethylaluminum compounds during the oligomerization center formation in the following systems:[39]

$$ZrY_4 + 4Et_3Al_2Cl_3 \rightarrow \underset{\text{I}}{EtZrCl_3{\cdot}EtAlCl_2{\cdot}EtAlClY} + 3[\underset{\text{II}}{Et_2AlCl{\cdot}EtAlClY}] \quad (9)$$

where Y = OOCR, $CH_2C_6H_5$, $C_5H_7O_2$.

If an excess of organoaluminum compounds is used, then reaction 10 occurs:

$$\text{I} + Et_3Al_2Cl_3 \rightarrow \underset{\text{III}}{EtZrCl_3{\cdot}EtAlCl_2{\cdot}EtAlCl_2} + \underset{\text{II}}{Et_2AlCl{\cdot}EtAlClY} \quad (10)$$

Complexes I and III are the ethylene oligomerization active center. Compound II is inert in ethylene oligomerization.

The oligomerization reaction succeeds when ethylene molecules insert into Zr–C bonds in the active complexes I and III.

$$\text{I} + nC_2H_4 \rightarrow \underset{\text{IV}}{C_2H_5(C_2H_4)_nZrCl_3{\cdot}EtAlCl_2{\cdot}EtAlClY} \quad (11)$$

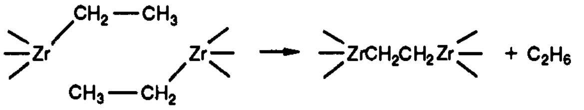
$$\text{III} + nC_2H_4 \rightarrow \underset{\text{V}}{C_2H_5(C_2H_4)_nZrCl_3{\cdot}EtAlCl_2{\cdot}EtAlCl_2} \quad (12)$$

The oligomer chain termination reaction occurs as a result of the oligomer chain on the monomer transfer.[13]

$$\text{IV} + C_2H_4 \rightarrow C_2H_5(C_2H_4)_{n-1}CH{=}CH_2 + \text{I} \quad (13)$$

$$\text{V} + C_2H_4 \rightarrow C_2H_5(C_2H_4)_{n-1}CH{=}CH_2 + \text{III} \quad (14)$$

The rates of cooligomerization reaction, solvent alkylation, and oligomer chain transfer on chloroethylaluminum derivatives were found to be very small. Simultaneously, ethylene oligomerization reaction rate in presence of the above catalysts was observed to decrease with the reaction time. The EPR investigations of the system $Zr(i\text{-}PrCOO)_4/Et_3Al_2Cl_3$ have shown that the reduction: Zr(IV) → Zr(III) does not occur but reaction 15 takes place.[40] This disproportionation reaction is responsible for this catalytic system's deactivation.



(15)

Additional information concerning this catalyst's deactivation was obtained from the electrical conductivity investigations in toluene. During oligomerization, ethylene and other α-olefins, were found to form cationic type centers R^+A^- which show little activity under reaction conditions as they dissociate to ions and disappear in subsequent reaction steps. An increase in the solvent's solvating properties in the decreasing order heptane < ligroin < cyclohexane < olefins < toluene increases oligomerization rate modestly but does not change the oligomer molecular weight.[40]

Investigations of the $Zr(i\text{-}PrCOO)_4/Et_3Al_2Cl_3$ (Al/Zr = 12) system showed that only 20% of the Zr compound is catalytically active.[40]

TABLE I. Oligomerization of Ethylene

catalyst	react condtn	products	yield	ref(s)
Titanium				
$TiCl_4$/alkylaluminum		olefins C_{4-24} = 70%, α-olefins = 56.27%		207
$TiCl_4/(C_2H_5)AlCl_2/AlCl_3$ (Al/Ti = 0.5–104)	xylene, C_6H_5Cl, 400 psig, 15–50 °C, 1 h	$\bar{M}_n$ olefins = 113–128, linearity = 91.2%	132 g (mmol of Ti)$^{-1}$	208
$TiCl_4/(C_2H_5)_3Al_2Cl_3$	toluene, 20–25 kg/cm^2, 10 °C, 85 min	olefins C_{6-28}, linearity = 96%		27, 209
$TiCl_4/(C_2H_5)_3Al_2Cl_3$ (Al/Ti = 2)	toluene, 2 MPa, 283 K, 1 h	α-olefins = 99%, $\bar{M}_n$ = 138	625 mol of olefins (mol of Ti)$^{-1}$ 432 g of product (g of Ti)$^{-1}$ 5.3 g of PE	24
$TiCl_4/(C_2H_5)AlCl_2$ (Al/Ti = 2)	hydrocarbon solvents, 500 psig, 150 °C, 4 h	oligomers, $\bar{M}_n$ = 70–300	166 g (g of $TiCl_4$)$^{-1}$ h^{-1}	17, 210
$TiCl_4/C_2H_5AlCl_2$ (Al/Ti = 8)	benzene, toluene, 20–80 °C, 15–37 min	$\bar{M}_n$ = 102–189	410 mol of oligomer (mol of Ti)$^{-1}$	61
$TiCl_4/C_2H_5AlCl_2$ (Al/Ti = 8)	benzene, 25 atm, 20 °C, 90 min	$\bar{M}_n$ = 127, α-olefins = 96%	1240 g (g of $TiCl_4$)$^{-1}$ 1.6% PE	19, 23
$TiCl_4/C_2H_5AlCl_2$ (1:8)	benzene, 6 atm, 40 °C, 88 min	α-olefins = 67.8%, $\bar{M}_n$ = 330	477 mol (mol of Ti)$^{-1}$	20
$TiCl_4/C_2H_5AlCl_2$ (1:4–12)	ethylene chloride, 2.5 atm, –20 °C, 30–100 min	$\bar{M}_n$ = 260–1700	50–248 mol (mol of Ti)$^{-1}$	26
$TiCl_4/C_2H_5AlCl_2$	toluene, 20–25 atm, 20–40 °C	olefins C_{12-18}	ethylene recycling	83
TiX_4/R_nAlX_{3-n}, TiX_3OR/R_nAlX_{3-n}, TiX_3OOCR'/R_nAlX_{3-n} (Al/Ti = 2–5); n = 1, 2; R and R′ = alkyl, X = halogen	50 psig, 5–25 °C, 1–2 h	linear α-olefins C_{12-20} = 60–100%, $\bar{M}_w$ = 90–150	40–150 g (g of $TiCl_4$)$^{-1}$ h^{-1}, traces of PE	211, 212
$TiX_3Y/(C_2H_5)_3AlCl/MCl_3$; X = Cl; Y = Cl, OR, OOCR; M = Fe, Sn, B, Ti, Al; R = alkyl	50 psig	linear α-olefins C_{12-20} = 97–98%; $\bar{M}_w$ = 110–120	200 g (g of $TiCl_4$)$^{-1}$ h^{-1}	213
$TiCl_4/(C_2H_5)_3AlCl/C_2H_5AlCl_2$/$t$-BuOH (6:6:1:1)	chlorobenzene, xylene, 55–500 psig, –20 °C	linear olefins C_{12-20} = 70–100%	90–147 g (g of $TiCl_4$)$^{-1}$ h^{-1}	17
TiX_3Y/R_nAlX_{3-n}/M or MX_m; X = Cl, Br; Y = Cl, OR, OOCR′; M = Fe, B, Sn; n = 1, 2		% olefins in product = 30–50, $\bar{M}_w$ = 120, olefins C_{12-20} = 96%	PE = 1%	214
$TiCl_4/C_2H_5AlCl_2$/L, L = acetylacetonate (AA), dimethylformamide (DMF), ethylene glycol dimethyl ether (EGE), diethyl ether (DE)	650 psig, 0–50 °C, 1 h	olefins $C_{<30}$ = 23–55%, $C_{>30}$ = 25–50%, linearity = 90%	40–272 g of product (g of $TiCl_4$)$^{-1}$ h^{-1}, PE = 5–52%, catalytic activity is of the order when L = EGE > DMF > AA > DE	215
$TiCl_4/(C_2H_5)_3Al$ or $C_2H_5AlCl_2$/ferrocene/(monochloromethyl)cyclopentane (50:100:16:183 mol)	140 atm, 54 °C	α-olefins C_{18-22} = 36.5% in product		216
$TiCl_4/C_2H_5AlCl_2$/styrene or α-methylstyrene	aromatic solvents			217
$TiCl_4/C_2H_5AlCl_2(C_2H_5)_3AlCl$/L (2:1:6), L = anthracene, mesitylene, hexamethylbenzene	40 atm, 20 °C	$\bar{M}_n$ = 212–220		218
$TiCl_4$/chloroorganoaluminums/L (1:1–10:0.2–2), L = amines, nitriles, ethers, ethylacetate, ketones, diketones		olefins C_{4-8} = 0.9–6%, C_{8-20} = 78–88% in product, linearity = 68–95%		219
$TiCl_4$/chloroorganoaluminums/mercaptanes, thioethers, amines		olefins C_{8-20} ≈ 70%, linearity ≈ 90%		220
$TiCl_4/D(C_2H_5)_3Al_2Cl_3/C_2H_5AlCl_2$/L, D = acetone, acrylonitryle, $(C_2H_5)_3P$; L = ethylmercaptane, Ph_2SO_2, thiophenol	–30 to 50 °C	olefins C_6 = 21%, C_{8-20} = 72%, linearity = 96%		221
$TiCl_4/C_2H_5AlCl_2/(C_2H_5)_3AlCl)/Bu_3P$ (1:1:0.5:100)	38.7 kg/cm^2, 20 °C	olefins C_{40-100}		224
$TiCl_4/R_nAlX_{3-n}/PX_3$, X = Ph, alkyl; n = 1, 2		olefins C_{8-20} = 90%, linearity = 94%		224, 225

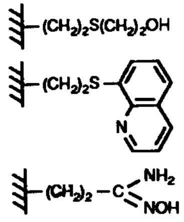
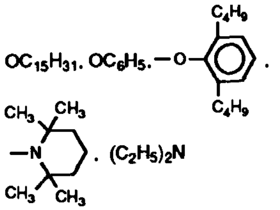
$TiCl_4/C_2H_5AlCl_2/PCl_3$	toluene, 450 psig, −5 to 20 °C	olefins C_{4-20} = 92–97%, linearity = 90%, $\bar{M}_n$ = 119		223
$TiCl_5^-R_3C^+/(C_2H_5)_3Al_2Cl_3$ (1:0.5–50), R_3C^+ = carbonium salt				226
$(C_2H_5O)_3TiCl/C_2H_5AlCl_2$ (1:5)	toluene, 12 atm, −20 to 0 °C, 1 h	olefins C_8 = 32% (α-olefins = 90%), C_{10-50} = 67.1% (α-olefins = 85%), $\bar{M}_n$ = 153	10–15 mol of C_2H_4 (g of catalyst)$^{-1}$ h^{-1}, ethylene conv = 17.8%	22, 228
$(CH_3O)_4Ti/(C_2H_5)_3Al$	12 kg/cm^2, 40 °C	olefins C_4 = 73%, C_6 = 26%, α-olefins = 100%	ethylene conv = 82%	12
$(BuO)_4Ti/(C_2H_5)_5Al$	n-heptane, H_2, and C_2H_4, mixture, 2.5 atm, 57 °C, 1 h	olefins C_4 = 77.6%, C_6 = 22.0%, PE = 0.4%		444
$TiCl_nY_m/R_aAlCl_{3-a}$ (Al/Ti = 23.5–125), a = 1–2; R = C_2H_5, C_4H_9; n = 0–3; m = 1–4; Y = $(A)_2NC({=}S)S-$, $AOC({=}S)S-$, $(AO)_2P({=}S)S-$, A = C_2H_5, C_3H_7, C_4H_9, C_6H_5	aliphatic or aromatic hydrocarbons, 10–35 atm, −10 to 80 °C	paraffins = 5–13%, olefins = 77–90% (α-olefins = 75–87%), C_{6-8} = 20–30%, C_{12-22} = 27–55%, $C_{>24}$ = 10–35%	1112–2042 g (g of Ti)$^{-1}$ h^{-1}	30
$TiX_4/C_2H_5AlCl_2/MY_n/MgZ_m$ (1:15–100:0.1–10:0.5–10), X = Cl, Br, acac; n = 2, 3; M = Ni, Co, Fe, Cu, Cd, Ca, Zn, Mg; Y = $A_2NC({=}S)S-$, $AOC({=}S)S-$, $(AO)_2P({=}S)S-$; A = C_2H_5, C_3H_7, C_4H_9, C_6H_5; Z = Cl, SO_4; m = 1, 2	hydrocarbon solvents, 5–50 atm, 0–80 °C, 1 h	olefins C_{4-40}: $CH_2{=}CH-$ = 28–35%, $-CH{=}CH-$ = 30–70%, ${=}C{=}CH-$ = 1–40%, $\bar{M}_n$ = 56–560	2407–14 166.6 g (g of Ti)$^{-1}$ h^{-1}	227
$TiCl_4$(surface ligands)/$(C_2H_5)_2Al_2Cl_3$ (Al/Ti = 2–3), surface ligands = 	hexane, 30 atm, −10 to 5 °C	olefins C_{8-18} = 17–58%; linearity = 57–85%	122–603 mol of C_2H_4 (mol of Ti)$^{-1}$ h^{-1}	33
$TiCl_4$ supported on borosilicate modified with (aminoalkyl)alkoxysilane/$C_2H_5AlCl_2$ (Al/Ti = 10)	heptane, 35 atm, −8 °C	olefins C_{6-18} = 55%, $C_{>18}$ = 25%	15 g of C_2H_4 (g of Ti)$^{-1}$ h^{-1}	34
$TiCl_4$ attached to graft polystyrene/ p-(diaminomethyl)polystyrene/$C_2H_5AlCl_2$	10 atm, 7 °C	olefins C_{6-18} = 59%, linearity = 70%	218 g of C_2H_4 (g of Ti)$^{-1}$ h^{-1}	35
$(C_5H_5)_2TiCl_2$ supported on 1,2-polybutadiene/$C_2H_5AlCl_2$ (Al/Ti = 8–20)	heptane, 0.4–2.1	olefins C_{4-16} (C_{8-16} = 50%), linearity = 50%	4 g (g of catalyst)$^{-1}$ h^{-1}	31
	Zirconium			
$ZrCl_4/(C_2H_5)_3Al_2Cl_3/Bu_3P$ (1:5:2)	benzene, 35 kg/cm^2, 100 °C	olefins C_{12-18} = 10%, $C_{>20}$ = 26.3%	50 g (g of catalyst)$^{-1}$ h^{-1}	230
$ZrCl_4/(C_2H_5)_2AlCl/CH_3SSCH_3$	chlorobenzene, 35 kg/cm^2, 100 °C	olefins C_{12-20} = 44%	530 g (g of catalyst)$^{-1}$ h^{-1}	231
$ZrCl_4/(C_2H_5)_3Al_2Cl_3$/thiophene	benzene, 35 kg/cm^2, 100 °C, 1 h	olefins C_{10-18} = 33%, $C_{>20}$ = 4.8%	1530 g (g of $ZrCl_4$)$^{-1}$ h^{-1}, without thiophene: 2600 g (g of $ZrCl_4$)$^{-1}$ h^{-1} 15% wax	232
$ZrCl_4/(C_2H_5)_3Al_2Cl_3$/BuONa (Al/Zr = 10)	90 °C, 2 h	α-olefins = 80%, linearity = 84%	1293.3 g (g of Zr)$^{-1}$ h^{-1}	48, 49
$ZrCl_aBr_b$/donors/$R_{3-n}AlX_n$ (R_2Zn); R = C_{1-20} alkyl; X = Cl, Br, a, b = 0–4; $a + b$ = 4	toluene, 500–5000 psig, 50–300 °C, H_2O, Zr/H_2O (20:1)	α-olefins, $\bar{M}_n$ = 108		234
$ZrCl_4/(C_2H_5)_2Zn$ (Zn/Zr < 1)	n-heptane, 7 MPa, 130 °C, 30 min	linear α-olefins in C_{12-20} = 99.2%, $\bar{M}_n$ = 199	5100 g (g of $ZrCl_4$)$^{-1}$ h^{-1}	44

TABLE I (Continued)

catalyst	react condtn	products	yield	ref(s)
$ZrCl_4/(C_2H_5)_3Al$ (2:1)	120 °C		18800 g (g of $ZrCl_4)^{-1}$ h^{-1}, 4.8% PE	44
$ZrCl_4/(C_2H_5)_2AlCl$ (Al/Zr = 4)	120 °C, 7 MPa	linear α-olefins in C_{12-20} = 95.5%	32000 g (g of $ZrCl_4)^{-1}$ h^{-1}	43, 44, 208
$ZrCl_4/(C_2H_5)_2AlCl/C_2H_5AlCl_2$/*n*-BuOH	chlorobenzene, 890 psig, 70 °C, 30 min	C_{12-20} = 33.2%	1275 g (g of catalyst)$^{-1}$ 30 min^{-1}	43, 29, 235
$ZrCl_4/R_3CCl/(C_2H_5)_3Al_2Cl_3$, R = alkyl, aryl				226
$Zr(OR)_4/(C_2H_5)_3AlCl/C_2H_5AlCl_2$ (1:1:4), R = C_3H_7, C_4H_9	toluene or xylene, 5.6–7 MPa, 120 °C, 15–30 min	olefins $C_{>20} \approx 50\%$, $\bar{M}_n$ = 254	17400–39600 g (g of $Zr(OC_4H_9)_4)^{-1}$ h^{-1}	29, 237
$ZrCl_4/R_2AlR'$ (4:1), R = alkyl; R′ = RO, C_6H_5O, $N(C_2H_5)_2$	heptane, 7 MPa, 130 °C, 30 min	linear α-olefins in C_{12-20} = 99.2%, $\bar{M}_{mw}$ = 290	10300 g (g of $ZrCl_4)^{-1}$ h^{-1}	233, 236
$ZrCl_4/(C_2H_5)_2AlX$; X = OC_2H_5.  	*n*-heptane, 7 MPa, 130 °C, 30 min	linear α-olefin = 99%, $\bar{M}_n$ = 218–290	1000–13900 g (g of $ZrCl_4)^{-1}$ h^{-1}	50
$Zr(OC_3H_7)_4/C_2H_5AlCl_2/(C_2H_5)_3AlCl$ (1:1:4)	heptane, 1000 psig, 110 °C, 30 min	linear α-olefins in C_{12-20} = 98.6%, $\bar{M}_n$ = 242		237
$(\pi\text{-}C_3H_5)ZrBr_3$ or $(C_6H_5CH_2)ZrBr_3/(C_2H_5)_2AlCl$, $(C_2H_5AlCl_2)$		olefins C_{4-40}		238
$Zr(acac)_4$/alkylbenzene/$C_2H_5AlCl_2$ (1:7–50:20–50)	50–100 °C			239, 229
$Zr(acac)_4$/alkylbenzenes/$C_2H_5AlI_2(C_2H_5AlCl_2)$ (1:7:30)	30 MPa, 90 °C, 5 h	70% olefins, bp = 348–500 °C	order of reactivity: toluene > mesitylene > benzene > *p*-xylene > PPh_3	45
$Zr(acac)_4$/mesitylene/$C_2H_5AlCl_2$ (1.16:2.3:9.3)	chlorobenzene	oligomers, flash point = 215 °C, pour point = −20 °C		46
ZrR_4, $(C_3H_7O)_2ZrCl_2$, $Zr(acac)_4/(C_2H_5)_3Al_2Cl_3$, R = OC_4H_9, $OC_{18}H_{35}$, $(C_4H_9)_2N$	heptane, 25 atm, 80 °C	α-olefins, C_{4-30}	13000 mol of C_2H_4 (mol of Zr)$^{-1}$ h^{-1}	36, 240
$Zr(OCOR)_4$, or $Zr(OSOR)_4/(C_2H_5)_3AlCl_3$ (1:4), R = alkyl, aryl	5–30 atm, 60–100 °C	olefins C_{4-30}	PE < 0.1%	242
$Zr(OCO\text{-}i\text{-}C_3H_7)_4/(C_2H_5)_3Al_2Cl_3$ (Al/Zr = 17)	toluene, 2 MPa, 80 °C	linear α-olefins = 95–98%, $\bar{P}_n$ = 506	2500–3856 mol of C_2H_4 (mol of Zr)$^{-1}$, PE = 0.01–0.55%	42
$Zr(OCO\text{-}i\text{-}C_3H_7)_4/(C_2H_5)_3Al_2Cl_3$ (Al/Zr = 17–25)	2 MPa, 80 °C	linear α-olefins = 95–98%, C_{4-8} = 45–67%, C_{10-20} = 30–45%	solvent influence on catalytic activity: toluene ≫ *n*-heptane > cyclohexane > gasoline > decene-1; max activity: 17.7 × 10^3 mol of C_2H_4 (mol of Zr)$^{-1}$ h^{-1}	41
$Zr(OC_3H_7)_4/(C_2H_5)_3Al_2Cl_3$ (0.55:2.5)	toluene, 20–30 atm, 80–90 °C, 1 h	linear α-olefins = 95%, olefins C_{12-18} = 93–96%	1030 g of C_2H_4 (0.5 g of Zr)$^{-1}$ h^{-1}	83
$Zr(O\text{-}n\text{-}C_4H_9)_2(OC_6H_4Cl)_2/(C_2H_5)_2AlCl/PPh_3$ (8.3:46:1)	toluene, 9 kg/cm^2, 50 °C, 1 h	olefins C_4 = 58%, C_6 = 29%, C_8 = 13%		241
$Zr(OCH_2C_6H_5)_4/(C_2H_5)_3Al_2Cl_3$	toluene, 40–80 °C	α-olefins		243
$ZrCl_2Y_2/R_aAlCl_{3-a}$, a = 1–2; R = C_2H_5, C_4H_9; Y = $A_2NC({=}S)S$–, $AOC({=}S)S$–, $(AO)_2P({=}S)S$–, A = C_2H_5, C_3H_7, C_4H_9, C_6H_5	toluene/heptane, 10–35 atm, −10 to 80 °C	α-olefins = 75–85%, C_{12-22} = 19–26%, C_{24-50} = 36–60%; $\bar{M}_c$ = 56–980	1527 g (g of Zr)$^{-1}$ h^{-1}, wax, and PE = 10–27%	30

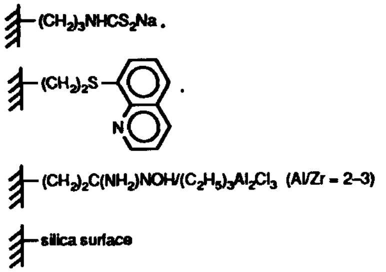
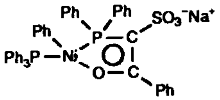
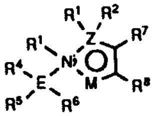
$Zr(acac)_4/C_2H_5AlCl_2/[(C_2H_5)_2NCS_2]Ni/MgCl_2$ (1:25:1:10)	heptane, hexane, 20 atm, 80 °C, 90 min	olefins C_{4-40}, α-olefins = 28–35%, $\bar{M}_c$ = 56–560	2415 g (g of Zr)$^{-1}$ h^{-1}	227
$ZrCl_2X_2/C_2H_5AlCl_2$; X = $(CH_3)_2NC({=}S)S-$, $C_2H_5OC({=}S)S-$, $(C_6H_5O)_2P({=}S)S-$, (Al/Zr = 18.5–50)	chlorobenzene, 10–40 atm, 80–100 °C	α-olefins, C_{4-50} = 55–83%, $\bar{M}_n$ = 56–700	max activity: 6590 g (g of Zr)$^{-1}$ h^{-1}	244
$Zr(acac)_4$, $Zr(acac)_3Cl$, or $Zr(CH_2C_6H_5)_4$ attached to  	tube reactor, 30 atm, −10 to 5 °C	olefins C_{8-18} = 30–40%, linearity = 30–78%	max activity: 451 mol of C_2H_4 (mol of Zr)$^{-1}$ h^{-1}	33
MX_3A/R_nAlX_{3-n}; M = Zr, Hf; X = Cl, Br; A = OR, OOCR; R = alkyl, aryl	100–1000 psig, 0–50 °C	olefins linearity = 90%; $\bar{M}_{mw}$ = 200–400		215
$MX_n/R_2AlCl/R_3CX$, X = Cl, Br; R = alkyl, aryl; M = Ti, Zr, V, Cr, Mo, W, Fe		olefins C_{12-22} = 38–50%		245
Nickel				
$NiCl_2$ or $Ni(OAc)_2/NaBH_4$/phosphinobenzoic acid (B/Ni = 2; Ni/ligand = 2)	$HO(CH_2)_4OH$, 20–70 °C, 500 psig	olefins C_4 = 8–20%, C_{6-10} = 30–50%, C_{12-20} = 15–35%		246
$NiCl_2{\cdot}6H_2O/NaBH_4/Ph_2PCH_2COOH$	$HO(CH_2)_4OH$, 500 psig, 25 °C for 15 min, 75 °C for 75 min	olefins C_4 = 26%, C_{6-10} = 31%, C_{12-20} = 20%	2350 g (g of Ni)$^{-1}$ h^{-1}, 1000 g (g of Ni)$^{-1}$ h^{-1}	247, 248, 262, 264, 265
$NiX_2/NaBH_4/Ph_2PCH_2CH_2COOH/PPh_3$, X = Cl, Br	$HO(CH_2)_4OH$, 40 atm, 100 °C	olefins C_{4-8} = 41%, C_{10-18} = 40.5%, C_{20} = 18.5%		250
$NiX_2/NaBH_4/Ph_2PCH_2CH_2COOH$ (Ni/B = 1)	glycols, 40 atm, 100 °C	olefins C_{12-24} = 23%, C_{22-42} = 50%, $C_{>42}$ = 25%		251
$NiCl_2/NaBH_4/2Ph_2PC_6H_4COOH$	$HO(CH_2)_4OH$	olefins C_{40}		252
$Ni[P(OC_6H_4\text{-}o\text{-}R)_3]_2C_2H_4/H_2SO_4$ (1:25), R = C_{1-3} alkyl, alkoxy	chlorobenzene, 0–50 °C			253
$Ni[OP({=}O)(OR)_2]_2/(C_2H_5)_3Al_2Cl_3$, R = C_{1-8} alkyl	benzene, 100 psig, 50 °C	olefins C_{12-20} = 90%		254, 255
$NiCl_2{\cdot}6H_2O/NaBH_4$/*o*-diphenylphosphinophenol	dimethylacetamide, 4.7 bar, 90 °C, 2 h	olefins C_{8-18} = 67%, α-olefins = 95–100%, linearity = 100%	conv = 81–95%	256, 257, 259
$NiCl_2{\cdot}6H_2O$/sodium bis[diphenylphosphino]-4-methylbenzenesulfonate/$NaBH_4$ (Ni/B = 1)	C_2H_5OH, 950 psig, 80 °C	olefins C_{4-8} = 25.3%, C_{10-18} = 8.9%, α-olefins = 95%		258
$L_nNi/[o\text{-}(R)HOC_6H_4PR_2]$, L = COD, R′—CH═C—R′; allyl, RR′—CCR′—CCR′, R = alkyl, aryl; R′ = alkyl	benzene, 250–1000 psig, 70–80 °C, 2–4 h	olefins $C_{>10}$ = 70–80%, linearity = 70–96%	conv = 70–95%	260, 261
$Ni(acac)_2$/haloorganoaluminums/halohydrocarbons (Ni/Al = 1:1–100)	hydrocarbons, 32–250 atm, 80–250 °C	$\bar{M}$ = 30–300		263, 266
$Ni(acac)_2/(C_2H_5)_3Al_2Cl_3/PPh_3$ or PBu_3 (1:3:1–20)	−10 to 0 °C, 3 h	olefins C_{4-8}, $C_{>8}$ = 13–15%		94, 266
$Ni(CO)_4/(C_2H_5)_3Al_2Cl_3/PPh_3$	benzene, 400 psig	olefins $C_{>8}$ = 35.72%		267
$Ni(sacsac)PR_3Cl$, R = C_2H_5, C_4H_9, octyl, decyl	1 atm, 293 K		conv = 4 × 10^6 mol of C_2H_4 (mol of Ni)$^{-1}$ h^{-1}	268
$(\pi\text{-}C_3H_5)NiBr/P(i\text{-}C_3H_7)(t\text{-}C_4H_9)_2/(C_2H_5)_3Al_2Cl_3$	1 atm, −20 °C	olefins $C_{>8}$ = 50%		51, 54
$Ni(acac)_2$ supported on $(SiO_2/Al_2O_3)/(C_2H_5)_3Al_2Cl_3$	100 psig, 30–70 °C	olefins $C_{>6}$ = 34%		270, 271
$Ni(acac)_2/(SiO_2/Al_2O_3)/(C_2H_5)_3Al_2Cl_3/PPh_3$ or PBu_3	145 °F, 3 h	olefins C_{4-8}	conv = 50%	94
$\pi\text{-}C_3H_5NiCl$ anchored on $\gamma\text{-}Al_2O_3/(C_2H_5)_3Al_2Cl_3$ (1–3% by wt Ni, Ni/Al = 1:2)	1 atm, 20 °C	olefins C_{8-14} = 16–22%	178.7 g (g of Ni)$^{-1}$ h^{-1}, conv 80–85%	272–274
$Ni(COD)_2/(C_6H_{11})_2PH$/heptafluorobutyric acid	pentanol, 700 psig		1860 g (g of Ni)$^{-1}$ h^{-1}	275

TABLE I (Continued)

catalyst	react condtn	products	yield	ref(s)
$Ni(COD)_2/P(CH_2CO_2H)_3$ or $PhP(CH_2CO_2M)_2$, M = Na, H	$HO(CH_2)_4OH$, 50 bar	α-olefins		276, 277
Ni(4-cycloocten-1-yl)bis(trifluoroacetamido)		linearity = 85%	11.5 mol of C_2H_4 (mol of Ni)$^{-1}$	278
$L_2Ni/CF_3COCHCOCF_3$ or CF_3COOH L = COD, π-allyl, RCH=CHR + Al_2O_3 or not	toluene, 500 psig, 25 °C, 10 h	olefins C_{4-10} linearity = 90%	32 g (g of catalyst)$^{-1}$ h^{-1}	280, 281
$Ni(COD)_2/CH_3P(C_6H_4COOH)_2$		olefins C_{4-10} = 5%, PE = 75%; M_w = 95 000		282
$Ni(COD)_2/RP(OR)CH_2COCH_3$, R = alkyl		olefins C_{4-10} = 97%	conv = 80%	249
$Ni(COD)_2/P(X)OR(R)$ supported on SiO_2, MgO, ZrO_2, Al_2O_3; X = carboxymethyl; R = alkyl	benzene, 500 psig, 50–100 °C	linearity = 90%	activity of catalyst: $SiO_2 > MgO > ZrO_2 > Al_2O_3$	249
$Ni(COD)_2$ or $Ni(\pi\text{-allyl})_2$/9-(carboxymethyl)-9-phosphabicyclo[3.3.1]nonane	aromatic solvents	linear α-olefins = 99.6%	6000 mol of C_2H_4 (mol of Ni)$^{-1}$	284, 285
$Ni(COD)_2/RP(OR)CH_2X$, X = hydroxymethyl, mercaptomethyl, hydrocarbonyl, hydrocarboxycarbonyl; R = alkyl	benzene, 500 psig, 100 °C	linear α-olefins = 91–95%, C_{4-8} = 37%, C_{8-12} = 34%, C_{12-20} = 29%	conv = 53%; 2.4 g (g of Ni)$^{-1}$ h^{-1}	286
$Ni(COD)_2/RPCH_2C(=O)NA_2$, R = alkyl, phosphine group; A = hydrogen, aromatic group, e.g., $Ph_2PCH_2C(=O)NPh_2$	*n*-heptane, 500–700 psig, 50 °C, 15 h	α-olefins = 96%, linearity = 98%, C_{4-8} = 34.3%, C_{10-18} = 41.7%, $C_{>20}$ = 24%	conv = 68%; 6.5 g (g of Ni)$^{-1}$ h^{-1}	287, 279
$Ni(COD)_2/Ph_3P{=}CHC(=O)X$, X = OH, OC_2H_5, NPh_2	benzene, 500 psig, 25–100 °C	olefins C_{4-20} = 50%, $C_{>20}$ = 50%; linearity = 92%		288
$Ph(PPh_3)Ni[Ph_2PCHC(Ph)O]$ or $Ni(COD)_2Ph_2PCH_2COOH$	toluene, 50 bar, 50 °C	α-olefins = 98%, linearity = 99%, C_{4-24} = 98–99%	6000 mol of C_2H_4 (mol of Ni)$^{-1}$	55, 291, 292, 294
$Ni(COD)_2/Ph_2PCH_2COOH$	benzene, 10–80 bar, 75 °C	α-olefins = 99%, C_{4-22}	conv = 93%	290, 293
$Ph(Ph_3P)Ni[Ph_2PCHC(Ph)O]$ or $(COD)Ni(Ph_2PCH_2COO)$ supported on Al_2O_3/SiO_2(SS) or binding over the phosphine or $\overset{\frown}{P\ O}$ chelate ligands to polystyrene (PS)	(SS)-flow reactor, 68 bar, 50 °C	α-olefins = 7–64%, linearity = 26–92%, C_{6-16}		60
	(PS)/toluene, 40 bar, 75 °C	α-olefins = 96–99%, linearity = 99%, C_{6-16}		60, 307
$Ni(COD)_2/Ph_3P/L$, L = $Ph_3As{=}CHCOPh$, $Ph_3As{=}C(COPh)_2$, Ph_2AsCH_2COOH	toluene, 15 bar, 40 °C	α-olefins = 70%, linearity = 95%	1600 mol of C_2H_4 (mol of Ni)$^{-1}$ h^{-1}	56
$(COD)Ni[CH[C(R)O]_2]$, R = CH_3, CF_3	toluene, 75 °C, 5 MPa	α-olefins = 17–24%, linearity = 67–82%, C_{4-24} (C_{10-24} = 21%)		53, 55
$[Ph_2PCH_2(CF_3)_2O]NiH(PCy_3)$	toluene, 50 bar, 50 °C	α-olefins = 98%, linearity = 99%, C_{4-30}	5000 mol of C_2H_4 (mol of Ni)$^{-1}$ h^{-1}	201
 $(C_2H_5)_nAl(OC_2H_5)_{3-n}$, *n* = 0, 1, 2	aromatic solvents, polar solvents, 14.6 atm, 50 °C, 120–180 min	α-olefins = 91%	without Al complex 2 × 10^4 g (g of complex)$^{-1}$; for Al/Ni = 200–5.2 × 10^5 g (g of complex)$^{-1}$	57, 58, 289, 295–297, 378
	80 °C, 500–1000 psig, 80 °C	linear α-olefins		295, 377
R^1–R^8 = H, C_{1-24} alkyl, C_{6-20} aryl; M = S, O; E = P, As, Sb, N; Z = P, As, Sb	CH_3OH/H_2O (0.5–20% H_2O), 20–100 °C, 10–300 psig	olefins C_{6-8} = 48%, C_{10-18} = 52%	selectivity – 90%	445
$(CPD)_3Ni_3(CO)_2$ supported on Al_2O_3/SiO_2	benzene, 450 psig, 150 °C, 1 h	olefins C_{4-14}, C_{8-14} = 29.5%	10^5 mol of C_2H_4 (mol of catalyst)$^{-1}$ h^{-1}	296–299

(CPD)Ni(π-C_6H_7) supported on Al_2O_3/SiO_2	heptane, 14–21 atm, 50–60 °C, 1 h	olefins C_{8-10} = 16%, C_{12-22} = 10%	conv = 84%	300, 301
		olefins C_{10-22} − 17%		302
(CPD)Ni(π-C_5H_7) supported on $Al_2O_3/SiO_2/CH_3SSCH_3$ or SNi(octanoate)$_2$/$(C_2H_5)_3Al$	800–1000 psig, 90 °C	internal olefins C_{14-30} which are isomerized and metathesized and recycled		205
Aluminum				
$(C_2H_5)_3Al$		oligomers	temperature effect on product distribution	304
$(C_2H_5)_3Al$/i-Bu_3Al	200–2000 psig, 100–150 °C	α-olefins C_{4-10}, C_{8-10} = 19.3%	2–6 mol of C_2H_4 (mol of Al)$^{-1}$	305
$(C_2H_5)_3Al/Bu_3Al$ 5% in solvent	n-tetradecane, 500–700 psig, 120 °C	olefins C_{10-40}, (1) reactor growth, (2) reactor ethylene displacement		306, 317
$R_3Al/(i\text{-}Bu_2Al)O$, R = alkyl C_{6-8}	500–1250 bar, 160–230 °C	α-olefins C_{10-40}		65
$(C_2H_5)_3Al$	kerosene, 248 °F, 1500 psig, 15 min	α-olefins = 62%		308
$(C_2H_5)_3Al$ (0.6 mol/L)	20–60 kg/cm^2, 180 °C, 3–7 h	olefins C_{10-20} = 70–77%, linearity = 75%	conv of C_2H_4 = 40–140 L/h	310, 313
$(C_2H_5)_3Al$	60 kg/cm^2, 180 °C, 7 h	olefins C_{6-20} (Ethyl Corp. Process)		78, 311
$(C_2H_5)_3Al$	n-heptane, diisobutane, 395–1000 atm	linear α-olefins C_{4-40}, max C_{12-18} (Gulf Research Process)	conv = 53–55%	79, 312
$(C_2H_5)_3Al/Ph_2NH$, R_2S (0.25–500 parts/(10^6 parts of $(C_2H_5)_3Al$), R = alkyl C_{8-16}	4–40 atm, 285–615 °F	olefins C_{4-40}	amine prevents PE formation	66, 67, 314
$(C_2H_5)_3Al$/Ni, Co, Pt	100 °C	α-olefins C_{2-24}		315–318
$(C_2H_5)_3Al$/polyethers	50 atm, 150 °C	linear α-olefins = 65% in C_{6-18} oligomers		319
$(C_2H_5)_3Al$/polyvinylalcohol or phenolic resins	40 atm, 100 °C, 150 min	α-olefins C_{6-50}, C_{6-18} = 75%		68
Al_{plate}/CCl_4 (1:0.05–1)	hydrocarbons, 40 atm, 130 °C	oligomers $\bar{M}_w$ = 100 (35%), $\bar{M}_w$ = 380 (17%)	6.6 g (g of Al)$^{-1}$	320, 321
Ruthenium				
(π-allyl)Ru(CO)$_3$X, X = Cl, Br		olefins C_{4-14}, C_{4-8} = 63%, C_{8-14} = 34%		62
Palladium				
$[Pd(CH_3CN)_4](BF_4)/CH_3CN$	1200 psig, 40 °C	olefins C_{4-10}		322
Mercury				
$Hg(OAc)_2/(C_2H_5)_2NH/HOCH_2CH_2NH_2$	50–70 atm, 70–200 °C	olefins C_{6-8}		63
Heterogenous Inorganic Systems				
BF_3/Al_2O_3 (BF_3 1–20% by wt)	100 psig, 150 °C		conv = 51.4%	192
hydrogen mordenite	500 K	olefins, aromatic hydrocarbons, polyphenylene		329
Ni/(Al_2O_3/SiO_2) (0.72% by wt Ni)	3500 kP, 115 °C, 2 h	olefins C_{10-20} = 41.1%	conv = 99.3%	323
MoO_3/Al_2O_3		olefins C_{12-14} (max C_{14})		324
Ni/NaY zeolite	3500 kPa, 100–150 °C	olefins $C_{>10}$ = 26%		325
$NiO/Al_2O_3/SiO_2$, $NiO/Al_2O_3(H_2)$		oligomers		75, 76
K/graphite, K/KCl, K/Na_2O	500 lb/sq, 200–300 °C	olefins C_{8-14} = 85%	PE = 15%	326
H/ZSM-5, HNaY	300–373 K	olefins, paraffins, aromatic hydrocarbons		137, 327, 328
H/ZSM-5 zeolite	flow reactor, 300–390 °C	olefins $C_{>30}$		71–74, 141
OGO-1 zeolite	flow reactor, 0.1 MPa, 390–400 °C, 200 h	olefins $C_{>5}$ = 65–75%, aromatic hydrocarbons = 20%	conv = 50–60%	408

The system $Zr(i\text{-}PrCOO)_4/Et_nAlCl_{3-n}$ (n = 1.5–2) served as a model for the study of the influence of reaction conditions on the ethylene oligomerization reactions.[39–42] The maximum oligomerization rate was observed for the system with $n = 1.7$. A change of n from 1.5 to 1.7 results in an increase of branched olefins (with internal C═C bonds) content in the products. The main reason for this phenomena is the relatively higher concentration of forming α-olefins in comparison with that of ethylene in the reaction medium caused by the very high activity of the catalysts. This enhances the catalyst reaction with higher α-olefins.[42] Increasing n from 9.5 to 17.3 decreased the yield and the molecular weight of the oligomers.[41]

An increase of the alkyl (R) chain length in the $Zr(RCOO)_4$ salts decreases the catalyst activity.[42] Raising the reaction temperature from 333 K to 373 K results in increase of the reaction rate, the reaction yield and the average molecular weight of the α-olefins. A higher reaction temperature (393 K) did not increase the reaction yield, but increased the α-olefin chains.[41]

When the ethylene pressure is raised during the ethylene oligomerization, a higher reaction rate and selectivity with unchanged oligomer molecular weight is achieved.

Catalyst activity and selectivity of $Zr(RCOO)_4/Et_nAlCl_{3-n}$ system is altered when the solvent is changed and increases in the order toluene > n-heptane > cyclohexane > ligroin. This is related to the lower ethylene solubility in these solvents, resulting in competitive, higher α-olefins cooligomerization. The same relationships are observed for other zirconium catalysts. For the $ZrCl_4/Et_2AlCl$ system increasing of Al/Zr ratio from 0.25 to 4.0 gave better yields (6000 to 32 000 g of oligomer (g of Zr)$^{-1}$ h^{-1}), lower average molecular weights, (224 to 150) and higher α-olefin selectivity (95.5–99.9%), respectively.[43] When Et_2AlCl is changed to Et_2Zn in this system, lower yields are obtained (6300 g oligomer (g of Zr)$^{-1}$ h^{-1}) with a higher α-olefin selectivity (99.1–99.8%) and higher oligomer molecular weight (229–285).[44]

Catalysts, giving C_{6-20} olefins in very high yield and purity (95%), containing Zr halides, organoaluminum compounds and sulfides, disulfides, thiophenes, thiourea, phosphines or primary amines, are described in Idemitsu Petrochemical Co. Ltd. patents.[230–232]

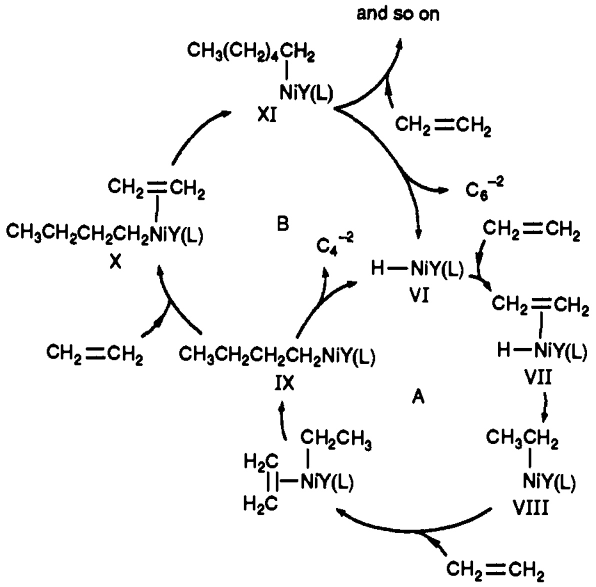
The $ZrCl_4/EtAlCl_2$ system is not active in the ethylene oligomerization and the catalysts $ZrCl_4/BuLi$ and $ZrCl_4/Bu_2Mg$ exhibit very small activity in this reaction.[44] When Et_3Al is used as modifier for $ZrCl_4$, a very active but relatively less selective (4.8% of polyethylene in the products) oligomerization catalyst is obtained.

Similar catalytic behavior is observed in the case of the $Zr(acac)_4/EtAlCl_2$[45–46] and $(C_3H_7)_4Zr/Et_3Al_2Cl_3$[36] catalysts.

The He and co-workers[48,49] EPR investigations of the systems $ZrCl_4/Et_2AlCl$ and $ZrCl_4/Et_3Al_2Cl_3/BuONa$ have indicated that it is possible to combine the catalysts deactivation with the reduction reaction namely, Zr(IV) to Zr(III).

In the system $ZrCl_4/Et_2AlX$[50] where X = OEt, $OC_{15}H_{31}$, OC_6H_5, (2,6-di-*tert*-butylphenyl)oxy, NEt_2, and 2,2,6,6-tetramethylpiperidine, the catalyst activity in ethylene oligomerization depends strongly on the ligands around aluminum. The bulky ligands decrease catalyst activity. The best yield was obtained for X = NEt_2(M_n = 285). All the catalyst systems with Et_2AlX as modifier were more active than those Et_2AlCl. Thus a replacement of chlorine acceptor ligand in Et_2AlCl with a donor ligand X results in higher oligomerization yields. Whereas with the $TiCl_4/Et_2AlX$ systems, the presence of acceptor X ligands resulted in a more active catalyst.

SCHEME VI. Catalytic Cycle of Ethylene Oligomerization in the Presence of a Nickel Catalyst[1,59]

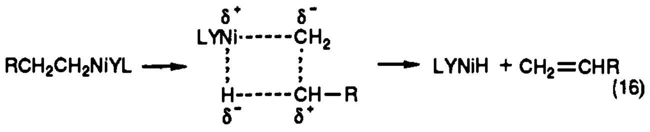


In conclusion, it can be stated that zirconium catalysts are generally more active than titanium ones. The catalyst activity for ethylene oligomerization in presence of zirconium catalysts is in the range, 15–30 kg (g of Zr)$^{-1}$ h^{-1}.[41,44,50] Selectivity to linear α-olefins approaches 99%. A constant ethylene supply is necessary to avoid the formation of branched olefins with internal C═C bonds. Such olefins are the products of the higher olefins cooligomerization and isomerization when the ethylene concentration is too low in the reaction medium.

III.1.3. Nickel

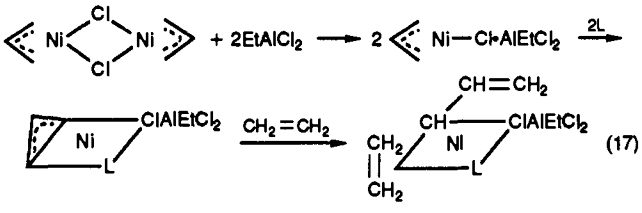
Nickel complexes are the most common group of the olefin oligomerization catalysts exhibiting the highest activity and selectivity to linear α-olefins. The oligomers follow a Schulz–Flory type distribution. The nickel catalyst complexes can be divided into two groups: nickel(II) compounds modified with alkyl or hydride main-group metal derivatives (Ziegler–Natta type catalysts) and chelated nickel compounds with a Ni–C bond.

The ethylene oligomerization catalyst cycle in presence of nickel catalyst, HNiYL where, Y = acyl, carboxyl, halogen; L = phosphine, is shown on Scheme VI. Ethylene coordination to the complex VI with the Ni–H bond, which is the catalyst's active center, gives the complex VII. The coordinated ethylene insertion into the Ni–H bond with formation of $Ni–C_2H_5$ group (complex VIII) begins the catalytic cycle via complexes IX, X, and XI. The chain transfer occurs through the β-hydrogen elimination from the oligomer chain in the complex XI by the nickel atom whereby the Ni–H bond is restored and oligomer liberated e.g.



(16)

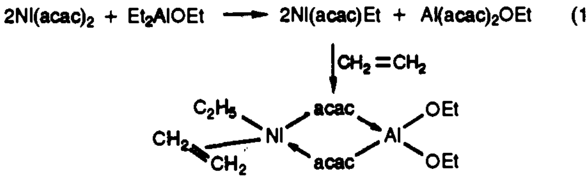
Formation of the Ni–H or Ni–alkyl bonds in nickel compounds is responsible for their catalytic activity in olefin oligomerization. This process for the system: $(\pi\text{-}C_3H_5)NiCl/Et_nAlCl_{3-n}$ (n = 1,2) is proposed as follows:[1]



(17)

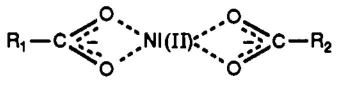
L = phosphine

In the system: $Ni(acac)_2/Et_2AlOEt$ (1:1) nickel alkylation occurs according to reaction 18:[51]



$$2Ni(acac)_2 + Et_2AlOEt \longrightarrow 2Ni(acac)Et + Al(acac)_2OEt \qquad (18)$$

Muzzio and Löffler[52] have proposed the following mechanism of the Ni–H bond formation for the catalyst XII:



XII

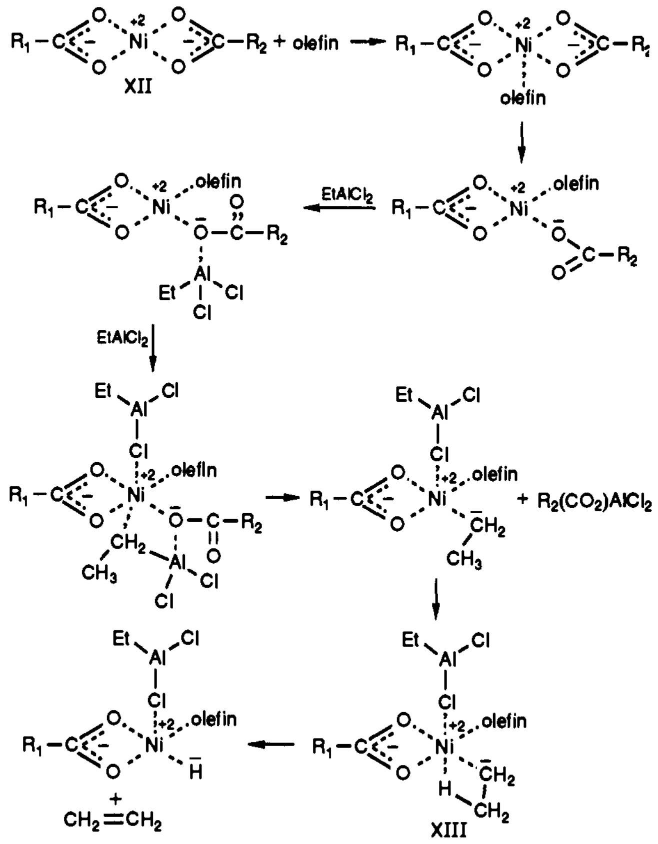
R_1 = alkyl of 5 or more carbon atoms
R_2 = haloalkyl of 1–3 carbon atoms

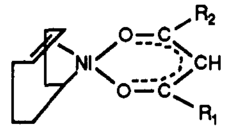
$EtAlCl_2$ and Et_2AlCl as a mixture are the necessary cocatalysts in this system. The mechanism of its action is presented on Scheme VII.

The reaction was carried out by adding at the beginning the nickel salt XII to the olefin. Next the organometallic compound was added. If the nickel salt were mixed with the organometallic compounds with no olefin present, the nickel salt would be reduced and would lose its catalytic activity. The first step of the reaction consists of the olefin coordination to the nickel atom. This helps to avoid reduction of the nickel in the complex XII with added organoaluminum compound. At first $EtAlCl_2$ complexes with one of the oxygen atoms in the complex XII. Additional aluminum compound is coordinated to the nickel through the chlorine bridge; and thus, is able to neutralize negative charge on the oxygen atom which in turn helps the salt $R_2COOAlCl_2$ to split off. Thus the nickel in the complex XIII is coordinatively unsaturated. Internal rearrangement leads to formation of Ni–H bond.

Many chelated nickel complexes are highly active and selective in the ethylene oligomerization without added organoaluminum compound e.g.

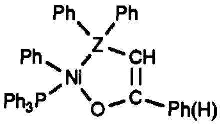
SCHEME VII. Mechanism for Hydride Formation in a Nickel-Catalyzed Olefin Oligomerization[52]





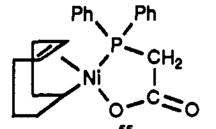
XIV[55,53]

XIV A: $R_1 = R_2 = CH_3$
B: $R_1 = CH_3$; $R_2 = CF_3$
C: $R_1 = R_2 = CF_3$

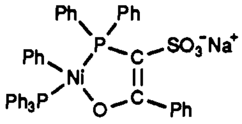


XV

Z = P[55,59,291], As[56]



XVI[55]

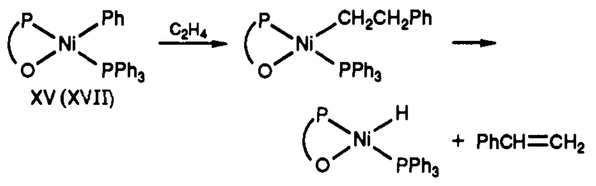


XVII[57,58]

Complexes of type XIV are very active catalysts for the oligomerization of ethylene. Linearity of 80% can be obtained in the C_8 oligomers[53] (XIV C). Complex XV has been found as the most interesting ethylene oligomerization catalyst. It converts ethylene at 50 °C and 10–100 bar to α-olefins possessing 99% linearity and >95% α-olefin content.[291] The geometric distribution of olefins can be modified by pressure and addition of Ph_3P. Increasing the Ph_3P/Ni ratio decreases the catalyst activity. Substitution Ph_3P in complex XV by trialkyl phosphine inactivates the system. When $(\alpha\text{-naphtol})_3P$ substitutes Ph_3P, 70% of linear PE is obtained in the products of ethylene oligomerization.[294]

Complexes similar to XV may be formed on reacting bis 1,5-cyclooctadiene nickel(0) with $Ph_2PCH_2CO_2H$,[446] thiolactic acid,[447] o-mercaptobenzoic acid,[448] phosphorous ylides,[449] or $Ph_2PCH_2C(CF_3)_2OH$.[201] All these systems have been patented by Shell and are effective in the Shell higher olefin process.[80]

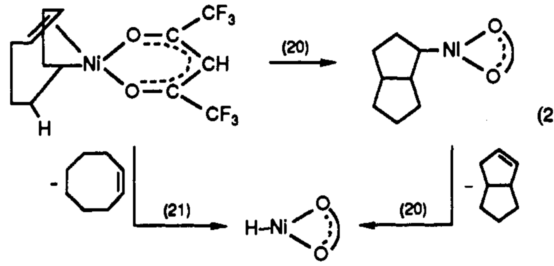
The XV and XVII derivatives do not have Ni–H bonds. These bonds are formed during oligomerization reaction probably through ethylene insertion into the Ni–Ph bond and the immediate split off of a styrene molecule[58,59] (eq 19):



XV (XVII)

(19)

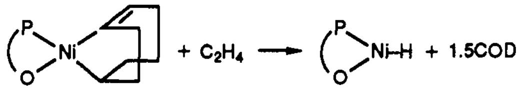
In the chelated complexes XIV the Ni–H bond is formed as a result of reactions 20 and 21.[53]



(20,21)

As stated earlier, reaction 20 is more favored than reaction 21. During ethylene oligomerization in presence of the complex XIV mainly bicyclo(3.0.0)octene-2 (beside a small amount of 1,5-cyclooctadiene) was found.[53]

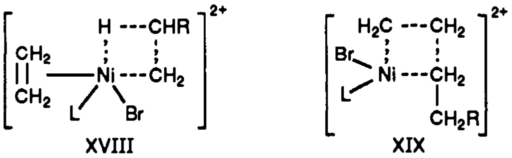
The Ni–H bond in the reaction of ethylene with the complex XVI is formed as follows:[59]



(22)

XVI

Active nickel complexes in the ethylene oligomerization have generally a square-planar structure. Their activity and selectivity depend on the nature of ligands surrounding the nickel ion. The more basic the phosphine (L) ligands and greater their bulk in the complex, (π-C_3H_5)NiBrL/$Et_3Al_2Cl_3$, the higher the oligomer molecular weight is.[51,54] This phenomena is explained by the β-hydrogen elimination from the five or more coordinated intermediate XVIII, whereas the olefin insertion into the nickel–alkyl bond occurs through the less-hindered intermediate XIX:



XVIII XIX

An increase in steric volume of the phosphine L helps in the formation of the structure XIX and the growth of the oligomer chain. A similar effect of an increase in the oligomer molecular weight is observed when there is a decrease in the electron density in the nickel ion in the complex XIV. An exchange, in this complex, of donor alkyl ligands for CF_3, which causes the withdrawal of electron from the nickel ion, diminishes the insertion reaction barrier and therefore the growth of the oligomer chain and its linearity.[55]

TABLE II. Modification of XVII by Aluminium Alkoxides[57]

aluminium alkoxide	blank run	$AlEt_2$-OEt	AlEt-$(OEt)_2$	Al-$(OEt)_2$
Ni ylide (XVII), g	0.0025	0.0025	0.0025	0.0025
Al/Ni, mol	0	200	200	200
temp, °C	50	50	50	50
reaction pressure, atm	14.6	14.6	14.6	14.6
reaction time, min	120	180	180	185
yield of oligomers g (g of XVII)$^{-1}$	700	18000	16700	14800
yield of oligomers mol (mol of XVII)$^{-1}$	2×10^4	5.2×10^5	4.8×10^5	4.2×10^5
1-alkene, content, %		90.3	90.7	90.2

In the complexes XV and XVI, donor character of the O͡P ligand weakens the Ni–H and Ni–C bonds. However, this effect does not influence the β-H-elimination reaction. In summary, these complexes oligomerize ethylene to long-chain α-olefins without C=C bond isomerization; so, the obtained selectivity for linear α-olefins is very high 99–100%.[55]

A very high selectivity of ethylene oligomerization is also obtained when $[[Ph_2PCH_2C(CF_3)_2]O]NiH(PCy_3)$ is used as a catalyst, i.e. 99% of linear and 98% α-olefins C_{4-30} are products of this reaction.[201] This high selectivity of the nickel complex is connected with the steric effects of the bulky phosphines rather then with their electronic properties.[55]

The ylide nickel complexes XV, XVI, and XVII are known to be the most active and selective catalysts of the olefin oligomerization. The recently described modification of the complex XVII with alkoxyalkylaluminum compounds gave one order of magnitude higher active systems (Table II).[57] In this case, the main products are linear α-olefins C_{4-40}. Some internal C=C bond olefins are also obtained.[58,59] Other ethylene dimers and trimers were obtained when other organoaluminum compounds (Et_2AlCl, i-Bu_2AlCl, or $EtAlCl_2$) were used as cocatalysts. The system XVII modified with Et_2AlOEt loses with time its catalytic activity and faster at higher temperatures.[57]

Using strong polar solvents as glycols[246–248,265] pentanol,[275] methanol,[378] and methanol/H_2O (0.5–20% H_2O)[445] for the catalytic system similar to XV and XVII allows the catalyst solution to separate in better grade from oligomer phase.

The complexes $Ph(Ph_3P)NiOCHPhCHPPh_2$ (XV), and (η^3-C_8H_{13})$NiOOCCH_2PPh_2$ (XVI) were heterogenized on alumina–silica and polystyrene supports. The systems supported on alumina–silica gels were less active than their homogeneous analogues. However, complex XV, bonded to the polystyrene chain through phosphine or P͡O ligands, forms active and highly selective (99%) catalysts, giving high molecular linear α-olefins.[60]

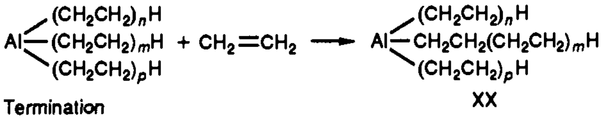
III.1.4. Other Metals

(π-CH_2=$CHCH_2$)$Ru(CO)_3X$ (X = Br, Cl) oligomerize ethylene to C_{14} linear and branched olefins.[62] The mercury complex $Hg(OOCCH_3)_2 + HOCH_2CH_2NH_2 + (C_2H_5)_2NH$ is only a slightly active in this reaction.[63]

III.2. Aluminum

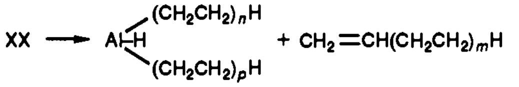
Ethylene oligomerization in the presence of alkylaluminum compounds occurs according to the following reactions:[64]

Propagation



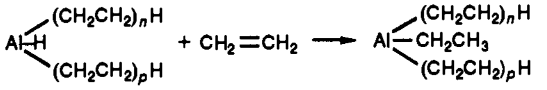
$$\mathrm{Al}\left<\begin{matrix}(\mathrm{CH_2CH_2})_n\mathrm{H}\\ (\mathrm{CH_2CH_2})_m\mathrm{H}\\ (\mathrm{CH_2CH_2})_p\mathrm{H}\end{matrix}\right. + \mathrm{CH_2{=}CH_2} \longrightarrow \underbrace{\mathrm{Al}\left<\begin{matrix}(\mathrm{CH_2CH_2})_n\mathrm{H}\\ \mathrm{CH_2CH_2(CH_2CH_2)}_m\mathrm{H}\\ (\mathrm{CH_2CH_2})_p\mathrm{H}\end{matrix}\right.}_{\mathrm{XX}} \tag{23}$$

Termination



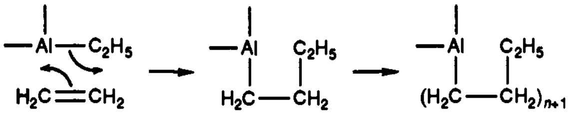
$$\mathrm{XX} \longrightarrow \mathrm{Al}\left<\begin{matrix}(\mathrm{CH_2CH_2})_n\mathrm{H}\\ \mathrm{H}\\ (\mathrm{CH_2CH_2})_p\mathrm{H}\end{matrix}\right. + \mathrm{CH_2{=}CH(CH_2CH_2)}_m\mathrm{H} \tag{24}$$

Thermal decomposition of the aluminum–alkyl bond yields the Al–H bond and α-olefin. At the end of the process the hidridoaluminum compound reacts very fast with ethylene, as follows:



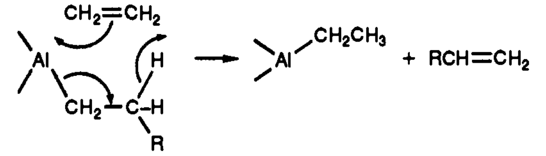
$$\mathrm{Al}\left<\begin{matrix}(\mathrm{CH_2CH_2})_n\mathrm{H}\\ \mathrm{H}\\ (\mathrm{CH_2CH_2})_p\mathrm{H}\end{matrix}\right. + \mathrm{CH_2{=}CH_2} \longrightarrow \mathrm{Al}\left<\begin{matrix}(\mathrm{CH_2CH_2})_n\mathrm{H}\\ \mathrm{CH_2CH_3}\\ (\mathrm{CH_2CH_2})_p\mathrm{H}\end{matrix}\right. \tag{25}$$

The Al–CH_2CH_3 bond can initiate the oligomer chain growth by inserting the next ethylene molecule, and thus beginning a cycle of ethylene oligomers production. The chain growth occurs through a four-center intermediate:[65]



(26)

The chain-termination reaction involves a six-center transition state:



(27)

Thermal decomposition (reaction 24) of the Al–R bond is considerably slower than the ethylene insertion into the Al–H bond (reaction 25). Thus, at lower temperatures, the oligomer growth reaction gives mainly high molecular weight products. At higher temperatures, 463 K, thermal decomposition of the Al–R bond begins to dominate the C_{12} olefins becomes the main products.[69] The product composition as a function of the reaction temperature is shown on Figure 2.[64]

An increase in the reaction pressure increases the ethylene conversion and the amount of linear long-chain oligomers.[65] To avoid polyethylene formation, sulfur (R–S–R)[66] or nitrogen compounds are added to the reaction mixture.

Triethylaluminum was heterogenized by binding to polymers possessing hydroxy groups such as polyvinyl alcohols[68] or phenol resins.[68,69] The ethylene oligomers obtained in their presence are C_{8-18} olefins with 75% content of α-isomers.

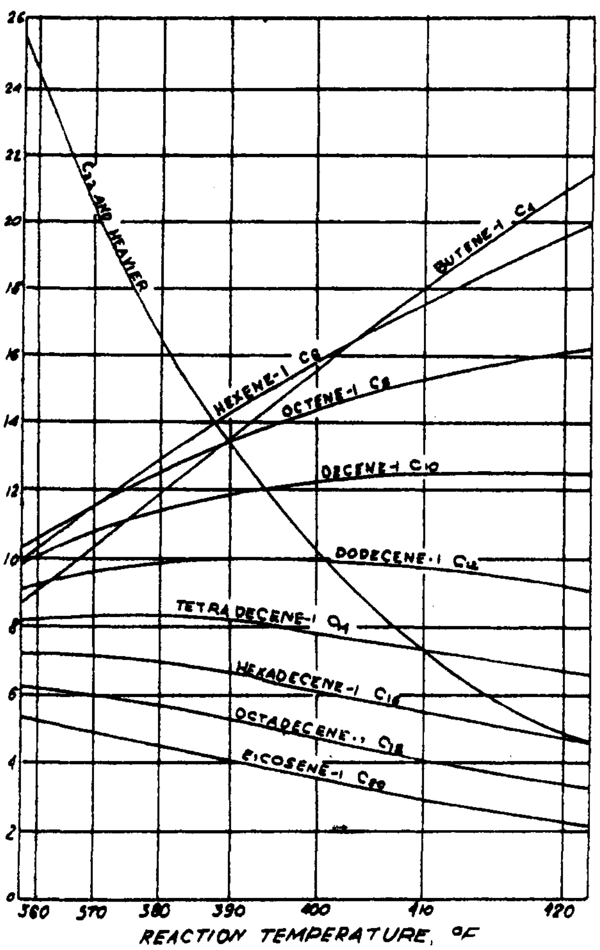


Figure 2. Effect of temperature on product distribution in ethylene oligomerization in the presence of $(C_2H_5)_3Al$, the Gulf Process.[64]

III.3. Inorganic Heterogeneous Catalysts of Ethylene Oligomerization

Various zeolites, e.g. H-ZSM-5, have been investigated as ethylene oligomerization catalysts.[70-73] They possess some of the positive heterogeneous catalyst properties like the possibility of carrying out reactions in a flow system, easy catalyst regeneration, and product separation but they have shown poor selectivity to α-linear olefins; a large amount of branched and cyclized olefins, paraffins, and aromatics is in the products especially when ethylene oligomerization is carried out at higher temperatures, 570 K.[70,71] Hydrocarbon cracking is also observed at these temperatures. Only in presence of high silica zeolites possessing strong Brönsted acid sites are linear oligomers obtained. In this case, mechanism of the ethylene oligomerization assumes cationic character.[74]

Transition-metal oxides and salts, supported on inorganic gels such as alumina and alumina–silica, oligomerize ethylene to α-olefins C_{6-10}. On the surfaces of these catalysts Brönsted acid and coordinative centers exist, which together are responsible for the olefin oligomerization. EPR investigations suggest that Ni(I) ions are the ethylene oligomerization centers in the $NiO–Al_2O_3$ and $NiO–Al_2O_3–SiO_2$ systems.[75,76]

III.4. Industrial Ethylene Oligomerization Processes

Large industrial scale production of α-olefins is carried out by Gulf Oil Chemical Co.,[64,79] Ethyl Corp.[77] and by Shell Oil Co.[59,77,80,81,82] The Gulf and Ethyl processes use Et_3Al as a catalyst although they differ in some details. In the Ethyl process unlike in the Gulf process the products are recycled in order to increase the amount of the most desirable linear α-olefins C_{6-14}. It

TABLE III. Analyses of α-Olefins from Ziegler-type Oligomerization of Ethylene with Recycle (Data from Ethyl Corp.)[77]

	wt %						
	C_6	C_8	C_{10}	C_{12}	C_{12-14}	C_{14-16}	C_{16-18}
linear α-olefins	97.5	96.5	96.2	93.5	87.0	76.9	62.7
linear olefins with internal double bonds	0.6	1.2	1.6	1.5	4.2	5.6	8.2
β-branched α-olefins	1.9	2.3	2.2	5.0	8.8	29.0	29.1
paraffins	0.1	0.6	0.3	0.4	0.4	0.4	0.8

leads, unfortunately, to higher branched olefins content in the products as a result of higher α-olefins reaction with alkylaluminum compounds.[77]

The Ethyl[78] process is carried out at 393 K under 210 psig pressure and the Gulf process at 463 K under 4000 psig uses 14% Et_3Al in heptane solution as catalyst. The ethylene conversions reach 85%. The product composition of these two processes is given in Tables III and IV.[77]

The most modern ethylene oligomerization process—SHOP (Shell Higher Olefins Process) consists of three steps: ethylene oligomerization, oligomers isomerization, and cometathesis.[59,80,82,294] (This process scheme is presented on Figure 3. Ethylene oligomerization is a catalytic process, with a homogeneous catalyst consisting of nickel chloride and the potassium salt of o-(diphenylphosphino)benzoic acid in 1,4-butanediol. The oligomerization reactors are operated at 80–120 °C and 1000–2000 psig. The ratio of reaction is controlled by the rate of catalyst addition. High partial pressure of ethylene is required for good rate of reaction and high linearity of the α-olefins product. Catalyst for oligomerization is dissolved in a solvent that is largely immiscible with the α-olefin product. After the reaction, a product is separated from catalyst solution and excess ethylene gas. Catalyst and ethylene are recycled. The oligomerization reaction provides a range of α-olefins with an even numbers of carbon atoms from C_4 to C_{40}. These are fed into a distillation column and split into three fractions, a C_{4-8} fraction, the desired C_{10-14} fraction, and a heavy C_{16-40} fraction. The light and heavy fractions are fed to an isomerization reactor where α-olefins are isomerized to internal olefins:

$$CH_3CH_2CH{=}CH_2 \xrightarrow[80-140\ ^\circ C,\ 50-250\ psig]{MgO} CH_3CH{=}CHCH_3 \quad (28)$$

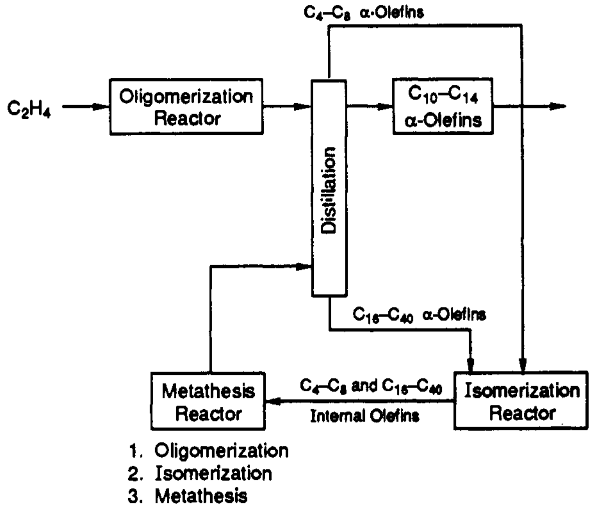
The internal olefins pass to the metathesis reactor where the short- and long-chain internal olefins disproportionate:[82]

$$CH_3CH{=}CHCH_3 + CH_3(CH_2)_8CH{=}CH(CH_2)_8CH_3 \xrightarrow[80-140\ ^\circ C,\ 50-250\ psig]{MoO_3/Al_2O_3} \text{or} \xrightarrow{Re_2O_7/Al_2O_3} 2CH_3CH{=}CH(CH_2)_8CH_3 \quad (29)$$

When higher internal olefins are reacted with ethylene α-olefins are obtained:[294]

$$RCH{=}CHR_1 + CH_2{=}CH_2 \rightarrow RCH{=}CH_2 + H_2C{=}CHR \quad (30)$$

The C_{10-14} olefin fraction is fed into a hydroformylation reactor where it is converted to the corresponding straight-chain aldehydes and then to alcohols. When the cobalt carbonyl complex catalyst is used causing the internal C═C bond migration to α-position in the olefins, the C_{10-14} internal olefins are passed to the hydroformylation reactor.



a. Shell higher olefin process (SHOP)

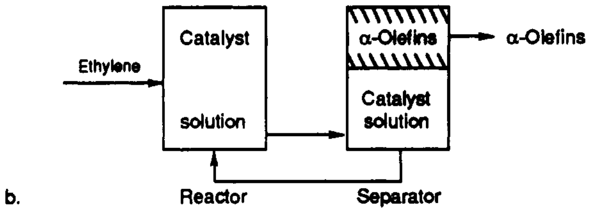


Figure 3. Shell higher olefin process (SHOP)[59,82]. Part a shows the Shell higher olefin process. Part b shows catalyst recycling making the most of two-phase solvent system.

TABLE IV. Composition of α-Olefin Mixture from Catalytic High-Temperature Ethylene Oligomerization (wt %) (According to Data from Gulf Oil Chemical Co.)[77]

	wt %						
	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
linear α-olefins	97.0	96.0	95.0	94.0	93.0	92.0	91.0
β-branched α-olefins[a]	1.4	2.5	3.4	4.6	5.6	6.6	7.8
paraffins	1.4	1.4	1.4	1.4	1.4	1.4	1.4

[a] Including very small amounts of olefins with internal double bonds.

α-Olefin oligomerization products are characterized by a geometric molar growth factor defined as

$$K = (\text{moles of } C_{n+2} \text{ olefin})/(\text{moles of } C_n \text{ olefin}) \quad (31)$$

Weight distribution of various α-olefin oligomerization product fractions is function of K.[80] Control of K factor is the key to the process, since it not only sets the product distribution in α-olefin oligomerization, but also determines the average carbon of the entire SHOP product. K factor can be readily varied by adjusting the catalyst composition. The SHOP process gives highly pure linear α-olefins of the range C_{6-18} as is shown in Table V.[77]

For comparison, the products composition of the Gulf Corp., the Ethyl Corp. and the SHOP processes are presented in Table VI.[77]

A new ethylene oligomerization process, using as a catalyst the nickel salt of organic acids/Et_3Al system,[205] has been recently patented in the United States. Also, in the USSR, the systems $Zr(OPr)_4/Et_3Al_2Cl_3$ and

TABLE V. Typical Quality of α-Olefins from SHOP Process[77]

	composition, wt %						
hydrocarbon type	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{18}	C_{18}
n-α-olefins	97.0	96.5	97.5	96.5	96.0	96.0	96.0
branched olefins	1.0	1.0	1.0	2.0	2.5	3.0	3.0
β-internal olefins	2.2	2.4	1.0	1.5	1.5	1.5	1.5
paraffins	0.1	0.1	0.1	0.05	0.05	0.05	0.05
conjugated dienes	0.1	0.1	0.1	0.05	0.05	0.05	0.05
aromatics	0.1	0.1	0.1	0.05	0.05	0.05	0.05
total monoolefins	99.9	99.9	99.9	99.9	99.9	99.9	99.9

$TiCl_4/EtAlCl_2$ have been patented as catalysts for the industrial ethylene oligomerization processes.[83] In this case the following conditions must be maintained: 20–30 atm, 353–363 K, and toluene as a solvent. After a 1-h reaction 515 kg of α-olefins (18% C_{4-6}, 30% C_{8-10}, and 38% C_{12-18}) per kilogram of Zr are obtained. For the titanium catalyst, the product consists of 18% C_{4-8}, 42% C_{8-10}, and 35% C_{12-18} α-olefins (102 kg (kg of Ti)$^{-1}$ h^{-1}) when the reaction was carried out at 293–313 K under 20–25 atm. The C_{4-6} fraction recycled with unreacted ethylene resulted in an increase of the desirable C_{12-18} fraction to 93–96%, with the content of α-olefins reaching 95% in the final products. Also zirconium catalytic systems described in the Idemitsu patents are a base for commercial use.[230-232]

IV. Oligomerization of Propylene

The propylene oligomerization literature is considerably poorer than for the ethylene oligomerization. The catalysts of oligomerization of propylene and conditions of this reaction are summarized in Table VII.

Most of these catalysts are also active in the ethylene oligomerization (they were partly discussed earlier). Also in this case the titanium, zirconium, and nickel complexes are the most popular catalysts. Propylene oligomers are more structurally diverse than ethylene oligomers (see Scheme VIII). The propagation step of the propylene oligomer growth in presence of transition-metal complexes occurs through four intermediates, wherein propylene inserts into the metal–hydrogen and metal–alkyl bonds. Also, in the chain-termination reaction (Scheme VIII) β-hydrogen can be eliminated from CH_3, CH_2, or CH groups of the oligomer chain. All these possibilities give rise to various olefin isomers.

IV.1. Transition-Metal Complexes as Catalysts of Propylene Oligomerization

IV.1.1. Titanium

Propylene shows outstanding inclination toward the cationic oligomerization. Therefore, the acidic system $TiCl_4/EtAlCl_2$ oligomerizes propylene to irregular strongly branched olefins.[2] A change of the chlorine atoms, in this system whether the one next to titanium or aluminum for the donor ligands, e.g. C_2H_5O, leads to yield of linear olefins.[2] Both actions increase the electron density in the titanium ion and linearity of obtained oligomers.

Investigations of the $TiCl_4/EtAlCl_2$ system during the cooligomerization of ethylene with propylene indicated that, depending on the reaction temperature and solvent, anionic–coordination and cationic centers coexist.

TABLE VI. Oligomers Composition of the Gulf, Ethyl, and SHOP Processes[77]

	Gulf	Ethyl	SHOP
α-olefins	91.0–97.0	63.0–97.5	96.0–97.5
branched olefins	1.6–78.0	1.9–29.1	1.0–3.0
internal olefins	–	0.6–8.2	1.0–2.4
paraffins	1.4	0.1–0.8	0.1
total monoolefin	98.6	99.0	99.9

$AlCl_3$ formed as a product of the $TiCl_4$ alkylation or a reaction of $EtAlCl_2$ with halogenohydrocarbon solvent[25,26] (reactions 32[61] and 33) can form the cationic

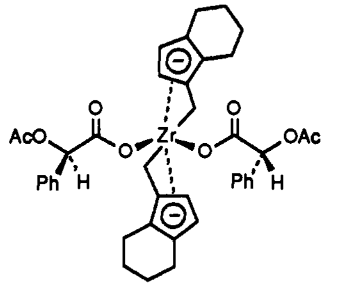
$$TiCl_4 + EtAlCl_2 \rightarrow EtTiCl_3 + AlCl_3 \rightleftharpoons (EtTiCl_2)^{-}(AlCl_4)^{-} \quad (32)$$

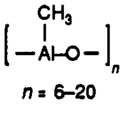
$$EtAlCl_2 + RCl \rightarrow AlCl_3 + RH + C_2H_4 \quad (33)$$

center for propylene oligomerization. It is assumed that the $TiCl_4/EtAlCl_2$ system oligomerizes olefins to a lesser or greater degree according to a cationic mechanism, in which the oligomer chain has a positive charge and forms an ionic pair with a negative counterion, e.g. $AlCl_4^-$.[61] A decrease in the Ti(IV) ion electron affinity decreases its acidity and increase a coordination mechanism contribution in the whole oligomerization reaction, which in turn causes an increase of the product linearity. During the investigations of the propylene oligomerization in the presence of the $TiCl_4/i\text{-}Bu_2AlCl$ system in toluene it was proved that the solvent participated in the oligomer chain termination reaction as the chain-transfer agent. This is the reason why a part of the obtained product has oligomers with toluene moiety as end groups.[84]

IV.1.2. Zirconium

Propylene oligomers have different lengths depending on the kind of the zirconium catalyst used. In presence of the $Zr(acac)_4/Et_3Al_2Cl_3/R_3P$ (R = alkyl or aryl) system, low molecular C_{6-9} oligomers are obtained.[85] When the system bis(pentamethylcyclopentadienyl)dichlorozirconium activated with methylaluminoxanes[86] is used, longer chain oligomers, having more than C_{16} in the chains, are found in the products. (*S*)-[1,1′-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium bis(*O*-acetyl-(*R*)-mandelate) activated with methylaluminoxane (see below) is a stereospecific catalyst of the propylene and 1-butene oligomerization.[203]





The Zr–CH_3 bond is the active center of zirconium catalysts. It is formed in the methylation reaction of the zirconium ions in the complexes with e.g. methylaluminoxanes. The next steps of the catalyst action are olefin complexation and olefin insertion into the Zr–CH_3 bond (reaction 34). The chain termination reaction

TABLE VII. Oligomerization of Propylene

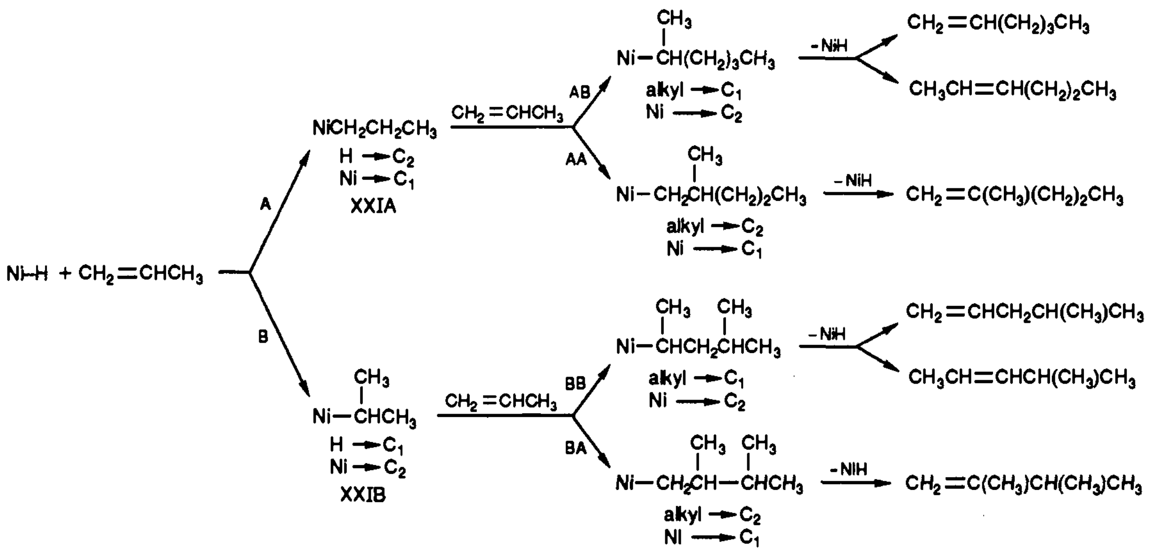
catalyst	react condtn	products	yield	ref(s)
		Titanium		
$TiCl_4/R_2AlCl$ (Al/Ti = 0.69), R = C_2H_5, $i\text{-}C_4H_9$	toluene, 60 °C, 15 min	olefins $\bar{M}_n$ = 92 (27%), 131 (36%), 163 (35%), 382 (2.7%)	conv = 95%, 430 × 10^{-3} L (g of $TiCl_4$)$^{-1}$ min^{-1} ethylene with propylene	25, 84
$TiCl_4/(C_2H_5)_3Al/RCl$ (Al/Ti = 10), R = alkyl	hexane, 40 °C, 15 min	oligomers	conv = 90%	163
$TiCl_4/(ONi)_5(OH)_n/C_2H_5AlCl_2$, n = 1, 2, 3		oligomers C_6 = 65%, C_9 = 25%, C_{12} = 8%, C_{15} = 2%		331
$TiCl_4/Ti(OBu)_4/Zr(OBu)_4/(C_2H_5)_3Al_2Cl_3$ (1:2:1:10)	hexane/toluene, 80 °C, 2 h	α-olefins = 72% of the product $\bar{M}_n$ = 114	conv = 86% (129 g), PP = 2 g	87
$(C_2H_5O)_2TiCl_2/C_2H_5AlCl_2$	benzene, 5 °C	olefins $\bar{M}_{mw}$ = 340, linearity = 49%		332
		Zirconium		
$Zr(acac)_4/(C_2H_5)_3Al_2Cl_3/PR_3$ (Al/Zr = 10–20:1)	100–600 psig, 150 °F	olefins C_{6-9}	conv = 60%	85
$Zr(\pi\text{-allyl})Br_3/(PhCH_2)ZrBr_3/(C_2H_5)_3Al_2Cl_3$		α-olefins C_6 and $C_{>6}$		238
(AcO)Ph$(CHCOO)_2$Zr[1,1′-ethylenbis(4,5,6,7-tetrahydro-1-indenyl)]/methylaluminoxane	toluene, 50 °C	olefins C_{9-21} = 53%		203
$[\eta^5\text{-}C_5(CH_3)_5]_2ZrCl_2$/methylaluminoxane$_n$, n = 6–20	8 atm, 50 °C, 4 h	oligomers C_9 = 15.5%, C_{12} = 5.9%, $C_{>15}$ = 78.5%		86
		Nickel		
$C_2H_4Ni[P(OC_6H_4R\text{-}o)_3]_2/H_2SO_4$, R = alkyl, alkoxy C_{1-3}	haloaromatic, 0–50 °C	oligomers		253
$(\pi\text{-}C_3H_5)NiBr/(C_6H_{11})_3P/C_2H_5AlCl_2$	−75 and +55 °C	olefins $C_{>12}$ = 10–15%		333
$(\pi\text{-}C_3H_5)_2Ni/SiO_2\ Al_2O_3$, $Al_2O_3/SiO_2/CH_3AlCl_2$ (Al/Ni = 1:4, Ni/OH = 1)	−40 and +50 °C, 2.5 h, propylene flow rate = 360 cm^3/min	olefins C_6 = 25–67%, C_9 = 17–43% C_{12} = 14–32%		96–99
$(\pi\text{-}C_3H_5)Ni/Al_2O_3/SiO_2$ (Ni/OH = 1)	−14 and +40 °C, propylene flow rate = 360 cm^3/min	olefins C_6 = 40.5%, C_9 = 56%, C_{12} = 3.5%		98
$(\pi\text{-}C_3H_5)NiCl$/Lewis acids		oligomers		
$Ni(RCOO)_2/(C_2H_5)_2AlCl$, RCOO = octanoate, oleate	n-heptane, 40 °C	branched olefins C_9, C_{12}	conv = 99	89, 338
$Ni(acac)_2$ supported on $SiO_2/(C_2H_5)_3Al_2Cl_3/Ph_{3-n}PCl_n$, n = 0, 1	90–380 psig, 150 °F, 3 h	olefins $C_{>9}$ = 40%	conv = 80%	92, 340
$Ni(acac)_2$ supported on $Al_2O_3/SiO_2/(C_2H_5)_3Al_2Cl_3/Ph_3P$ or Bu_3P (Al/Ni = 3)	145 °F, 3 h	oligomers $C_{>12}$ = 21%	38 g (mol 439 Ni)$^{-1}$ h^{-1}	93, 94, 154, 439
$Ni(acac)_2$ supported on $Al_2O_3/SiO_2/(C_2H_5)_3Al_2Cl_3$	toluene, 1–100 atm, 0–130 °C	olefins C_6 = 62%, C_9 = 25%		95
$[CH[C(CF_3)O]_2]_2Ni/(C_2H_5)_2Al(OEt)$	40–80 °C	olefins C_6 = 77%, C_9 = 17%, C_{12} = 3%	2384 mol of C_3^{2-} (mol of Ni)$^{-1}$ h^{-1} (80 °C)	90
$(COD)Ni[CH(C(CF_3O]_2]$	toluene, 75 °C, 0.75 h	oligomers C_6 = 59%, C_9 = 32%, C_{12-15} = 9%	conv = 73%, 7220 mol C_3^{2-} (mol of Ni)$^{-1}$	53
$Ni(sacsac)(Bu_3P)Cl/(C_2H_5)_2AlCl$	chlorobenzene	oligomers		341
NiX_2 or $PdX_2/(C_2H_5)_2AlCl$ or $NaBH_4$, X = −SR, =CRC(SR)=, RSC_6H_4F, e.g., $C_6F_5OH/NiOAc\cdot4H_2O/Et_2AlCl$	chlorobenzene, 110 psig, 60 °C, 20 h	oligomers C_{6-9} = 73%, C_{12-18} = 18%, $C_{>21}$ = 9%	linearity = 80%	206
$NiCl_2\cdot H_2O$/alumina spheres/$(C_2H_5)_2AlCl$	toluene, 700 lb/sq, 35–50 °C	olefins $C_{>6}$ = 20%	conv = 88, 7–99.8%	159
Ni/microfibrous carbon fibers/haloalkylaluminum	40–150 °C	oligomers		372
		Lanthanides		
$Lu[\eta^5\text{-}C_5(CH_3)_5]_2CH_3/(C_2H_5)_2O$	toluene or cyclohexane −30 and +20 °C	high oligomers		100
$[[\eta^5\text{-}C_5(CH_3)_5]_2MH]_2$, M = La, Nd	cyclohexane, 293 K	high branched oligomers		62
$[[(CH_3)_2Si[\eta^5\text{-}C_5(CH_3)_4]_2LuH]_2$	cyclohexane, 298 K	high oligomers		102

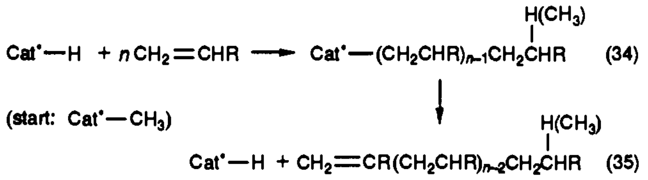
Ruthenium				
(π-C_3H_5)Ru(CO)$_3$X		high branched oligomers		62
Aluminum				
R_nAlX_{3-n}/chlorohydrocarbon, n = 1, 2, 3; R = hydrocarbyl, RO, RC(=O)–; halogen	pentane, 28 °C, 30 min	oligomers $\bar{M}_w$ = 592		343
R_3Al or R_2AlH; R = alkyl C_{2-18}	40–150 atm, 120–180 °C	α-olefins C_{7-9} = 25%, C_{10-14} = 37%, C_{15-18} = 19% (branched)		367
B, Al, Ti, and Zn Halides Systems				
BF_3/H_3PO_4, BF_3/HPO_3, $BF_3/H_4P_2O_7$	100 °C, 1 atm	oligomers C_{9-18}		125–127
	60–70 °C	oligomers C_{12}		
BF_3/ROH, R = CH_3, C_4H_9	CH_2Cl_2, $C_2H_4Cl_2$, CCl_4, $PhNO_2$	oligomers C_{12-30}	influence of solvent on oligomer yield: $C_2H_4Cl_2$ > $PhNO_2$ > CCl_4	128–130
BF_3-HF	4–60 °C	oligomers C_{12-15}		350
BF_3/H_2O	5 atm, 100 °C, 60 min	oligomers C_{12-18} = 72%, $C_{>20}$ = 9%	5 g (mmol of BF_3)$^{-1}$	136
BF_3/polyolefins (0.2–0.4%)	40 °C	oligomers C_{19-20}		351
BF_3/ZSM-5 (SiO_2/Al_2O_3 = 70)	150 °C	oligomers C_{4-8} = 28.7%, C_{7-10} = 55% without aromatic hydrocarbons	conv = 99%	
BF_3/TiO_2		oligomers		349
$AlCl_3$	70 °C	oligomers C_{6-24}		131
$AlCl_3/CH_3C_6H_5/C_2H_4Cl_2$ (1:3.5:2.5)		oligomers $\bar{M}_w$ = 1074	conv = 84%	364
$AlCl_3$/graphite	600 psig, 200 °C	oligomers C_9		359
$AlBr_3$, $AlBr_3$/HBr	–50 and +100 °C	oligomers		352–354
$TiCl_3$	95–315 °C			356
TiF_4/Al_2O_3	300 °C	oligomers		330
$ZnCl_2$		mainly oligomers C_9		132–134
H_3PO_4 Acid and Others				
H_3PO_4		oligomers		346
H_3PO_4/SiO_2	70 atm, 125–150 °C	olefins C_9 = 60–80%	conv = 80–90%	105
H_3PO_4 (65%)/SiO_2 (1.5:1)	30–80 atm, 170–250 °C	oligomers C_6 = 25%, C_9 = 55%, $C_{>12}$ = 20%		107–109
	30–80 atm, 183–230 °C	oligomers, C_{12} = 75%		
H_3PO_4/SiO_2 (P_2O_5 = 36.1%)	220 °C	oligomers C_6 = 6%, C_9 = 56%, C_{12} = 36%	0.155 mol (g of catalyst)$^{-1}$ h^{-1}	104
H_3PO_4/SiO_2/graphite		oligomers, C_{9-12}	high conversion, traces of PP	110
H_3PO_4/SiO_2		oligomers C_{12-16}		362
$H_3PO_4/Al_2O_3/SiO_2$ or Al_2O_3	two-step process			113
$H_4P_2O_7/SiO_2$/NaA zeolite	180 °C	oligomers C_{12}		347
HF	400–0 psig, 20–30 °C	oligomers C_{7-14}		348
H_2SO_4	25 °C	oligomers	conv = 99%	105
mineral acids	205–315 °C			344
Inorganic Oxides Systems				
CuP_2O_7	150 °C			357
Cu/Zr/aluminum phosphate	propene/butene mixture, 100 °C	oligomers C_{5-12}		375
TiO_2/SiO_2				355
$Al_2O_3/SiO_2/MoO_3$, WO_3, UO_3, Cr_2O_3, NiO, FeO, or ZnO		oligomers		358
MoO_3/Al_2O_3		oligomers C_{10-18}, max C_{13}		324
10%NiO/Al_2O_3/SiO_2		oligomers C_6 = 24%, C_9 = 48%, $C_{>10}$ = 42%	conv = 41%	149

TABLE VII (Continued)

catalyst	react condtn	products	yield	ref(s)
$TiO_2/ZrO_2/Ni$ (0.1%)	800 min	oligomers $C_{>10} = 72.8\%$		148, 371
sulfided Ni/mica/montmorillonite (N-SMM)		oligomers C_{12-21}		370
Ni/HZSM-5	1600 psig, 130 °F	oligomers C_{6-15}, max C_{6-9}		142, 303
Ti/Al/silicalite ($SiO_2/Al_2O_3 = 161$, $SiO_2/TiO_2 = 46$)	260 °C, flow rate = 0.6 h^{-1}	oligomers, $C_{>7} = 54\%$	conv = 98%	365
SiO_2/Fe_2O_3(573), SiO_2/TiO_2(46) (Ti, Fe silicalite)	310 °C, flow rate = 0.6 h^{-1}	oligomers $C_{>6} = 35\%$		366
ferrerites $M_{x/n}(TO_2)_x(SiO_2)_{36-x}$, M = cation, T = B, Al, Fe(III); $x = 0.05–6.6$; n = valence of M, (1.25% F)	4 MPa, 330 °C	oligomers $C_{6-9} = 35\%$, $C_{10-17} = 62.4\%$, $C_{>18} = 2.6\%$		373
zeolites		branched oligomers	branched oligomers in the product decreases in order: omega > HY > mordenite ⩾ ZSM-5 > offretite > boralite	138
zeolites: H, NaHY, NaMgY	313 K	oligomers, aromatics		137, 144, 145, 204, 328
zeolite NaX/30%Ni(II)	200 °C, 0.0125 h cont time	oligomers $C_6 = 24\%$, $C_9 = 57\%$, $C_{12} = 19\%$	conv = 62%	149
KO-10/4	150–200 °C	oligomers C_{9-12}	conv = 99%	140
zeolite 25 M	1 atm, 530 °F, flow rate = 0.6 h^{-1}	oligomers C_{3-11}	conv = 95%	360
	500 psig, 400 °F	oligomers C_{9-15}		
HZSM-5	1 atm, 270–330 °C, space velocity = 0.873–1.75 h^{-1}	olefins, aromatic hydrogen, paraffins		222
HZSM-5	300–500 K	oligomers C_{5-20}		36, 71, 72, 141, 202
zeolite Y (dealuminated, $SiO_2/Al_2O_3 = 75$)	1000 psig, 510 °F	oligomers bp = 330 °F (19.8%), bp = 330–650 °F (64.3%), bp > 650 °F (9.1%)		368
ZSM-23/trialkylpyridine or organophosphite	200 °C	oligomers $C_{>12}$	0.25 g g^{-1} h^{-1}	369, 446
HZSM-12	600 psig, 100–150 °F	oligomers $C_9 = 59\%$, $C_{12} = 27\%$, $C_{15} = 8.7\%$	conv = 61–99%	442
zeolites (ZSM-5, boralites, offretite·HY, mordenite, or omega)/20% sepionite	30–50 atm	oligomers $C_{6-12,>12}$, low selectivity		374
SiO_2		oligomers		88

SCHEME VIII. Reaction Paths of Propylene Oligomerization in the Presence of a Nickel Catalyst[51]





$$\text{Cat}'\text{—H} + n\text{CH}_2\text{=CHR} \longrightarrow \text{Cat}'\text{—(CH}_2\text{CHR)}_{n-1}\text{CH}_2\overset{\text{H(CH}_3)}{\text{C}}\text{HR} \quad (34)$$

(start: Cat'—CH$_3$)

$$\text{Cat}'\text{—H} + \text{CH}_2\text{=CR(CH}_2\text{CHR)}_{n-2}\text{CH}_2\overset{\text{H(CH}_3)}{\text{C}}\text{HR} \quad (35)$$

occurs as a result of the β-hydrogen elimination reaction and the Zr–H bond restoration (reaction 35).[203]

The mixed systems consisting of titanium and zirconium halides and alkoxyls (Ti:Zr = 3–1:1) modified with $Et_3Al_2Cl_3$ exhibit high activity in the linear propylene α-oligomerization. The products of this reaction contained, beside high molecular oligomers, polypropylene. The propylene conversion was in the range of 78–93%.[87]

IV.1.3. Nickel

The structures and mechanisms of the nickel complexes action in the propylene oligomerization are the same as in the ethylene oligomerization. The bonds Ni–H and nickel–alkyl are the active centers of the catalysts. The catalytic propylene oligomerization begins with olefin insertion into the Ni–H bond Scheme VIII. Hydrogen from the Ni–H bond can be bonded to the carbon C_1 or C_2 forming, respectively, branched or linear alkyl groups bonded to the nickel ion. These alkyl groups can migrate to the propylene molecule in two modes: to the propylene carbons C_1 or C_2. These possibilities are responsible for the branched products. It is possible however to control these reactions with the help of the phosphine ligands,[51,54] as it occurs in the system $[(\pi\text{-}C_3H_5)NiBr]_2/Et_3Al_2Cl_3/L$ where L = PMe_3, PEt_3, PBu_3, $P(i\text{-}Pr)_3$, PCy_3, and $P(tBu)_2(i\text{-}Pr)$. Only very bulky $P(t\text{-}Bu)_2(i\text{-}Pr)$ changes the first step of the oligomerization—propylene insertion into the Ni–H bond from the iso mode—the Markovnikov mode insertion product XXIB – into 1-propyl mode – to the anti-Markovnikov insertion product XXIA (Scheme VIII, path B and A, respectively). More bulky phosphine ligands favor less volume branched alkyl in the formed nickel–alkyl group during the olefin insertion reaction. In this situation nickel ion's bonding to the C_2 carbon of the propylene molecule is blocked. Thus, when nonbulky phosphines, PMe_3, PEt_3, or $P(n\text{-}Pr)_3$, were used as the ligands highly branched oligomers were the products of the propylene oligomerization.

Detailed investigations[1,54] of this kind of catalysts have unequivocally established that the phosphine influence on the oligomer structure has steric, not electronic character. More bulky phosphines in these catalysts are responsible for formation of more linear oligomers.

Generally, nickel complexes do not oligomerize propylene to higher molecular weight olefins. Mainly dimers and trimers are the products of this reaction.

Highly branched oligomers, dimers, and trimers are obtained when the system nickel octanoate/$EtAlCl_2$ is used as a catalyst.[89] The same product composition but with linearity of 50–70% was obtained by using (η^4-cycloocten-1-yl)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)nickel without cocatalysts.[53] Modification of this catalyst with Et_2AlOEt[90] or $(i\text{-}Bu)_2AlH$[91] raised the catalyst's activity but without a change of product's composition. In this type of nickel catalyst, activity of olefin oligomerization increases with acidity of organoaluminum compounds and decrease of β-ketone ligand donor properties. Chevron Research reported a catalyst prepared by contacting Ni or Pt salt with a fluoroorganothiol or sulfide followed by addition of organoaluminum halide or alkoxide or borohydride. For example, the bis(pentafluorophenylthiolato)nickel/Et_2AlCl catalyst system gives high yield of propylene oligomers (C_{6-9}, 70%) having ≥ 80% linear olefins.[206]

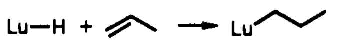
C_9 (40%) and higher propylene oligomers were the products of oligomerization reaction in presence of heterogenized catalyst $Ni(acac)_2/Et_3Al_2Cl_3/Al_2O_3SiO_2$.[92–95]

By changing the alumina–silica gel composition in the heterogenized π-allyl nickel systems it was possible to oligomerize propylene without organoaluminum compounds as cocatalysts. This catalytic activity was exhibited in supports containing 50% by weight Al_2O_3 to 70% by weight Al_2O_3. Modification of all these systems with chloroalkylaluminum compounds, $TiCl_4$, or $AlBr_3$ gave highly active catalysts for propylene oligomerization in the flow system.[92–95]

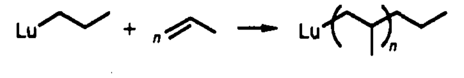
Hydrated iron group metal salts supported on porous carriers after drying and calcination modified with organoaluminum compounds are used as catalysts in Huels-UOP—"Hexall" and "Octol" processes for propylene oligomerization and propylene—butene co-oligomerization minly to dimers 60%. These reactions are carried out at 35–50 °C, 700 psig. The most effective catalysts contain nickel surface complexes.[159,161,162] $Ni(NO_3)_2$ or $NiCl_2 \cdot 2H_2O$ on alumina spheres calcined and activated with Et_2AlCl or $AlCl_3$ oligomerizes propylene to dimer (80%) and higher oligomers (20%).[159] The calcination temperature affected the catalyst selectivity.[159]

IV.1.4. Various Metals

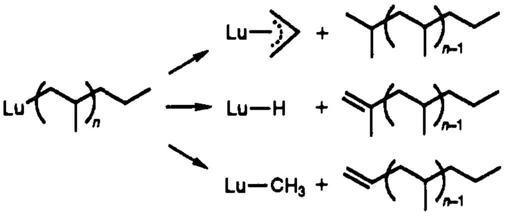
Lutetium complexes: $(\eta^5\text{-}C_5Me_5)_2LuCH_3\cdot$ether (XXII),[100] $[(\eta^5\text{-}C_5Me_5)_2LuH]_2$ (XXIII),[101] and $[[(CH_3)_2Si(\eta^5\text{-}C_5Me_4)]_2LuH]_2$ (XXIV)[102] are catalytically active in the propylene oligomerization. The complex XXIV is 10-fold more active than the XXIII. The oligomers having more than 21 carbons in their chains were products of these system. The propylene oligomerization mechanism in such catalysts is similar to that described for other transition-metal complexes. It proceeds in the following way:



(36)



(37)



(38)

(39)

(40)

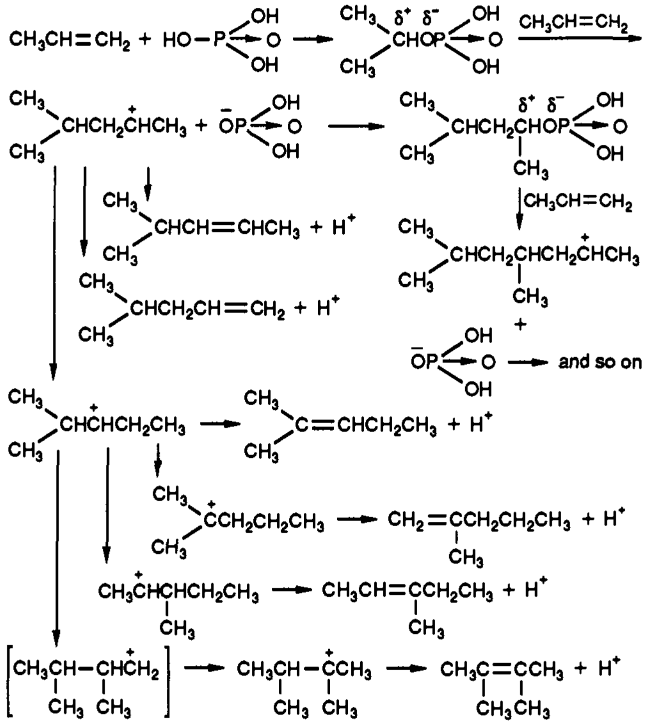
The oligomer chain termination step occurs thanks to the olefin metalation, β-hydrogen elimination, and β-methyl group elimination (reactions 38, 39, and 40, respectively).

$(\pi\text{-}CH_2{=}CH\text{-}CH_2)Ru(CO)_3X$ (X = Br, Cl) oligomerizes propylene to highly branched C_{9-15} oligomers.[62]

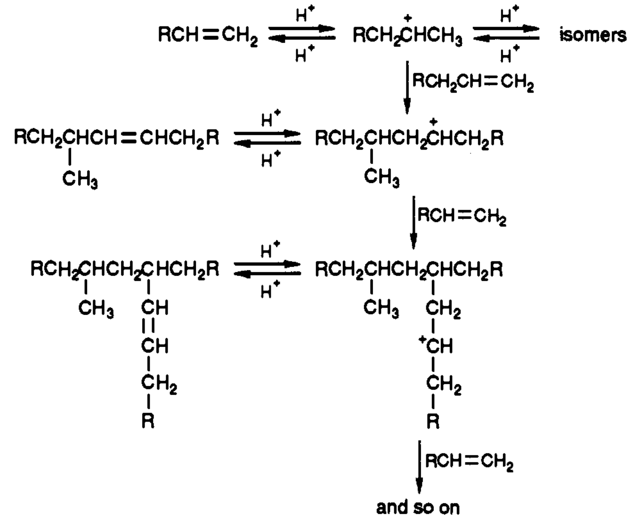
IV.2. Cationic Oligomerization of Propylene

In 1933 Universal Oil Products Co. developed the supported catalytic system H_3PO_4/SiO_2 for propylene oligomerization.[103] Amount of supported phosphoric acid is of the range 62–65% by weight. Also, asbestos can be used as carrier in this reaction. Use of neutral carrier such as active carbon leads to the formation of alkyl phosphates which volatilize from the catalyst bed. Thus H_3PO_4 is removed from the catalytic system. This does not occur when acidic carriers are used. Silica,[104–110] kaolin,[111] silicon, silicon carbide, marble, glass, quartz,[112] and alumina–silica[113] were investigated as supports of H_3PO_4. Also, some processes for propylene oligomerization using only H_3PO_4 as a catalyst have been described.[114,115] The reaction mechanism for kind of oligomerization is presented in Scheme IX. Dimers, trimers, and tetramers are found when the reaction is carried out at lower temperatures (520 K). At higher temperatures longer chain oligomers are formed. Propylene hydropolymerization reactions, yielding paraffins, begin to occur when the reaction temperature is higher than 580 K. The addition of steam to the reaction mixture at this temperature reduces the paraffin content in the products. The molecular weight of oligomers grows when the reaction pressure is raised.

SCHEME IX. Mechanism of Propylene Oligomerization in the Presence of H_3PO_4 as a Catalyst[104]



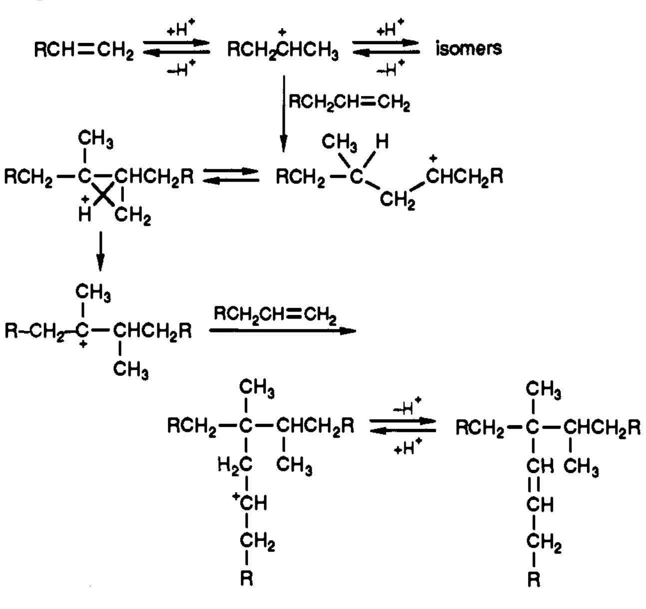
SCHEME X. Cationic Mechanism of α-Olefin Oligomerization in the Presence of the System BF_3/n-BuOH[128]



Repas[104] has proved that addition of water to the system H_3PO_4/SiO_2 increased the propylene oligomerization product yield. He has also proposed a mechanism for this reaction in which surface propylene phosphate esters are the catalytic centers for propylene oligomerization. This catalytic system is often modified with cupric,[116–118] nickel,[117,121] and calcium[116] salts, manganese derivatives,[122] and amines.[123–124]

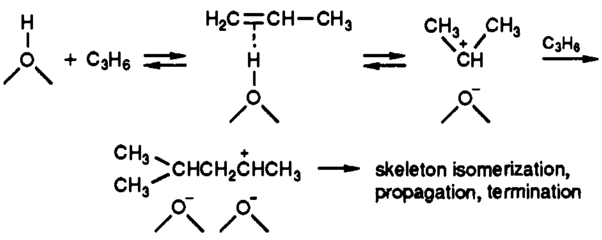
Many other acidic catalysts possessing a Lewis acid as a component are active in propylene oligomerization. The most popular are BF_3/H_3PO_4,[125–127] BF_3/H_2O,[128,136] $BF_3/MeOH$,[129] $BF_3/BuOH$,[130] $AlCl_3$,[131] and $ZnCl_2$,[132–134]

SCHEME XI. Shubkin's Mechanism of Cationic α-Olefin Oligomerization in the Presence of a Lewis Type Catalyst[136]



and they are listed in Table VII. The cationic mechanisms of propylene oligomerization in presence of Lewis acids are in Schemes X and XI. In this case, an increase in reaction temperature causes a decrease in oligomer molecular weight.[136]

Propylene oligomerization in presence of alumina-silica gels and zeolites, e.g. HNaY,[137] are initiated on the surface of acidic Brönsted type sites after propylene adsorption. An increase in the amount of the acidic centers on the carrier surface and their acidic strength results in increasing of the propylene oligomerization rate and greater branching of the product. The oligomer chain branching depends on the carrier porosity. The following order of decreasing branching with pore size was established for zeolites: omega > HY > mordenite > ZSM-5 > offretite > boralite.[138-143] Omega with the largest (10 Å) pore opening gives the most branched oligomers.



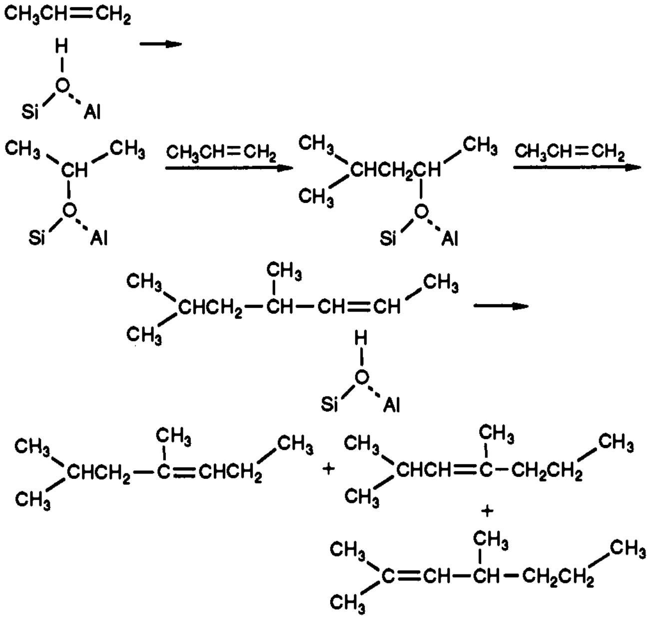
(41)

In the presence of these catalysts mainly low molecular weight oligomers are formed. Some paraffins and aromatics are formed as products of the side reactions, namely, isomerization, cracking, aromatization, and hydrogen transfer.

The propylene oligomerization on HY zeolites at 213–313 K occurs through surface alkoxy derivatives formed in the reaction between protonated alkenes and surface oxygens of the zeolite. Carbocations are not intermediates in this case. The mechanism of this reaction is presented on Scheme XII.[204]

A point of some interest in propylene oligomerization is the selective poisoning of sites on the outside of zeolite HZSM-23 particles with trialkylpyridine or organo phosphite compounds having an effective cross section larger than that of the pores. In this case propylene is oligomerized in zeolite pores, improving in this way linearity of product.[369,446]

SCHEME XII. Mechanims of Propylene Oligomerization in the Presence of Zeolite HY[204]



The following systems have been described as catalysts of propylene oligomerization: MoO_3/Al_2O_3,[146] $TiO_2/ZrO_2/Ni$,[148] $NiO/Al_2O_3/SiO_2$,[149] and Fe, Co, and Ni oxides on alumina/silica.[147,150,151]

V. Oligomerization of Higher α-Olefins

The dimerization and trimerization of higher olefins are classified in this article as the oligomerization reactions. The catalytic systems for higher α-olefin oligomerizations are presented in Table VIII. Olefin reactivity, in this reaction, decreases in the following order: ethylene > propylene > 1-butene > 1-hexene > 1-octene > 1-decene.[53,58] Longer chain α-olefins undergo a more difficult oligomerization reaction than ethylene and propylene. The selectivity of this reaction in the case of higher α-olefins is lower. This is a result of the fact that higher α-olefins can form a greater amount of isomers than ethylene and propylene in the oligomerization cycle as is shown in Scheme XIII. Catalysts similar to that used for ethylene or propylene oligomerization can be used for higher α-olefin oligomerization. Among the most popular are titanium, zirconium, and nickel complexes, homogeneous and heterogenous Lewis and Brönsted acids, and inorganic oxides.

V.1. Organometallic Complexes as Catalysts of Higher α-Olefin Oligomerization

V.1.1. Titanium and Zirconium

The system $TiCl_4/R_nAlCl_{3-n}$ (n = 1,2,3; R = alkyl) oligomerizes 1-hexene.[168] Modification with halogenohydrocarbons, phosphoro- and sulfuroorganic compounds, alkali metal hydrides, and nickel salts gave reactive catalysts in the 1-decene,[163] $CH_2{=}CH(CH_2)_nCH_3$ (n = 1–5),[164] C_{6-14} α-olefin,[165] and C_{3-6} α-olefin[167] oligomerization.

TABLE VIII. Oligomerization of Higher α-Olefins

catalyst	olefin/react condtn	products	yield	ref(s)
	Titanium			
$TiCl_4/(C_2H_5)_{3-n}AlCl_n/3RCl$, $n = 0, 1, 1.5$	olefins C_{3-14}/42 °C, 15 min, hexane	oligomers C_{35-350}	conv = 90%	163
$TiCl_4/(C_2H_5)_3Al_2Cl_3$	1-hexane/30 °C, toluene	vinylidene olefins = α-olefins = 5.3%; $\bar{M}_w = 186$	conv = 38.5%	168
$TiCl_4/AlCl_3/LiH$	1-butene, 1-octene/100–120 °C	oligomers, index viscosity = 131, flash point = 210 °C		165
$TiCl_4$/Ni (salt)/organoaluminums (2–20:1–5:5–86)	α-olefins C_{3-6}/20–180 °C, contact time = 0.1–34 s			167
$TiCl_4$/P,S,N-hydrocarbons/$R_3Al_2Cl_3$, $RAlCl_2$ (1:0.1–4:1–5)	$CH_2{=}CH(CH_2)_nCH_3$, $n = 1–5$	oligomers		164
$TiCl_4/(OBu)_4/Zr(OBu)_4/(C_2H_5)_3Al_2Cl_3$ (1:2:1:10)	1-decene/80 °C, 4 h	oligomer $\bar{M}_n = 356$	conv = 86%	87
$TiCl_4$/propylene oxide/$(C_2H_5)_3Al_2Cl_3$ (Al/Ti = 1.25)	1-octene/hexane	olefins C_{24} = 65%	conv = 80%	170
	Zirconium			
$Cp_2ZrCl_2/(CH_3)_3Al/H_2O$	1-hexene/10 psig, 20 °C, toluene			392
$ZrCl_4(HfCl_4)/AlCl_3$ (Al/Zr = 1)	1-decene/99 °C, 1 h, heptane	oligomers C_{30-50} = 45–51%	conv = 93%	169
	Nickel			
$Ni(CF_3COCHCOCF_3)_2$ $(C_2H_5)_3Al_2Cl_3/Ph_3P$ or $Ni(CF_3COCHCOCF_3)_2/(C_2H_5)_3AlOC_2H_5$	1-butene (isomerization of 1-C_4 to 2-C_4)	olefins C_8 = 78%, C_{12} = 17.6%, C_{16} = 4.4%	conv = 31.3%	153, 379
$Ni(COD)(CF_3COCHCOCF_3)$	1-butene, 2-butene, 1-hexene, 1-octene/70 °C, 0.5–2 h	dimers and trimers, linearity = 36–85%	62–330 mol olefins (mol of Ni)$^{-1}$ h^{-1}	53, 55
$Ni(HCOO)_2/(C_2H_5)_3Al$ (Al/Ni = 40)	1-hexene/60 °C, 4 h, toluene	α-olefins = 89%, $\bar{M}_w = 174$	conv = 38.3%	168
$Ni(acac)_2/(C_2H_5)_3Al_2Cl_3/Ph_3P$ or not	1-hexene/60 °C, 4 h, toluene	α-olefins = 50%; $\bar{M}_w$ = 172–271	conv = 63%, without Ph_3P = 47.7%	168
(COD)Ni(1,2-diketones)$RCO_2NiO_2CR_1$, R = C_5 hydrocarbyl; $R_1 = C_{1-3}$ haloalkyl, e.g., CF_3CO_2Ni(2-ethylhexanoate)/$C_2H_5AlCl_2$ (31:194)	1-butene	oligomers C_{8-12}		160
	olefins C_{4-8}, e.g., hexene/65 °C	olefins C_{12} = 97%	conv = 5%	155 206
	1-butene	olefins C_8 (85%), C_{12} (12%), C_{16} (3%)	conv = 75% 0.11 L or product (mol of catalyst)$^{-1}$ h^{-1}	155
$Ni(octanoate)_2/C_2H_5AlCl_2$	butene	oligomers C_8		338
$Ni(acac)_2$ supported on $SiO_2/Al_2O_3/(C_2H_5)_3Al_2Cl_3$/monoolefins, diolefins	α-olefins C_{2-10}, e.g., butene/toluene, 0–130 °C, 1–100 atm	olefins C_8 (89%), C_{12} (10%), C_{16} (1%)		95
Ni(carboxylate 11% Ni)/$C_2H_5AlCl_2/CF_3CO_3H$, $(CF_3CO)_2O$	1-butene + 2-butene/isohexane, 42 °C, 5 bars, 4 h	olefins C_{8-16}	conv = 67–98%	156, 381
$Ni(acac)_2$ supported on $SiO_2/Al_2O_3/(C_2H_5)_5Al_2Cl_3/Ph_3P$ or Bu_3P (1:1–20:>3)	1-butene/isooctane, 145 °F, 15 bars, 3 h	olefins C_{8-12}	conv = 50%	94, 154
$(COD)_2Ni_3(CO)_2$ supported on Al_2O_3/SiO_2 (12–87)	1-hexene/cyclohexane, 150 °C, 1.4 h	olefins C_{12} (78%), C_{18} (17%), C_{24} (4%)	1552 g of oligomer (g of Ni)$^{-1}$ h^{-1}	376
5% $NiO/Al_2O_3/SiO_2/C_2H_5AlCl_2$ (Al/Ni = 1)	butenes/50 °C	olefins C_8 (50%), C_{12} (13%), $C_{>16}$ (37%)	conv = 63%	382
$Ni/Al_2O_3/AlCl_3/(C_2H_5)_2AlCl$	60% n-butenes–40% butane/54 °C, 6 h	olefins C_8 (60%), $C_{>12}$ (40%)	conv = 79%	162, 161

	Tungsten			
$W[OCH(CH_2Cl)_2]_2Cl_4/(C_2H_5)_2AlCl/D$; D = $(C_4H_9)_2O$, $(C_2H_5)_2O$, $CH_3OC_6H_5$	2-methyl-1-pentene	olefins C_{12-24} D donor strength ↑ $\bar{M}_{mw}$ ↓, α↓	conv = 35–56%	172
$WCl_6/LiAlH_4$	1-hexene/25 °C, 75 min, chlorobenzene	branched-chain oligomers, $\bar{M}_w = 1230$	conv = 100%	171
WF_3/branched-chain aliphatic alcohols	1-butene/42 °C, 40 min	olefins C_{12-16} (10%), C_{20-24} (21%), $C_{>26}$ (69%)	conv = 85%	383
	Chromium, Iron, Cobalt, Nickel			
Cp_2M supported on $Al_2O_3/SiO_2/(C_2H_5)_3Al_2Cl_3$, M = Cr, Fe, Co, Ni (Al/M = 0.5)	butene-butane/70 °C, 30 min	olefins C_8 (80%), C_{12} (12%), C_{16} (8%), linearity = 78%	conv = 75–99%	270
	Aluminum			
$C_2H_5AlCl_2/RCl$ (1:1.5–2)	1-hexene/293 K, 90 min heptane/hexane = 1:1	high branched-chain oligomers	conv = 50–100% RCl activity: *t*-BuCl > allyl Cl > PhCl > Ph_3CCl	177
R_nAlX_{3-n}/RCl; X = halogen; R = H, alkyl, alkoxy; $n = 0$–3	olefins C_{3-11}			343
R_nAlX_{3-n}/R^1Cl, R = alkyl C_{1-18}, aryl C_{6-10}; R^1 = alkyl C_{1-24}, cycloalkyl C_{5-6}, alkenyl C_{3-30}, aryloalkyl C_{7-9}; X = Cl, Br, I	1-decene/18–22 °C			179
$R_3Al_2X_3$ or $R_nAlX_{3-n}X_2$, *R* = hydrocarbyl; X = Br, I; $n = 1, 3$	1-decene/42 °C, 15 min, hexane	oligomers viscosity = 82.86 csT (100 °C)		385
$AlCl_3$/alkylaluminum halide (0.7–1.5%)	α-olefins C_{6-18}/70–80 °C			283
R_3Al/RCl, R = hydrocarbyl	α-olefins $C_{\geq 3}$/hexane	1-decene oligomer, viscosity = 20.5 csT (100 °C)		178
AlX_3 or $RAlX_2$/haloalkanoic acid, X = Cl, F	1-hexene/70 °C, 24 h, nonpolar solvent	olefins C_{12} (20%), C_{18} (40%), C_{24} (10%)	conv = 95%	174, 176
$(C_2H_5)_2AlOC_2H_5$/zeolite (10×)	isobutene/160 L (kg of catalyst)$^{-1}$ h^{-1}, 40 °C	olefins C_8 (65%), C_{12} (25%)	conv = 100%	386
$AlCl_3/i\text{-}C_3H_7OH$ (19:0.7)	1-dodecene/25 °C, 3 h	oligomer viscosity = 96.4 csT (37.8 °C)	conv = 98%	182
$AlCl_3$	olefins C_{4-10}/50 °C, 1.5 h, heptane	oligomer viscosity = 77.58 cSt (38 °C)	conv = 88%	166, 388
$(C_2H_5)_3Al_2Cl_3$, $C_2H_5AlCl_2$	fraction C_4H_{10}–C_4H_8/–60 and +25 °C, heptane	$\bar{M}_w = 1000$		173
$AlCl_3/Al_{powd}/AcO(CH_2)_nOAc$, n = 2, 3, 4	olefins C_{6-10}/100 °C, 5 h		conv = 95%	183
$AlCl_3$/alkyl aromatic hydrocarbons containing O and N ligands	1-decene		act energy = 0.3 kJ/mol	389
$AlCl_3$	1-hexene,1-decene/103 °C, 1 h	oligomers viscosity = 41.7 cSt (40 °C)	conv = 80%	390
$AlCl_3/Al_2O_3$	olefins C_{4-6}			391
$AlCl_3$/alkyl aromatic hydrocarbons	1-butene/–20 to +5 °C, *n*-hexane	oligomers vinylidene (53–58%), trans C=C (30–33%), trisubstituted C=C (10–16%)	conv = 100%	180, 181
AlH_3/Davison SiO_2 (3.8% Al)	isobutene/65 °C, 1 atm	oligomers C_8 (3%), C_{12} (81%), C_{16} (16%)	conv = 98%	397
	BF_3 Systems			
BF_3/alcohols C_{5-6}	1-decene (61% in feed-stock)/–10 and +40 °C, fixed-bed reactor	olefins C_{20-50} (max C_{30-40})		184
$BF_3/n\text{-}BuOH$, $CH_3COC_2H_5$, or $HO(CH_2)OH$	1-decene/20 psig, 49–50 °C	oligomers C_{20} (10.6%), C_{30} (58.3%), C_{40} (19.9%), C_{50} (3.9%)	conv = 92.7%	187

TABLE VIII (Continued)

catalyst	olefin/react condtn	products	yield	ref(s)
BF_3/BuOH	linear olefins: C_{3-4}, internal C_{13-15}/85–86 °C, 105 min	dimers (61.3%), trimers (25.1%)	conv = 87.1%	186, 409
BF_3/C_2H_5OH or C_4H_9OH	1-decene/10 psig, 20–25 °C, 4–6 h, continuous process	olefins C_{30} (59–60%), C_{40} (23–19%)		410
$BF_3/SiO_2/H_2O$	1-decene/29–36 °C, 12 h, 45 cm^3/h	olefins C_{20} (37.8%), C_{30} (49%), C_{40} (10%)	conv = 84.4%	411, 415
$BF_3/O_2/SiO_2$	1-decene/10–15 °C	olefins C_{20} (12–14%), C_{30} (53–58%), C_{40} (18–19%), C_{50} (3–6.6%)		191, 194
BF_3(1–20%)/Al_2O_3	2-butene/100 psig, 150 °C	olefins C_8 (81%)	conv = 51.4%	192
BF_3/cocatalysts	1-decene/two-step oligomerization			412
BF_3/CH_3OH	2-butene/CH_2Cl_2	oligomers C_{8-20} (60%)		188
BF_3, H_2O/BF_3(gas)	1-octene/7 °C, 2 h	oligomers C_{16} (0.6%), C_{24} (7.2%), $C_{>32}$ (92.2%)	conv = 93.4%	413
BF_3/H_2O or alcohols	1-alkenes			414
BF_3/mannitol (3.1:1)	1-decene	oligomers		189
BF_3/H_2O, alkanoic acids	1-hexene, 1-decene, 1-tetradecene/30 °C	high branched-chain dimers to pentamers	conv = 70%	195, 418
BF_3(gas)/$BF_3 \cdot 2H_2O$	1-hexene/1–1.5 psig, 20–50 °C	olefins C_{12} (1.8%), C_{18} (68.4%), $C_{>24}$ (29.5%)	conv = 99%	417
BF_3/*n*-BuOH	1-butene, 1-pentene, 1-decene/50 psig, 50 °C	dimers	conv = 40%	135
BF_3/Al_2O_3	butene/30 bar, 75 °C		conv = 32–92%	419
BF_3/NiO, CuO, Cr_2O_3, $CoCO_3$, or NiF_2, CoF_2	α-olefins $C_4/C_{10}/C_{14}$ (4:1:1)	oligomer C_{20-22}		420
BF_3/*n*-BuOH, C_2H_5COOH	α-olefins $C_4/C_6/C_{8-18}$ (3.6:1:1)/23–49 °C, 1–2.5 h	oligomers C_{8-30}		130, 421
BF_3/Naftion 501	α-olefins C_{13-15}/85 °C, 2 h	dimers (59%), trimers (15%)		422
BF_3/CH_3OH, C_2H_5COOH, H_3PO_4, or H_2O (1:1)	3-methyl-1-butene/0–70 °C, hexane	dimers to hexamers		423
$BF_3/(CH_3OH/BF_3)$	1-decene/2 psig, 30 °C, 2 h, 0.2 mol of catalyst per 100 g of 1-decene	oligomers C_{30} (84%)	conv = 97%	170
	Heterogeneous Inorganic Systems			
Ni/mordenite (Si/Al = 9)	butenes (butane–butadiene)/16 bar, 42 °C, 0.29 mg of catalyst L^{-1}	liquid oligomers		393
0.1–1.5% by wt Ga/ZSM-5	olefins C_{2-5}	oligomers bp = 343 °C		394
SiO_2, Al_2O_3, MgO, or TiO_2/H_3PO_4	isobutene/170–293 K	oligomers C_{20-50}		395
Cd or Zn/Al_2O_3/SiO_2	olefins C_{2-6}/30 bar, 50–500 °C			396
Al_2O_3/TiO_2/F (Al/Ti = 90:10)	isobutene in butenes/120 °C, 30 min	oligomers C_8 (19.5%), C_{12} (55.2%), C_{16} (20.3%)	conv = 98.8%	398
WO_3/γ-Al_2O_3	isobutene/1 atm, 150 °C	oligomers C_{12-16}	conv = 74%	384
WO_3/Al_2O_3/F (Al/W = 100:0.5–10)	isobutene/120 °C, 30 atm	oligomers C_8 (18.2%), C_{12} (56.3%), C_{18} (21.4%)	conv = 99.1%	399
ZrO_2–MoO_3 (100:13)	isobutene/120 °C, 30 min	oligomers C_8 (29.3%), C_{12} (49.2%), C_{16} (19.2%)	conv = 90.4%	400
$K_2O/CaO/Fe_2O_3/Na_2O_2/Al_2O_3/SiO_2$	olefins C_{9-14}	oils		401
$MSO_4 \cdot nHCl$, M = Zn, Sn, Pb, Cu, Tl, Cd, Hg; *n* = 0.2–1.7	isobutene	internal olefins C_{8-24}		402
$CuSO_4$/2HCl (1:2) on mineral supports	isobutene/0–60 °C	oligomers C_{12}		363
5%Cr/Al_2O_3/SiO_2	1-hexene	oligomers C_{12-18}		403
12.9% $TaCl_5/SiO_2$	1-butene/500 psig, 150 °C	olefins C_8 (38%), C_{12} (31%), C_{16} (19%), $C_{>20}$ (12%)	conv = 95%	406

Ta_2O_5/Al_2O_3	1-butene/170 °C	olefins C_8 (7%), C_{12} (6%)		404
Zn/HZSM-5 zeolite	butenes, olefins C_{6-9}/800 psig, 120–230 °C, 0.5 LHSV	for C_4 olefins C_{16} (60%), for C_{6-9} olefins C_{12-18} (max C_{12}), 1% aromatic hydrocarbon	conv = 99%	440
Ni/HZSM-5	butene/120–230 °C	olefins C_{18}	conv = 60%	303
$TaCl_5/SiO_2$	1-hexene/100 psig, 100 °C	olefins C_{12} (69%), C_{18} (14%), $C_{>24}$ (17%)	conv = 59%	406
SiO_2, Al_2O_3, TiO_2, or ZrO_2/H_3PO_4	*n*-butene, isobutene/200 Torr, 20 °C		TiO_2 system the most active	395, 407
CeY zeolite	isobutene, cis-2-butene/80 °C	oligomers C_{8-12}		416
Bulgarien mordenite	butenes	oligomerization and metathesis products	conv = 50%	139
Wyoming bentonite (cation exchanged)	olefins C_{2-10}/85–100 °C	alkenes (80%), alkanes (3–17%), aromatic hydrocarbon (9–40%)		424
zeolite HKL	isobutene/150 °C	olefins C_8 (62.9%), C_{12} (36.5%)	conv = 82%	196
HZSM-5/Cr(V), V(IV), or Zn(II)	isobutene/320 °C, 10^{-5} mol of isobutene (g of catalyst)$^{-1}$ s^{-1}	oligomers C_{6-10} (60%)	conv = 36–98%	197
HZSM-5	1-hexene/359–593 K	oligomers C_{8-15} (max C_{12}) cracking, isomerization and aromatization products		342
HZSM-12	α-olefins C_5, C_8, C_{10}/200–400 psig, 392–482 °F	for C_5 olefins C_{10} (97%), for C_8 olefins (67%), C_{16} (84–88%), C_{24} (11–14%), for C_{10} olefins C_{20} (62–72%)	conv for C_5 = 76%, for C_8 = 53–59%, for C_{10} = 43–59%	442
ZSM-5	olefins C_{2-6}/30–100 bar, 200–300 °C	oligomers $\bar{M}_w$ low	conv = 75–85%	142
L and Y zeolites: mordenite, erionite, and pentasil	isobutene/50–200 °C	oligomers C_{8-12}		425
HM/mordenites (Si/Al = 6)	1-butene/51 bar, 473 K	oligomers C_8 (70%), C_{12} (23%), C_{16} (7%)	conv = 70–80%	426
Zeolon 100H (H-type mordenite)	isobutene		conv = 98.7	427
NaHY zeolite	butenes/293 K	highly branched oligomers		428, 335
NaY zeolite/(SiO_2/Al_2O_3 = 5.22)	butenes/293 K	reactivity: *trans*-2-butene < *cis*-2-butene < 1-butene		199
HCaNiY zeolite	isobutene/110 °C, 100 h^{-1}		conv = 86.2%	443
Y zeolites/Ca(II), Mg(II)	1-butene	linear and branched olefins		271
$Na_2O/SiO_2/Al_2O_3$ (114:1)/H_2O or *t*-BuOH (0.5%)	isobutene/35 atm, 80 °C	oligomers C_8 (92%), C_{12} (8%)	conv = 99.3%	433, 434
SiO_2/Al_2O_3 (20–50%)	isobutene/1–50 atm	oligomers C_8 (15.4%), C_{12} (5.4%)		435, 309
SiO_2/Al_2O_3 (15–85%)/F	butenes/14 bar, 160 °C			438
Cu, Zr, Al orthophosphate	butenes	oligomers C_{8-12}		375
$AlPO_4$/F	2-butene, 2-hexene/1000 psig, 300–350 °C	highly branched oligomers		432
BPO_4	1-decene	oligomers		269
	Cation Exchangers			
$MgCl_2$/KU-2-8 cation exchanger	olefins C_{4-6}			391
wofatite OK 80	isobutene	olefins C_8 (74%), C_{12} (11%), C_{16} (15%)		429, 430
benzylsulfonic acid siloxane	isobutene/1 atm, 130 °C	olefins C_8 (52%), C_{12} (40%), C_{16} (3%)	conv = 52%	31
amberlist 15	isobutene/7 bar, 60 °C		yield = 57.1%	438
nafion 425 (perfluorosulfonic acid resin)	isobutene/145 °C, 1000 h	olefins C_8 (50.8%), C_{12} (47.5%), C_{18} (1.8%)		380
nafion 501	α-olefins C_{14-20}	oligomers C_{26} and higher	conv = 83.6%	334

TABLE VIII (Continued)

catalyst	olefin/react condtn	products	yield	ref(s)
ion exchanger/SO_3H	isobutene/18 atm, 48 °C	oligomers		185
	Miscellaneous			
H_3PO_4/C_{act}	isobutene			436
Lewis and proton acids	2,4,4-trimethyl-1(or 2)-pentene	oligomers C_{16}		190
	Oligomerization of Strained Alkenes			
$(COD)_2Ni/PR_3$		dimers, trimers		447

The mixed catalytic system $TiCl_4/Ti(OBu)_4/Zr(OBu)_4/Et_3Al_2Cl_3$ (1:2:1:10) oligomerizes with high yield 1-decene to a product having an average molecular weight of M_n = 356.[87]

Octene trimers are the main products of the 1-octene oligomerization in the presence of the system $TiCl_4/Et_3Al_2Cl_3$.[170]

$ZrCl_4$ modified with $AlCl_3$ oligomerizes 1-decene to trimers and tetramers with yield of 93%.[169]

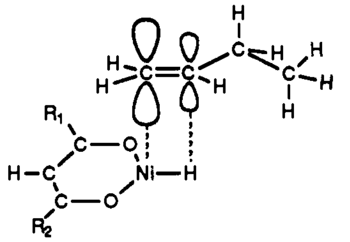
All of these titanium and zirconium catalysts have one deficiency: they promote alkylation of olefins with aromatic solvents. Zirconium catalysts are more active in this reaction, e.g. the $Zr(O\textit{i}\text{-}Pr)_4/Et_3Al_2Cl_3$ system alkylated toluene with 1-hexene with 100% efficiency (no 1-hexene oligomers) when the $TiCl_4/Et_3Al_2Cl_3$ system gave only 12% of the alkylation reaction products.[168]

V.1.2. Nickel

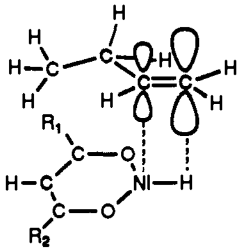
The sulfonated ylide nickel complex XVII activated with Et_2AlOEt cooligomerizes ethylene with higher olefins, e.g. 1-hexene, 1-heptene, 1-octene, and 1-decene. The mechanism of this reaction has been presented earlier (see Chapter III.1.3). Olefin insertion into the Ni–H bond is nonselective in this case (Scheme XIII, steps A and B). The chain-propagation step α-olefin insertion into the nickel–alkyl bond is also nonselective. Olefin insertion leading to the primary Ni–C bond formation (Scheme XIII, step A) is 60% more probable. Olefin reactivity in the propagation step decreases considerably together with their chain prolongation. The Ni–C bond reactivity in the olefin insertion reaction depends on the structure of an alkyl group bonded to the nickel ion. Relative reactivity in this reaction of the Ni–C bonds $NiCH_2CHRCH_2R'$ (R = C_8H_{17}), $NiCH_2CHRCH_2R'$ (R = C_4H_9), and $NiCH_2CH_2CH_2R'$ equals 0.5:0.7:1.0.[58]

Reactivity of the Ni–C bonds in the β-hydrogen elimination reaction depends strongly also on the alkyl group structure: β-hydrogen is eliminated at a rate 2.5 times faster from $NiCH_2CHRCH_2R'$ group compared to the $NiCH_2CH_2CH_2R'$ group.[58]

The complex XIV A $(\eta^3\text{-}C_8H_{13})Ni(CH_3COCHCOCH_3)$, XIV B $(\eta^3\text{-}C_8H_{13})Ni(CF_3COCHCOCH_3)$, and XIV C $(\eta^3\text{-}C_8H_{13})Ni(CF_3COCHCOCF_3)$—see Chapter III.1.3.— are very active in the 1-butene oligomerization.[53,55,160] Two 1-butene orientations; "n mode" and "iso mode" are possible during its insertion to the Ni–H bond.



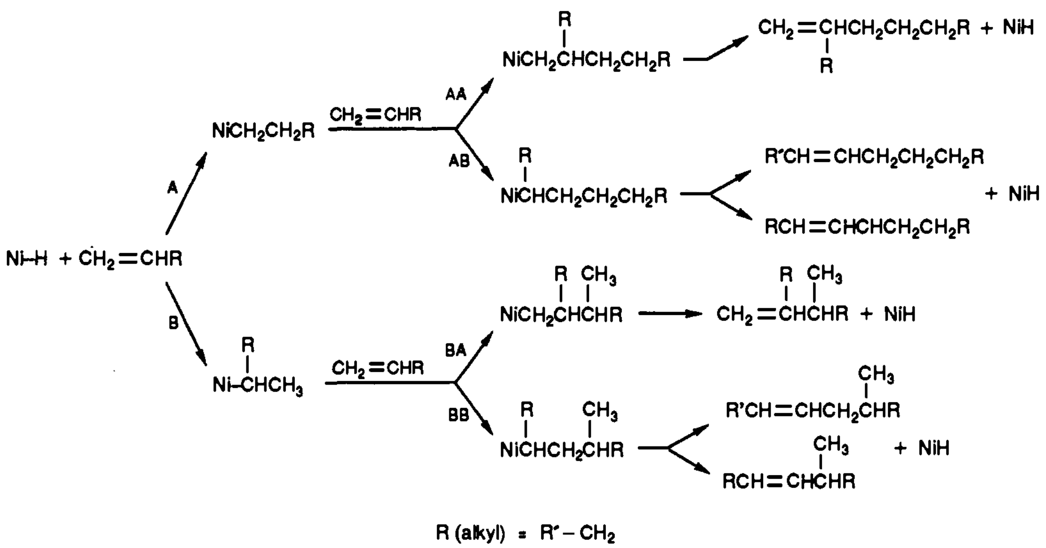
XIV n mode



iso mode

Reduction in electron density in the nickel ions in the complexes XIV A,B,C caused by an increase of the number of fluorine atoms in the acetylacetonate moiety, increase the catalytic activity of these complexes and the stability of the n-mode intermediate in the following

SCHEME XIII. High α-Olefin Oligomerization Mechanism in the Presence of a Nickel Complex Catalyst[53,55,a]



[a] (A) Addition of the olefin primary carbon to the nickel atom. (B) Addition of the olefin secondary carbon to the nickel atom.

order: XIV C > XIV B > XIV A and favors the occurrence of reaction A Scheme XIII.[53,54] The insertion of 1-butene into the Ni–H bond occurs mainly according to the Markovnikov rule—n mode (90%). Insertion of the next 1-butene molecule into the penultimate nickel–alkyl bond occurs with only 12% Markovnikov selectivity. This indicates that steric effects are more important than electronic influences in 1-butene oligomerization in presence of the complexes XIV.[55] Various solvents have been tested in this reaction and the following increasing order of effectiveness has been established: toluene > fluorobenzene > *n*-heptane. Polar solvents block the catalyst active centers; acetonitrile and DMF destroy these nickel complexes.[53]

The system Ni(acac)$_2$/$Et_3Al_2Cl_3$ is active in 1-hexene oligomerization. Its modification with donor ligands, e.g. PPh_3, increases the yield and molecular weight of obtained products, mainly trimers.[168] Similar systems with trifluoroacetylacetonate ligands and with PPh_3[153] or PBu_3[154] phosphines and the system RCOONiOOCR′/$EtAlCl_2$ where R = CF_3, R′ = 2-ethylhexanoate[155,158] gave dimers and trimers in 1-butene oligomerization.

In presence of sulfur ligand containing systems, Ni(*p*-toluensulfonato)$_2$/$EtAlCl_2$[157] and Ni(pentene-2,5-dithionato)/P($R^1R^2R^3$)X (R = alkyl or aryl, X = halogen), only butene dimers have been obtained.[158]

Heterogenized catalysts have also been tested in this reaction. Calcinated nickel salts supported on alumina and activated with (*sec*-BuO)$_3$Al or a $AlCl_3$ + Et_2AlCl mixture[159,161,162] oligomerized butenes to C_{8-12} olefins. Similar results have been obtained in the presence of the system Cp_2Ni/Al_2O_3–$SiO_2/Et_3Al_2Cl_3$.[270]

V.1.3. Tungsten

$WCl_6/LiAlH_4$[171] and W[OCH(CH_2Cl)$_2$]$_2Cl_4$/Et_2AlCl/ether (ether = Bu_2O, Et_2O, MeOPh)[172] catalytic systems oligomerize 2-methyl-1-pentene and 1-hexene.

V.1.4. Aluminum

Chloroalkylaluminum compounds are described as active catalysts for various olefin oligomerizations. The mixed system $Et_3Al_2Cl_3/EtAlCl_2$ was used for oligomerization of butenes.[173] 1-Hexene dimers, trimers, and tetramers are obtained in the presence of the following systems: $EtAlCl_2/Cl_3CCOOH$ and $EtAlCl_2/CF_3SO_3H$, which can be called superacids.[174-176]

Cationic mechanism of the 1-hexene oligomerization for the $EtAlCl_2$/RCl (R = alkyl or aryl) catalyst was established as follows:[177]

$$\begin{tikzcd} (CH_3)_3CCl + C_2H_5AlCl_2 \arrow[r, shift left] & (CH_3)_3C^+(C_2H_5AlCl_3)^- \arrow[l, shift left] \arrow[dl, shift left] \arrow[d, "XXV"'] \\ (CH_3)_3C^+ + (C_2H_5AlCl_3)^- \arrow[ur, shift left] & AlCl_3 + (CH_3)_3CH + C_2H_4 \end{tikzcd} \quad (42)$$

$$(CH_3)_3CCl + AlCl_3 \rightleftharpoons (CH_3)_3C^+(AlCl_4)^- \rightleftharpoons (CH_3)_3C^+ + AlCl_4^- \quad (43)$$

$$2XXV + 2C_2H_4 \longrightarrow 2(CH_3)_3CCH_2CH_2^+(C_2H_5AlCl_3)^- \longrightarrow$$
$$(CH_3)_3CC_2H_5 + C_2H_4 + (CH_3)_3CCH_2CH_2Cl + C_2H_5AlCl_2 + AlCl_3 \quad (44)$$

In the system $EtAlCl_2$/RCl the catalyst efficiency decreases in the following order: $(CH_3)_3CCl > CH_2{=}CHCH_2Cl > C_6H_5Cl > (C_6H_5)_3CCl$.[177] The products obtained with this catalytic system are branched. The same mechanism was proposed also for the 1-decene oligomerization.

V.2. Lewis and Brönsted Acids as Catalysts

$AlCl_3$ and BF_3 are catalysts for higher α-olefins' oligomerization.[180] For their action, they need the presence of labile proton cocatalysts in many cases. 1-Butene is oligomerized in presence of $AlCl_3$ modified with *n*-butylbenzene or xylenes.[181] An increase in catalyst concentration increases the reaction yield up to 100% when the catalyst concentration reaches 1.5% by weight. An increase in the reaction temperature causes a decrease in the oligomer molecular weight.

The system $AlCl_3$/tertiary or quaternary alcohols are described as 1-dodecene oligomerization catalysts.[182]

Another catalytic system $AlCl_3$/poly alcohol esters are successfully used in higher α-olefins oligomerization.[183] A change from $AlCl_3$ in these systems to BF_3 gives active oligomerization catalysts for 1-decene,[184,189] olefins C_{4-10},[130] butenes,[186] olefins C_{6-12},[187] and 2-butenes.[129,188] The mechanism of all of those reactions has a cationic character as shown in Schemes X and XI.

1-Hexene, 1-decene, and 1-tetradecene are oligomerized to highly branched di-, tri-, tetra-, and pentamers in the presence of the system BF_3/alkanoic acids.[195]

The heterogeneous systems BF_3/SiO_2 and BF_3/Al_2O_3 were used in the 1-decene[191,193,194] and olefins C_{4-6}[192] oligomerization.

V.3. Inorganic Oxides

Alumina–silica gels modified or unmodified with various metal ions are the most popular catalysts for higher α-olefins oligomerization.[395,396,401,403]

The zeolite HKL (SiO_2–Al_2O_3 = 5.2), partly decationized, is active in this reaction. Its activity depends on the amount of catalyst, not on the strength of acidic sites (Lewis and Brönsted).[196] These sites are mainly located on amorphous alumina–silica gel surface and macropores and in the zeolite channals and chamber walls. At temperatures higher than 573 K, besides oligomerization the olefin also undergoes cracking and aromatization reactions. Also the reaction products also take part in these reactions. The yield of aromatic products increases with temperature increase.

In the case of the H-ZSM-5 zeolite, modification with Cr(III), Cr(V), and Cr(IV) and Zn(II) ions decreases the OH groups (Brönsted acid center) concentration on the zeolite surface and on the channel walls. This results decrease in catalyst's activity in oligomerization of olefins because the reaction mainly occurs in the channels.[197]

Investigations of butene oligomerization in the presence of a zeolite (SiO_2–Al_2O_3 = 60.3) modified with various metal oxides allowed the establishment of the influence of oxides on this reaction.[198] SiO_2 and WO_3 localize on the zeolite crystal surfaces and practically do not change the reaction selectivity. Oxides like SnO_2, Cr_2O_3, and Bi_2O_3 localize on the channel walls and in this way block the Brönsted acid sites. This results in an increase of aromatic product yield. Addition of ZnO favors olefin dehydrogenation. The product of this reaction becomes the intermediates for subsequent aromatization reactions. The selectivity of oligomers in this case is very low.

For the NaHY zeolite, as a catalyst, the following reactivity of butenes in the cationic oligomerization reaction was established: 1-butene > cis-2-butene > trans-2-butene.[199]

Generally, all catalysts of this group have very low selectivity in the higher α-olefin oligomerization. Their activity, selectivity, and oligomerization reaction conditions are listed in Table VIII.

VI. Conclusions

The olefin reactivity in the oligomerization reaction decreases in proportion to the increase of the olefin length (ethylene > propylene > 1-butene > 1-hexene > 1-octene > 1-decene) and the C=C bond position (1-butene > 2-butene).

Only linear ethylene oligomers with 99% yields are obtained. In the case of higher olefin oligomerization mainly branched oligomers are the products.

Oligomerization catalysts can be divided into three groups: homogeneous and heterogeneous transition-metal complexes, trialkylaluminum compounds, and heterogeneous and homogeneous Lewis and Brönsted acids.

The Ti(IV), Zr(IV), and particularly Ni(II), Ni(I) complexes exhibit the highest activity and selectivity in the olefin oligomerization. Their activity and selectivity depend on electronic and steric factors of the central metal ion in these complexes.

An increase in positive charge on the central metal ion caused by acceptor ligands generally increases the catalyst's activity but decreases molecular weights of the obtained oligomers.

Donor ligands make olefin insertion into the metal–carbon bond much easier. This results in an increase of the oligomer length and linearity.

Large, bulky ligands favor the formation of intermediates from which the β-hydrogen elimination becomes more difficult and therefore the higher oligomers are obtained. The presence of these ligands in these complexes contributes to a relatively high linearity of the products.

Nickel complexes, particularly ylides, are most selective and active in the ethylene oligomerization to higher linear α-olefins. They have been recently applied industrially in the SHOP process.

There are many papers concerning titanium and zirconium complexes which are also very active and selective as catalysts of olefin oligomerization. Their main deficiency is polyethylene and branched oligomers formation as side products.

The systems consisting of other metal complexes, e.g. lanthanides, are less active or are being investigated at the moment.

Cationic catalysts homogeneous and heterogeneous (e.g. $AlCl_3$, metal oxides, zeolites, inorganic acids) are generally used for oligomerization of olefins possessing three or more carbons in the chain. These catalysts are less selective than transition-metal complex catalysts. In their presence, mainly high branched oligomers and products of the alkylation, cracking, aromatization, and isomerization reactions are obtained, particularly at higher temperatures.

Oligomers with high linearity are the products of the ethylene oligomerization using trialkylaluminum compounds as catalysts. Halogenoalkylaluminum compounds and the systems organoaluminum/halogenohydrocarbons are the catalysts of higher olefin oligomerization according to a cationic mechanism.

VII. References

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